Alfred Bader fonds Correspondence G 1993-2003

QUEEN'S UNIVERSITY ARCHIVES
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BOX 5
FILE 17

Subject: Re: Article about your talk at CHF
From: Neil Gussman <ngussman@dejazzd.com>
Date: Tue, 23 Sep 2003 18:10:27 -0400
To: Alfred Bader Fine Arts <baderfa@execpc.com>

Dr. Bader,

Thank you for your changes and corrections. The corrected copy is on the way to the editor of Chemical Heritage magazine.

Yesterday Marc Reisch of Chemical and Engineering News asked our photographer for additional photos from your talk. That's usually a good sign that there will be an article in the next issue of the magazine. I would think the article will be printed in the Sept. 28 or Oct. 6 issue of C&E News.

Thanks again,

Neil Gussman

> Dear Mr. Gussman,
>
> Thank you for sending me the draft of your article.
>
> On p.1, paragraph 2, please delete "have been married more than 50 years and" so that the sentence reads: Alfred and Isabel are constant companions.
>
> You will note in Chapter 6 of my autobiography that we were not married until 1982.
>
> Please change the second paragraph of p.2 to the following: Though Bader has helped his Canadian alma mater, Queen's University, to acquire a castle in England, the story of his success as an American entrepreneur actually begins with his deportation from the embattled British Isles in 1940. Bader had escaped Austria as the Nazis began their reign of terror in his homeland. The British interned him and sent him to Canada where he was educated first in the internment camp and then at Queen's University. After the war he became a graduate student in chemistry at Harvard and then a chemist at PPG Industries.
>
> The third paragraph on p.2 should be changed: The reply **from** Eastman-Kodak was a postcard saying, "Do not contact us again, we will send your order when we have the material."
>
> In the second last line on p.2, please delete the word "rare".
>
> In the second paragraph of p.3, please note that "The first Aldrich catalog was a single mimeographed sheet with **one** product offered for sale."
>
> The last sentence of p. 3 should be changed to: Eastman-Kodak no longer competes with Sigma-Aldrich.
>
> Please call me if you have any questions.

> Sincerely,
> Alfred Bader
>
> Neil Gussman wrote:
>
>> Dr. Bader,
>>
>> Attached is an article about your talk at CHF. Our magazine is on a short deadline. Could I ask you to review the article and return your comments this week?
>>
>> Thank you. I enjoyed the talk very much and it was a pleasure to meet you.
>>
>> Regards,
>>
>> Neil Gussman

University of Glasgow
Department of Chemistry
Joseph Black Building
University Avenue
Glasgow G12 8QQ

31 October 2001

Dr. Alfred Bader, CBE
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202

Dear Dr. Bader,

It is a great pleasure for me to express my gratitude for your generous donation. I really appreciate the opportunity to spend an academic year at the Chemistry Department, University of Glasgow, and to join Professor Kočovský's research group.

As I am interested in organometallic chemistry, stereochemistry, asymmetric synthesis and catalysis, this is a unique opportunity for me to gain priceless experience in the field by being a member of a renowned team. Thanks to your kind donation, I can fully devote my time to chemistry without the need of taking a part-time job.

I am convinced that a period of study at the University of Glasgow will help me a lot.

Many thanks and kindest regards.

Yours sincerely,

Filip Teplý

Dr. Alfred Bader
2961 North Sheppard Avenue
Milwaukee, Wisconsin 53211
USA

Prague, December 18, 2000

Dear Alfred,

After relatively long period, I am sending you this letter instead of the faster and more convenient e-mail. I am a little bit conservative and for longer messages I prefer using letters.

I have attended this year's Conference on Organic, Bioorganic and Medicinal Chemistry held at Liblice Castle, where the Bader Award was given. This annual conference is usually attended by many Czech chemists, especially younger ones, both from the Czech Academy of Sciences, all Czech Universities, and Industry. In the recent years I usually visited Liblice only for one day (it is a three days meeting) but this year I was invited to deliver a plenary lecture and therefore I was there all the time. Regarding the Bader Award, Dr. Vladimir Cirkva is undoubtedly an organic chemist, and, I believe that he was the best pick of the young chemist who had not been awarded yet. His lecture on "From radical and photochemical reactions to biocompatible compounds" reviewed all his chemical career. During the meeting I talked with him and found that he spent some time also at University of Illinois with a professor who knows you well...

I was also invited to a committee for evaluation of a competition of young students from a Prague chemistry high school (Masarykova prumyslova skola chemicka). I was quite surprised by high quality of the presented work. This activity is absolutely voluntary and the students, who are about 18 years old, work in their free time at selected laboratories at Prague Universities or Academic Institutions during a year. At the end of year they write a report similar to diploma work (of course much shorter). Three reviewers then review the report and the best students then present the work orally in the mentioned official competition. This year's competition was well organized; it was opened by prof. Zahradnik and the organizing school gave some money to three selected students. I was so impressed that I decided to take one student to my own lab. I am sure it will take some time to introduce him to the real organic chemistry but it can be the way to attract young people for this nice branch of science. In spite of the fact that this competition is only for students from one school, I believe that it deserves more support. By this I do not mean financial support, but I believe that a book or an official letter of appreciation signed by the founder of Aldrich would be a good idea. But we can discuss this matter during your next visit in Prague.

As I have mentioned in a previous e-mail, our Institute has been relocated into the Leciva site. Leciva, a Czech pharmaceutical company, bought the Institute from the state, reduced the staff substantially and sold all our buildings and other properties. All our original research activities were terminated and the rest of the Institute (about 70 people, 20 of them organic chemists) should work on development of generic substances for Leciva.

Fortunately, there is nothing new at home. Now we are busy to do everything necessary for Christmas and the New Year celebrations. Since I was really busy during the recent several months, I have no Christmas presents yet and I will have to do some shopping during the next several days. As usual, we will spend the first part in Prague with Majka's Mother and the second part with my parents near Pilsen.

I hope that everything is good also with you and Isabel. Of course I wish you a successful year 2001, and especially good health and vitality, you both are well known for.

Best regards,

Jan

FAX FROM:

Alfred Bader Fine Arts
924 East Juneau Avenue
Astor Hotel -Suite 622
Milwaukee, WI 53202
Ph: 277-0730
Fax: 277-0709
e-mail: baderfa@execpc.com

A Chemist Helping Chemists

February 4, 2000

TO: Dr. John R. Long
GFS Chemicals

Page 1 of _1__

FAX #: 614-225-1175

Dear John,

I am sorry that a trip to New York has delayed my thanking you for your fax of February 1st.

Give my best regards to Norbert Braunagel. As you know, he worked for a while at Aldrich in Germany but could not get along with David Harvey. In that he was not alone.

Most of my chemist friends in Germany have either retired or have died. The one man still in an important position is Dr. Axel Kleemann at Degussa in Frankfurt.

Isabel and I will be in England from March 22-30 and then in England and on the continent in June and July.

If you would like to send me a draft of your company brochure, I would be happy to look at it before it is printed.

We much look forward to seeing you in May.

With best wishes I remain

Yours sincerely,

Alfred Bader
AB/az

Fax

DR. ALFRED BADER CBE
2A Holmesdale Road
Bexhill-on-Sea
East Sussex TN39 3QE
England
Phone/Fax: 01424-222223

A Chemist Helping Chemists

Dr. John Lang
GFS Chemicals
Columbus, Ohio

November 19 2000

Dear John.

Regarding your proposal to explore novel naked-ion chemistry involving your perchlorate reagents, I will of course be happy to consult.

I'll be back in Milwaukee on December 22 and look forward to talking to you.

Best wishes

Fax

[illegible]

[illegible]

[illegible] if you think [illegible]
we [illegible] on a tentative [illegible] which will [illegible]
when the weather is comfortable, I will [illegible]
[illegible] and arranging accomodatio[illegible]. Let me know.

1785
The University of Georgia

S. William Pelletier
Director

Institute for Natural Products Research

Chemistry Building
Athens, Georgia 30602-2556,U.S.A.
Telephone (706) 542-5800
Fax (706) 542-5804

Dr. Clinton F. Lane, President
Aldrich Chemical Co., Inc.
1001 W. St. Paul Ave.
Milwaukee, WI 53233

Dear Dr. Lane:

I really enjoyed reading the history of Aldrich Chemical Co. in the recent issue of *Aldrichemica* Acta (vol. 34, no. 2). I note that about a dozen references refer to Dr. Bader's autobiography; *Adventures of a Chemist Collector*. I wonder if this book is available from Aldrich and if so, its catalogue number.

Aldrichemica Acta has been a favorite chemistry journal of mine over the years. It is always packed with interesting and useful material.

Sincerely,

S. W. Pelletier
S. William Pelletier

SWP:sdj
Aug. 16, 2001
bcc: Dr. Bader

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

October 14, 1997

Mr. William W. Gorman, Jr., P.E.
12418 First Street West
Treasure Island, FL 33796

Dear Mr. Gorman:

Thank you for sending me those fine photographs, which reminded me of our weekend in Las Vegas.

Unfortunately, I don't go to many professional meetings - not even of the ACS - because my calendar is so very full.

Thank you for your thoughtfulness.

Sincerely yours,

AB/cw

William W. Gorman, Jr., P.E.

Registered Professional Engineer

12418 First Street West
Treasure Island, FL 33706
Telephone & Fax (813) 360-9311
E-Mail wwgorman@gte.net

Florida Registration No.
020899
Illinois Registration No.
062-027616
Pennsylvania Reg. No.
PE-015686-E

Fellow, The American Institute of Chemists

Member, The American Association of Clinical Chemistry

Member, International Electrophoresis Society

October 6, 1997

Dr. Alfred Bader
924 E. Juneau Avenue
Milwaukee, WI 53202

Dear Dr. Bader:

Congratulations on your AIC Gold Medal award. It was a pleasure to meet you and your wife and I enjoyed your talk very much.

Enclosed are some of the photos of the event for your files.

We all hope we will see you at future AIC meetings.

Sincerely,

Bill

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

December 26, 1997

Professor Kevin W. Glaeske
Department of Chemistry
Wisconsin Lutheran College
8800 West Bluemound Road
Milwaukee, WI 53226

Dear Professor Glaeske:

I am happy that we could finally talk to each other and decide on the date of my talk on the History of Sigma-Aldrich, on Wednesday evening April 22, 1998.

For that talk I require one overhead projector.

Before that day I will ask you to send me directions how to come to the building where the talk will be held.

With all good wishes for 1998, I remain,

Yours sincerely,

AB/nik

FAX FROM [illegible]

WISCONSIN
LUTHERAN

[illegible]

No

Wed
April 22 98
Hist. EA

WISCONSIN
LUTHERAN
COLLEGE

Nov. 14, 1997

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202

Dear Dr. Bader:

After meeting with our Convocation Committee (which explains the long delay in replying, for which I apologize) we find that we can honor your request to move your talk from Jan. 28 to the middle of February. The dates from Feb. 17-19 provide us the best opportunity on our campus to hear your talk. Again the time would be at night and I shall send you the directions necessary for getting to our campus.

8800 West Bluemound Road
Milwaukee, Wisconsin 53226
FAX 414 443 3514
414 443 8800

I look forward to hearing from you, and remain,

Yours sincerely,

Kevin Glaeske

Kevin W. Glaeske
Assistant Professor of Chemistry
Wisconsin Lutheran College
8800 West Bluemound Road
Milwaukee, WI 53226
414-443-8893

[illegible] expecting [illegible] middle of Jan [illegible]

[illegible] committee [illegible]

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

October 13, 1997

Professor Ken Glazske
Wisconsin Lutheran College
8800 West Bluemound Road
Milwaukee, WI 53226

Dear Professor Glazske:

You will recall that we set January 28 for the date of my talk on The History of Aldrich. Unfortunately I have found out, since our discussion, that I have to be in New York City that week. Is it possible to move the talk either to earlier in January, say January 14th, or into the middle or end of February.

I look forward to hearing from you, and remain,

Yours sincerely,

AB/nik

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[illegible] Herrn Graefe

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[illegible]

Dear [illegible]

[illegible]

But [illegible]

I remember [illegible]

There appears [illegible]

With best regards [illegible]

Yours [illegible]

AB/[illegible]

Peroxid- [illegible] machen. mfg Ingo 09.09.97

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

September 29, 1997

Professor Dr. Helmuth Grössing
Universität Wien, Institut f.Geschichte
Dr. Karl Lueger-Ring 1
A-1010 Vienna
AUSTRIA

Dear Professor Dr. Grössing:

Thank you so much for your letter of September 22.

A few days ago my good friend Dr. Reinhard Schlögl telephoned me to inquire whether I would write an article on Loschmidt in German and I presume that his request is identical to yours, that is that this essay should be for the second volume to be published by Erasmus.

A year ago I talked about Loschmidt in German at the University in Vienna and an obviously very able group of students used a tape recording to put my talk on paper.

Dr. Schlögl then very kindly sent me the manuscript. I have made a very few corrections and enclose it for your consideration.

I am doing this because you will see that I am by no means perfect - either in spoken or in written German. Please do remember that I went to high school in Vienna for only four years and was 14 when I left Vienna for England.

If, despite this handicap, you and Dr. Schlögl would still like to have a manuscript in German, I would be happy to write this during the Christmas holidays and send it to you at the very end of the year - provided that you will help me by correcting obvious mistakes in German.

Thank you so much for sending me the first volume of your book to which I look forward very much.

With all good wishes, I remain,

Yours sincerely,

AB/nik

Enclosure

c: Dr. Reinhard Schlögl

ao.Univ. Prof.
Dr.phil habil Helmuth Grössing
Universität Wien, Institut f.Geschichte
A-1010 Wien, Dr.Karl Lueger-Ring 1
Tel. 4277/40834. FAX 4277-9408.
E-M: helmut.groessing@univie.ac.at

Herrn
Dr.Alfred Bader

Astorhotel Suite 622
924 East Juneau Av.
53202 Milwaukee, Wisconsin
USA

Wien, 22.9.1997

Sehr geehrter Herr Dr.Bader!

Als Präsident des von Dr.R.Reinhard Schlögl gegründeten Vereins "Institut für Wissenschafts- und Technikdokumentation" darf ich mich gelegentlich dieses Schreibens vorstellen und Ihnen für Ihre Mitgliedschaft danken.
Ich habe jüngst mit mehreren Mitarbeitern (darunter auch Reinhard Schlögl) ein Buch herausgegeben, das exemplarische Leistungen österreichischer Naturforscher, Mediziner und Techniker (historisch und aktuell) zum Inhalt hat. Ich erlaube mir, Ihnen - mit gleicher Post aber getrennt als Drucksache - einen Band als Präsent zu überreichen.
Wir planen inzwischen einen zweiten Band, der in meinem eigenen, im Vorjahr gegründeten Verlag ERASMUS erscheinen soll. Hierin ist eine Biographie Loschmidts vorgesehen (Umfang ca. 20-25 Seiten mit Apparat).
Ich habe vor zwei Jahren Ihren interessanten und sprachlich mitreißenden Loschmidt-Vortrag im alten chemischen Institut gehört und würde mich freuen, wenn ich Sie als Mitarbeiter an diesem, eher populär zu schreibenden Buch gewinnen könnte. (Wir können die Arbeit allerdings nur eher mäßig honorieren, dies hängt vom Verkaufserfolg ab.)
Gerne erwarte ich Ihre geschätzte Antwort und bleibe mit freundlichen Grüßen und
vorzüglicher Hochachtung

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

August 8, 1997

Mr. and Mrs. Steven Gill
4030 A. Rd.
Garberville, CA 95542

Dear Susie and Steven:

Isabel and I have only just returned from a long trip to Europe and hence, the delay in my responding to your long undated letter which Isabel and I enjoyed immensely.

Of course, it brought back many memories of our working together so happily.

You know about Robert Benkeser's reduction with calcium from page 188 of my autobiography. The reduction works quite well and Aldrich licensed the technology from Purdue and did quite a few in Milwaukee. Also, about 12 years or so ago, we had a full page advertisement for this technology and I will find this in one of our *Acta*s and send it to you.

Your letter raises two important questions: One very personal namely, whether you should go back to school; and the other a general question about which I have thought a good deal - namely the smoking of marijuana.

You are an excellent chemist and I just don't see why you should have to start studies at a university in the freshman or the sophomore year. You know far more chemistry than most graduates with a BSC degree and you have so much enthusiasm and love for chemistry. What is needed is to find a chemistry department that would allow you to start - at worst - in the junior year or - at best - in the senior. I just don't know how flexible and sensible chemistry departments are but as you have a good rapport with one academic at Purdue, why not try? I also have quite a few friends there and if you do apply, would write supporting letters to these friends. Also, of course, please use page 85 of my book and your wonderful article in the *Acta* to support your application.

To turn to the problem of marijuana.

Let me say, first of all, that I have *never* smoked *anything* - not even without inhaling - and I hope that I discouraged many hundreds of my Sunday School kids by thundering against the evil of smoking. Just think of your sensitive lung tissues and then hot mixtures of carcinogenic compounds descending into these tissues.

But I simply do not understand why we have put hundreds of thousands of people behind bars for smoking marijuana.

The most common argument made against soft drugs is that they are the gateway to hard drugs. That is probably so with a certain percentage of the population. But surely alcohol is the gateway to alcoholism and there can not be any person in the world who became an alcoholic without first drinking a small quantity. I am not an alcoholic but I certainly enjoy a Southern Comfort two or three evenings a week, and a glass of wine on the eve of the Sabbath.

What should happen I believe - and if I read your letter correctly it will eventually - is that marijuana be legalized and, of course, taxed the way cigarettes are. That way hundreds of thousands of people would not go to jail, billions would be earned by the government in taxes and the only people who would really object most strenuously to this would be the drug dealers. I understand that somewhere between five and 10 percent of the total world trade deals in drugs and, of course, the billions earned by drug dealers will give them a real incentive to thwart our attempts to legalize and tax marijuana.

Isabel and I met Dr. Sasha Shulgin only twice and read his interesting book. I have had some vague reports about his recent legal difficulties; do you have any details?

Have you read the book by Langston and Palfreman entitled "The Case of the Frozen Addicts"? It is a most interesting book and the case could not have been solved if I had not acquired the key compound in Quebec and put it into the Aldrich catalogue. It is a scary story and also so instructive.

We saw John Duberman recently but all too shortly and we do hope that you and he will visit us in Milwaukee before long or that we might meet in California.

With fond regards from house to house,

AB/nik

Enclosure

bc: David Bader
Daniel Bader,
Dean Marshall Goodman (UW-M)

(1)

Steven Hill P 85
R Beukers P 188

Dear Alfred and Isabel:

Imagine my suprise and delight when Josh Duberman brought "Adventures of a Chemist-Collector" to my attention. I had heard about your "dismissal" from Aldrich, and in fact tried to get your address from their website with absolutely no reply. Now with your book out, I can write to you directly and expect you to receive the letter.

Sadly, I can't say I'm suprised at the actions of Aldrich. It seems we are living in an age where profit and total disregard of the individual has replaced the blooming of social advances and (seeming) corporate willingness to at least to some extent care for their employees that seemed to be occurring for a few decades. In this day and age, most companies go to incredible extremes to assure profits including hiring temp workers to assure no benifits or medical plans are possible. In an age where the cost of living is almost out of sight for many people, the minimum wage is held at a level where few families can survive with just one wage earner.

Well, of course you've heard all this before, and I didn't intend to bombard you both with the political opinions of one who came of age in the 60's, and therefore is perhaps more idealistic than is possible in this day and age.

It was so interesting to hear an insider's reports of the growth and function of a chemical company, especially Aldrich, where your (Alfred's) inimitable style created an atmosphere of communication and collaboration rather than competition between chemists. When information is shared, it's potential to help is augmented. Of course inventers must realize their profits - and hopefully future partnerships between academia and industry will not impede the free flow of information. Needless to say I'm still totally grateful for all the help and encouragement I recieved both from you personally and from Aldrich.

Speaking of which, I was most interested to read of using calcium as a substitute for alkalai metals in liquid ammonia in the Birch reduction....do you have any references to this procedure? Next time I'm at the library, I'll look through chem abstracts - that would be an interesting route to (for instance) dihydrodiphenylanthracenes.....

As to what we have been doing, well, I wish I could report even a hundredth of the interesting life experiences you describe in your book, but perhaps I'm tending towards "midlife crisis" whatever that means - I'm 43 now, and in many ways I feel that I should have stayed in school - in fact, I'm considering returning to take some classes in computer science vis a vis molecular modeling and audio compression techniques.

Since we left the Bay Area, Susie & I have been homesteading a beautiful 40 acre piece of property in southern Humboldt County. Our place is about 25 miles inland from the Pacific at about 1800 feet elevation. The vegetation is mixed fir/manzanita/oak/madrone - the classic California highlands that I've loved my entire life. Problems of infrastructure here are many - we only have flowing water during the winter months (although we have a couple of ponds for agricultural use), there is no grid electricity, so we have a number of solar panels and batteries, and the phone service is very poor - I can use a modem on my computer, but modem speed is extremely limited, and every time I come back from the bay

area (where I have a delightful niece & nephew, for whom we purchased a computer for christmas a year ago) I'm struck again at how hard it is to do anything out here - though looked at another way, it's really a miracle - here we are out in a shack in the woods hooked up to the internet just as if we were downtown! Eventually the various systems will be upgraded, yet the problem is more what I should do with myself than how well things work here.

I love the peace & quiet out here, but there really are no jobs for chemists of course, and it would be next to impossible to start a company like we had in Richmond in this area, not to mention all the regulations that make it so hard to run any kind of small business.....So, much of my creative energy has gone into computers and music, while we make a living doing everything from textile arts (Susie is an avid silkscreen/tie-dyer) to consultation work with companies wishing to formulate herbal extracts, etc. This involves commuting to the bay area a bit, but I enjoy it down there (at least as a visitor). Still, the work is very infrequent, and I miss working on synthetic projects. What I'd really like to do is work with Dr. Nichols at Purdue (medicinal chemistry has always been one of my interests)

but I'd pretty much have to start over from square one, that is as a freshman or maybe a sophmore. I've never considered myself anything more than a dabbler, so I question whether it would be worthwhile for me to take six years of pregrad just to get to the point where I could start working there.....and as always I question whether I have an ability worth investing further time & money into. I've never been more that a fair to middlin' synthesist, and there are a million grad students out there that have not only more ability, but more time to spend on that path. The Heffter Institute will be able to hire the best ...and I can't wait to see what they come up with. Their current work with the benzodifuran analogs of dimethoxyphenethylamines is extremely exciting....it seems like they are "zeroing in" on the 5-HT2a receptor, if that's what it is. As always with psychobiochemistry, there's only so far you can go with theory before you confront the great mystery of consciousness itself.....and in a more enlightened future, I'm sure many of the tools David Nichols and Sasha Shulgin, as well as many others are developing will be added to the pharmacopoea for psychotherapy and consciousness research.

I was reminded of Sasha's recent legal predicament when I read in your book of Sigma's weight discrepancy and the fine they had to pay - for in essence being generous! I've always felt that was good practice in the chemical industry: To give slightly over the declared weight to make up for transfer losses......I wonder if Sigma still does that? Thank goodness Sasha and Ann's many friends were there to help with his legal expenses. Of course all his friends have looked up to Sasha as one who has been scrupulously honest in every way, so to see him singled out by the DEA was suprising.....but I suppose his book was frightening to the powers that be. I found his book to be quite interesting, and am looking forward to the next, TIHKAL. Of course, any chemist can make a medicinally active compound and divert it to the black market, and having a book like Sashas' will make very little difference to those who wish to make money in this way. But of course, bureaucracies don't think in this fashion.

Personally I think eventually most schedule I and II drugs will become legally avaliable, either in a controlled setting or to people with a license resembling a driver's license perhaps. Or a harm reduction model like that used in the Netherlands will apply....I've seen too many young people sent to prison for 20 years and up for first offenses or even peripheral involvement in minor amounts of controlled substances to ever agree with the "War on Drugs" model. It simply creates another "generation gap" as the children grow up in a "Do as I say, not as I do" world.

I see a great deal of this firsthand living in Humboldt County. It was quite famous for marijuana cultivation a decade ago, but now of course MJ cultivation is ubiquitous, so we're not so much the "center of the storm" anymore. There's a certain percentage of people out here that either do that full time, or augment whatever other kind of work they can with MJ earnings. Medicinally of course MJ is one of the less toxic plants around, but I think the long term effects of relatively easy money on the local community has not been altogether good. It's a very complex issue, but mostly I hate to see the kids get caught up in a livelihood that is somewhat of a dead end. When MJ is decriminalized (as there's little doubt it will be eventually) there'll be alot of young people who have little schooling and few skills to offer society. How they will support their young families then I don't know.

It's not an uncommon problem in today's world: Areas of depressed economic opportunities turn to drugs as a replacement for lost jobs, and though one problem is solved, others accrue, especially with the addicting substances such as heroin or cocaine. And then of course the gangster element becomes involved.......well, at least we don't have that problem here. For the most part, MJ growers are like farmers anywhere....there are no "turf wars" or "drivebys". It's very peaceful here, and most people don't even have locks on their doors. Of course this will change to some extent as the area becomes more populated, and I hope it doesn't get too crowded here - this area is exquisitely sensitive to geological disturbance because of the torrential winter rains and the fact that the hills are pretty much made of clay with a little Franciscan formation shale mixed in.....it erodes very quickly once any kind of disturbance occurs, and of course most people either can't afford or aren't willing to maintain the roads properly to minimize erosion. Eventually there will have to be laws regulating road upkeep.....which might make it impossible for some of us to live here! If everyone contributes it should be no problem though.....One of the sore points around here, to be sure.

I fear that returning to school will be hard for me....I've grown quite accustomed to the peace and quiet of no cars, really no noise at all except the birds and the wind, and whatever noise we make. I have to run a generator an hour or two a day this time of year if I want to do any computer work, but it's a small generator & fairly quiet. We hope to build a powerhouse at the end of our driveway (the sunniest spot) which will have more solar panels and batteries to supplement the set that are on the house. With about four more panels we'd almost never need a generator.

Mountain lions are common here - I've seen several, in fact I almost stepped on one during a night walk - it jumped out of the bushes next to the road right in front of me, then ran away - I happened to have a flashlight so I got a good look at it - I don't know which one of us was more scared by the encounter! Bobcats are common also, easily identified by their very short, ringed tails. It's claimed that they interbreed with the feral domestic cats around here - I've seen some kittens with bobcat tails, so who knows?

Black bears make their presence known once or twice a year - unfortunately this year one broke all the upper branches of three new trees we had planted. It came too late though: All the apples were already long gone. It made a nice hole in the fence where it entered - perhaps it was frustrated at missing out on all the fruit......

Raccoons, deer and the usual gray squirrels, deer mice and voles, gophers, and many migratory birds appear regularly. Various ducks, herons, and other birds use our pond as a stop on their migration. In the spring and fall this area really is a paradise on earth, and except in the summer (I'm not a thermophile - temperatures of over 90 degrees F pretty well incapacitate me) it's mild year-round. It snows once or twice a year, but other than that it's in the 40-70 degree range for half the year, then 60-110 the other half. We're about as far from the ocean as one would wish - any closer to the Central Valley and the summer temperatures would be just too much... Over 100 ' F for months at a time doesn't appeal to me. I grew up near the coast, and I'm happiest in coastal climates.

Apologies for turning a simple letter into a rant, but once I start typing it's hard to stop sometimes. You have our address now, and if you're both travelling in Northern California, please call. We share a comfortable house in Phillipsville with friends - It's right on Highway 101, so when people come through the area we usually stay down there, so it's avaliable if you ever happen to come by. Sorry to have not kept in touch more - perhaps I've felt embarrased that I haven't kept up in the chemical world......that may change in the future. The rapid development of molecular modeling has brought together my interest in chemistry and computers (and your chapter on the history of molecular modeling was absolutely fascinating, Alfred). I don't doubt that I might end up at HSU or some other school again ......why not? There's always more interesting things to learn!

A special hug from Susie to Isabel, and my warmest regards to your entire family.

So happy to have communicated again, Susie & I remain most respectfully.....

Your Friends, S & S

Steve + Susie
4030 A. Rd.
Garberville, CA 95542

USA 32
SAVE OUR ENVIRONMENT

Alfred + Isabel Bader
2961 N. Shepard Ave.
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53211/3433 61

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924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
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Fax: 414/277-0709

A Chemist Helping Chemists

October 11, 1995

Dr. Alfred Griesinger
Mittelrain 51
D89555 Steinheim am Albuch
Germany

Dear Alfred:

I haven't heard from you for quite a while, and I hope that you and the family are well.

May I ask you to send an Aldrich Chemie catalog, of course with German prices, to Professor Carlos Seoane at the Universidad Complutense de Madrid, Facultad de Ciencias Quimicas, Departmento de Quimica Organica 1, Ciudad Universitaria, 28040 Madrid, Spain?

Professor Seoane does joint research with chemists outside of Spain - I believe in Slovakia, Poland and perhaps other countries. Could he order chemicals from Aldrich Chemie to be sent to those countries but then billed to him in Madrid? Of course, it wouldn't make sense for him to get the chemicals from Steinheim to Madrid, only then to send them to another country.

With all good wishes to you and the family, I remain,

Yours sincerely,

AB/cw

Dr. Nick Gerasimchuk
chemist
Meadowbrook Apts.; DD317
Lawrence, KS, 66049-3906;

December, 17 / 94.

Alfred and Isabel Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

Dear Alfred and Isabel,

Let me send you what I have promised a long time earlier. We received this matter just a few days ago.

Enclosed please find the author's reprint from our with Prof.Kristin Bowman-James chapter into ***Encyclopedia of Inorganic Chemistry.*** I'm glad very much that I have participated in writing a contribution into this book. It is a big honor for me.

Also let me congratulate you with coming holidays and wish you all the best. Good health, and good luck to you in everything!

Yours sincerely,
Nick
Sincerely yours,
Nick.

Nick Gerasimchuk

Mixed Donor Ligands

Nikolay N. Gerasimchuk & Kristin Bowman-James
University of Kansas, Lawrence, KS, USA

1 INTRODUCTION

Mixed donor ligands comprise a vast area of coordination chemistry. The prerequisite is bi- or polydentate capability, and the variety of donor atoms is overwhelming, including the commonly found N, O, S, P, and the less extensively studied As, but also with possibilities from Group 14: Si, Ge, Sn, and Pb. For the purposes of this article the heteroatoms to be considered will be those nonmetals more commonly found as donors: N, O, S, P, and to a lesser extent Se and Te. This article will be divided into four sections: simple chelating ligands, Schiff bases, complexones, and amino acids. Not included are macrocyclic ligands with mixed donor atoms, which can be found in ***Macrocyclic Ligands***.

Mixed donor ligands can participate in bi-, tri-, tetra-, and higher dentate coordination modes, examples of the first three of which are shown in Figure 1. A, B, C, and D are nonmetals capable of forming coordination bonds to the central atom with significant σ-bond character. These heteroatoms are usually, although not always, linked through covalent bonds with carbon atoms forming chelate rings, as noted by solid lines.

Of major importance in the stability and chemistry of mixed donor ligands are two major concepts of coordination chemistry: the chelate effect and the *Hard & Soft Acid–Base Theory*. The chelate effect, operable for all multidentate ligands, is the increase in stability of a given type of complex as the number of chelate rings increases. The HSAB theory is particularly applicable to mixed donor ligands because of the general tendency for 'hard' nonpolarizable donors such as nitrogen and oxygen to bond preferentially to 'hard' nonpolarizable metal ions such as the first row transition series in higher oxidation states. Likewise, 'soft' polarizable ligands, such as sulfur, phosphorus, arsenic, selenium, and tellurium, have a greater tendency to bond to the low-valent, more polarizable metal ions of the second and third transition series.

Figure 1 Types of mixed donor ligands

2 SIMPLE CHELATING LIGANDS

An excellent review of the properties, structures, and stability of numerous bi-, tri-, and polydentate ligands, including mixed donor macrocycles, has been published.[1] A review of the synthesis and properties of different polyethers, polyamines, and various combinations as precursors for mixed donor cryptands, and other macrocycles, has also appeared.[2]

2.1 Bidentate Ligands

The scope of possible mixed donor bidentate ligands is virtually limitless (Figure 2). A review of bidentate mixed donor ligands can be found, which includes mixtures of N, O, S, and Se.[3]

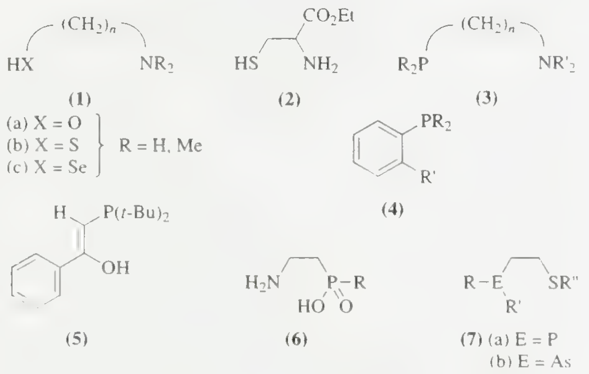


Figure 2 Simple bidentate ligands

List of General Abbreviations on back endpaper

2.1.1 Simple Donor Ligands

Amino alcohols are one of the most widely occurring examples of N,O donor ligands, and have been studied primarily because of their practical applications as bioactive compounds and catalysts. The simplest of these ligands, 2-aminoethanol, 2-aminopropanol, and the 3-aminopropanol derivatives (**1a**; R = H), usually form polynuclear complexes, a review of which has appeared.[4] In many cases, both protonated and deprotonated OH groups coexist in the same compound. The polynuclear complexes are often bridged through either the deprotonated alkoxides or via hydrogen bonding between an alcohol and alkoxide. The interaction between different metals or their oxides with amino alcohols leads to the formation of an interesting series of compounds extensively studied by Kokozey.[5] Monomeric complexes are also known, and a number of structures have been determined.[6]

Bidentate mixed donor sulfur ligands have been reviewed.[7,8] Thioalcohols and their simplest chelating agent, 2-aminoethanethiol (**1b**; R = H), were investigated in detail by Busch in the first attempts at the rational synthesis of macrocyclic ligands.[9] The deprotonated ligand forms complexes ML_2 (M = Cu, Ni, Pd),[10] and often this N,S bidentate donor forms trimeric compounds.[11] The structure of the tin(II) complex of a substituted aminoethanethiol (**2**) is shown in Figure 3.[12]

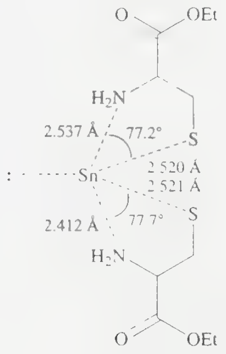


Figure 3 Structure of a Sn^{II} complex with a substituted aminoethanethiol

Selenocysteamine (**1c**) has received considerable attention in comparison with its oxo and thio analogs, and a variety of metal complexes have been reported.[13]

The coordination chemistry of aminophosphines (**3**) has been extensively developed during the last decade as a result of their importance as inert and bulky ligands for organometallic chemistry.[14] Additionally, N,P donor bidentate ligands are excellent stabilizers of unstable oxidation states of transition metals. P,O donors such as ligands (**4**) and (**5**) form complexes with platinum group metals such as Ru and Rh.[14,15] The coordination and chemical properties of different aminophosphonic acids (**6**) have been compared with their amino acid analogs.[16]

Complexes of palladium derived from the mixed donor complexes (**7a**) and (**7b**) display optical activity.[17] A fragment of the molecular structure of one of these complexes is shown in Figure 4. The ligands (**7a**) and (**7b**) are rare examples of the soft–soft P,S and As,S donor sets.[18]

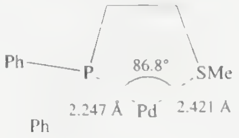


Figure 4 Structure of an optically active Pd^{II} complex with mixed donor ligands

2.1.2 Pyridine-, Pyrazine-, and Imidazole-Derived Ligands

Both 2-hydroxy- (**8a**) and 2-mercaptopyridine (**8b**) (Figure 5) form stable four-membered N,O or N,S chelates, respectively.[19] The latter ligand shows biological activity. The structure of the complex of (**8b**) with Sb^{III} is shown in Figure 6.[20]

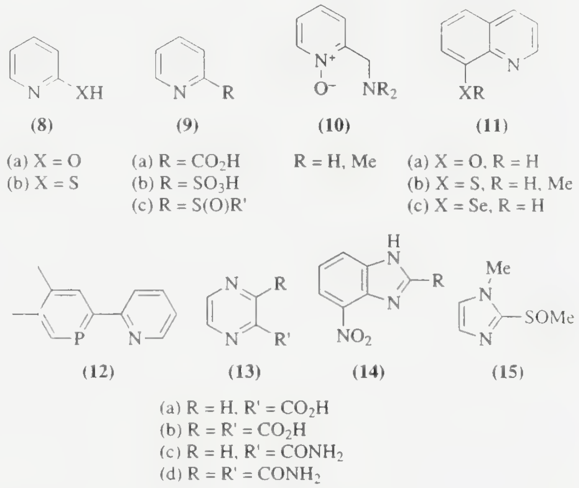


Figure 5 Pyridine-, pyrazine-, and imidazole-derived ligands

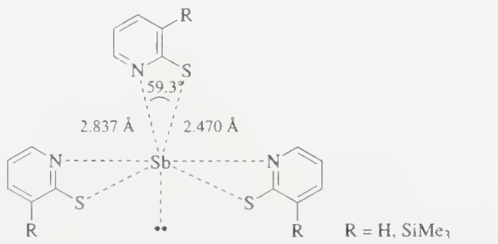


Figure 6 Structure of an Sb^{III} complex, the 2-mercaptopyridine

Another N,O ligand, 2-pyridinecarboxylic acid (**9a**), forms stable N,O bidentate chelates, and numerous complexes of this monoanionic ligand have been prepared and characterized.[21,22] Complexes with the neutral form of this ligand can be isolated from nonaqueous solutions.[21] The sulfonate analog of picolinic acid (**9b**) also acts as an N,O chelating ligand in the polymeric structure of the Ag^I complex.[23] The sulfoxide (**9c**) has been found to be a good ligand for a number of organotin compounds, and the crystal structures of several have been determined.[24]

A series of pyridine *N*-oxides (**10**) usually maintain N,O bidentate coordination with the formation of six-membered chelate rings.[25]

The series of ligands (**11a–c**) are excellent analytical reagents, and the oxine (**11a**) is probably one of the longest studied and most useful N,O bidentate ligand.[26] The crystal structure of a Mn^{III} tetranuclear complex with a bidentate oxine has recently been reported.[27] Thioxine (**11b**) forms stable, highly colored five-membered N,S chelates with metals for which the sulfides are insoluble. Usually these compounds are soluble in different organic solvents, which has provided widespread analytical applications.[9] The selenium analogs of oxine and thioxine (**11c**) have also received careful study, and the chromatographic behavior of numerous complexes has been investigated.[28]

The P,N analog (**12**) of the famous N,N bidentate ligand 2,2′-bipyridine has been prepared[29,30] and provides excellent stabilization of low-valent Pd, Pt, and Ir. Here is a combination of the hard–soft N,P donor atoms as seen earlier for the P,N ligands (**3**).

Numerous pyrazine-containing ligands (**13a–d**) are found to display N,O bidentate coordination, forming five-membered chelates with transition metals. The results of spectroscopic and structural studies have been reported.[31,32] Usually, complexes of (**13b**) and (**13d**) form insoluble 1:1 complexes with transition metal ions. Mono- and diamides of the related 2-picolinic acid and 2,3-pyrazinedicarboxylic acid at high pH demonstrate the result of deprotonation of the amide group, which leads to changing the donor set from N,O to N,N ligation.[32]

Imidazole-derived molecules can also behave as mixed donor ligands. For example, nitro compounds (**14**) have been found to act as chelating agents to a number of transition metals.[33] *N*-Methyl-2-imidazolyl methyl sulfoxide (**15**) forms stable five-membered N,O chelates with organotin(IV) derivatives.[24]

2.1.3 N-Hydroxide, Oxime, Cyanoxime, and N-Oxide Ligands

Examples of these ligands are given in Figure 7. The formation of three-membered chelate rings, while unusual, has been found for a number of mixed donor ligands.[34–40] Chelates of *N*-hydroxides such as hydroxylamine (**16a**), *N*-methylhydroxylamine (**16b**) or *N,N*-dialkylhydroxylamines are capable of forming three-membered chelate rings as shown in Figure 8.[35,36] However, when other potentially chelating groups are available, the three-membered chelate rings may or may not form, as shown in the nitrosophenol-derived structures in Figure 9.[37,38]

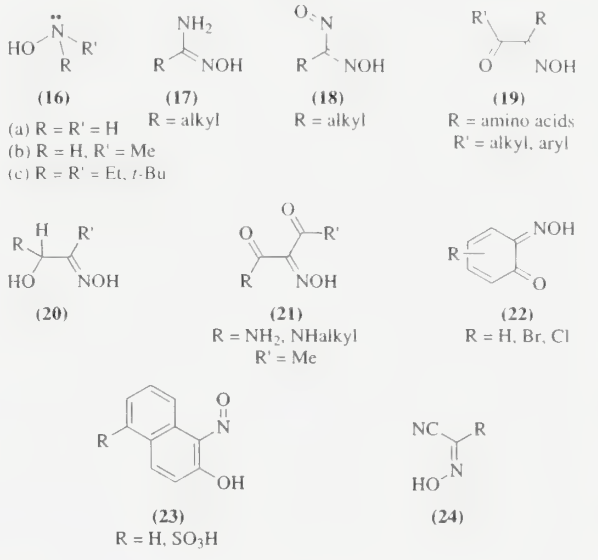


Figure 7 *N*-Hydroxide, oxime, cyanoxime, and *N*-oxide ligands

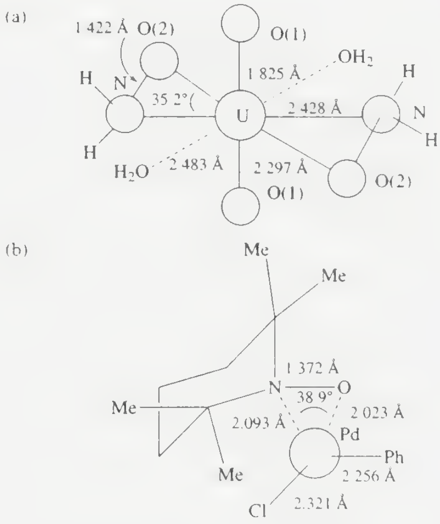


Figure 8 Three-membered chelate ring formation

The oximes (**17–22**) are examples of ambidentate groups which can be coordinated to a metal ion via both oxygen and nitrogen.[39] Nevertheless, the majority of oxime complexes are bound through nitrogen. Amidoximes (**17**) and hydroxy oximes (**20**) are widely used analytical reagents for complexation with metal ions such as copper(II).[40] The most famous is 'cupron' (**20**; R = R′ = Ph). Nitrosooximes (**18**) are also known, and the crystal structure of a tris complex of Mn^{II} has been determined

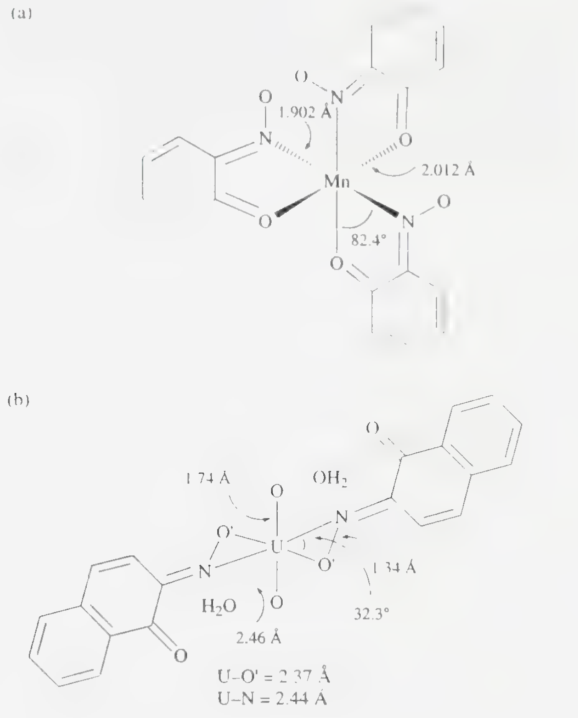


Figure 9 Nitrosophenol structures showing different forms of chelation

for R = Et.[41] Carbonyl oximes (**19**) are for the most part poor chelating ligands for bivalent transition metals. However, substitution of the alkyl group R as in (**19**) leads to new ligands combining the properties of ketones, oximes, and amino acids. Crystal structures and spectral properties of a number of these ligands have been reported.[42] A series of bidentate ligands based on malonamide oximes (**21**) have also been prepared.[43,44] In the tris complex with Fe^{II}, the simplest nitrosomalonodiamide acts as an N,O bidentate monoanionic ligand. The oxime of acetylacetone (**21**; R = Me) binds to numerous metal ions including Co^{III}, Fe^{II}, Pd^{II}, and Ni^{II}.

2-Nitrosophenols normally occur as carbonyl-oxime tautomers both in the free state and in complexes. The Mn^{III} complex with ligand (**22**; R = Br, Cl) exists as *mer* and *fac* isomers (Figure 9a).[37] On the other hand, 1-nitroso-2-naphthol exists in the nitroso form in solutions,[45] but adopts the carbonyl-oxime tautomeric form in other complexes. The structure of the UO_2^{2+} complex is shown in Figure 9b.[38] The classical Co^{III} complex of (**23**; R = H) exists as a mixture of *mer* and *fac* isomers as verified by ^1H and ^{13}C NMR.[46]

Cyanoximes (**24**) are a relatively little-studied class of ligands with the general formula N≡C–C(R)=N–OH, where R is an electron acceptor.[47,48] Examples of the commonly occurring R groups are shown in Figure 10. These ligands differ from other oximes as a result of the nitrile fragment being close to the oxime functionality. This leads to greater acidity compared to other oxime-containing ligands: the pK values are usually on the order of 4.5–5.5.

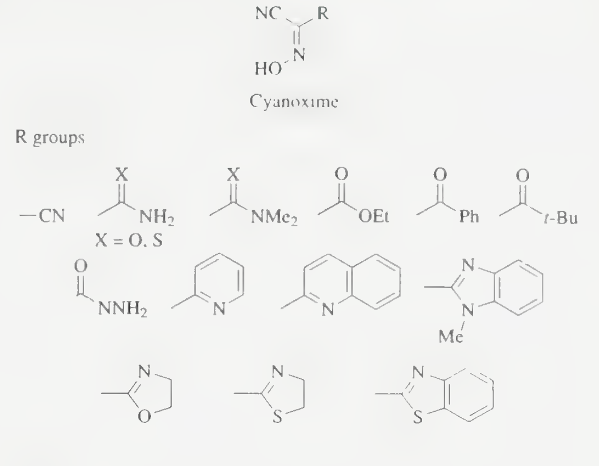
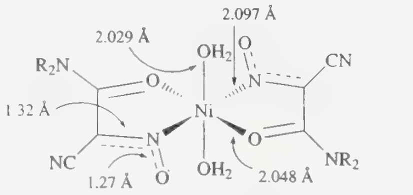
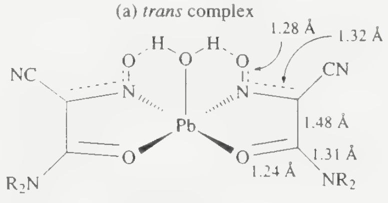


Figure 10 Cyanoximes and their commonly occurring R groups

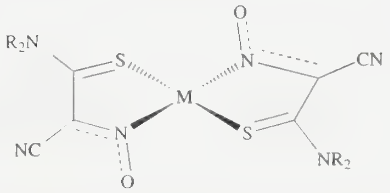
While cyanoximes often form bridging structures with monodentate coordination at two of the coordination sites, chelation is more usual for the 3d metals[49,50] as well as for Pb^{II};[51] both *cis* and *trans* geometries are observed (Figures 11a and 11b). Stabilization of the *cis* geometry is achieved by means of strong hydrogen bonding between protons of a coordinated H_2O and the oxygen atoms of the NO group.[51] Sulfur-containing cyanoximes form square planar complexes with Ni^{II} and Cu^{II} (Figure 11c).[52,53]



(a) *trans* complex



(b) *cis* complex



(c) $[MN_2S_2]$; R = Cu^{2+}, Ni^{2+}; R = H, Me

Figure 11 *Cis*- and *trans*-coordinated cyanoximes

2.1.4 Sulfur Donor Ligands

Examples of these are given in Figure 12. Thioalcohols (**25**) form similar complexes to amino alcohols. These are usually polymeric structures involving both O and S bridging. Monomeric complexes of Tc with 2-mercaptoethanol have been structurally characterized.[54]

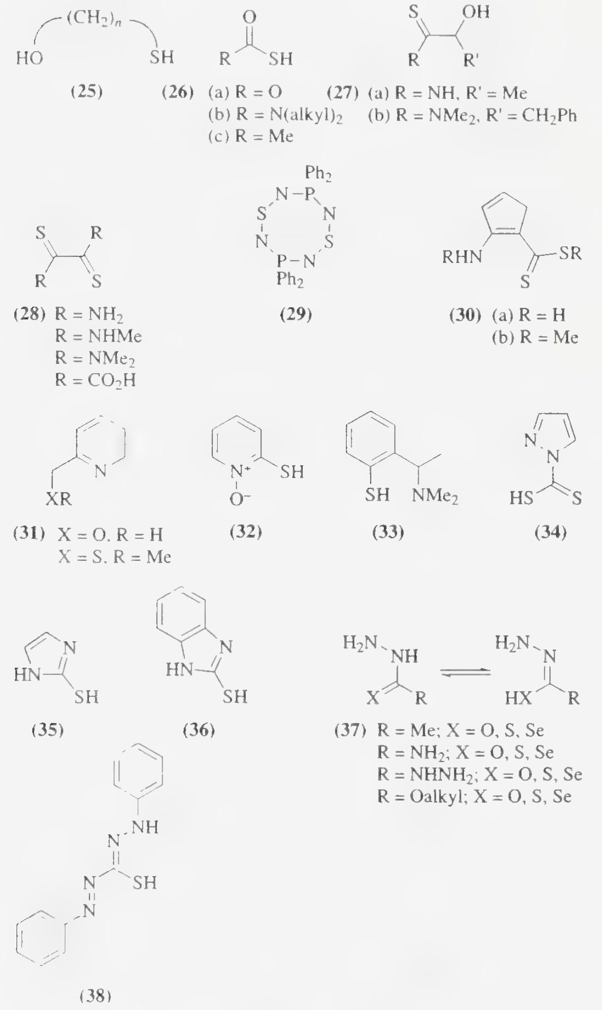


Figure 12 Sulfur ligands

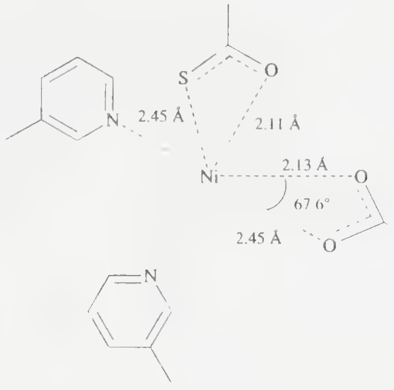


Figure 13 Examples of hard–soft O,S donors

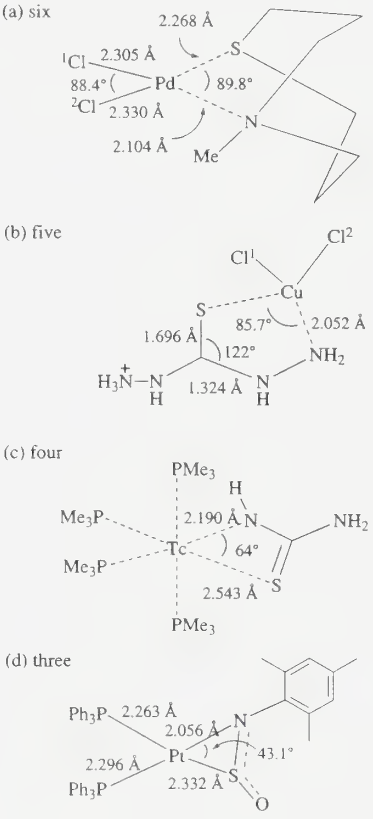


Figure 14 N,S donor ligand complexes illustrating the variety of chelate ring sizes

Examples of ligands with a hard–soft O,S donor set are thioacetic acid (**26a**)[55] (Figure 13), the monothiocarbonate anion (**26b**),[56] and the monothiocarbamates (**26c**).[57] Usually these ligands form four-membered chelate rings, but substituted thioacetic acids and their ethers, for example $HSCH_2CO_2H$ and $RS(CH_2)_2CO_2H$, form five- and six-membered chelates.[58]

Chelate ring sizes range from six to three for the N,S donors shown in Figure 14.[59–62]

Thiohydroxamic acids (**27a**,**b**) are traditional ligands for coordination chemistry, and have wide analytical and biological applications.[3] Reaction of NH_2OH with NCS^- anion in the presence of oxo-$Mo^{V,VI}$ salts leads to the formation of *N*-hydroxythiohydroxamic acid having both O,S five-membered rings and N,S four-membered rings.[63] Bidentate coordination of mono-deprotonated thiourea has been found recently in a phosphine complex of Tc^{III} (Figure 14c).[59]

The coordination of disulfide donors and related compounds to metal ions such as Co^{III} have been described in detail.[64] Usually ligands such as [HO$_2$C(CH$_2$)$_n$S]$_2$ do not coordinate in the expected tridentate fashion, but as bis-O,S bidentate chelates.

Dithiooxamide ligands are capable of coordinating either in the S,S or mixed donor modes. Derivatives of dithiooxamide such as (**28**; R = NH$_2$) form insoluble polymeric 1:1 chelates, which have analytical applications in metal ion detection.[3,65] Dithiooxalate (**28**; R = CO$_2$H) has been found as an O,S bidentate chelating ligand in complexes of Ag^I, Cu^{II}, and In^{III}.[66]

The chemistry of the cyclic compound S$_4$N$_4$ as a precursor to bidentate ligands has been intensively developed due to the strong biological activity of such ligands and their numerous complexes.[67] The ligand (**29**) reacts with Pt and Pd phosphine complexes with the insertion of the phosphine into the N$_4$S$_4$ core. Different types of mixed donor or same donor complexes can be formed, as well as dimeric compounds.

N,S bidentate chelation has been found for (**30**) and its *N*-alkylated derivatives.[68] With R and R′ as methyl groups the ligand becomes an N,S chelate, forming six-membered rings, for example with Rh^{III}.[69]

Octahedral complexes of the 3d metals with neutral ligands of (**31**) have been obtained with both O,N and S,N five-membered chelation.[3,70] The coordination chemistry of copper(I) complexes of thioethers, including (**31**; X = S, R = Me) has been reviewed.[70] The related 1-oxidopyridinium-2-thiol (**32**) has received considerable attention because of its useful biological applications.[16] In different complexes of Sn, Al, Zn, Pt, Pd, and Ni this ligand acts as a monoanionic S,O bidentate ligand with formation of five-membered rings. A unique example of the coordination of a thioether and a tertiary amine group is shown in Figure 14a.[60] A six-membered ring forms in complexes of Cu^{I,II} with the thiol (**33**), for which structures and luminescence properties have been reported.[71]

A review of pyrazole-derived ligands includes 1-thiocarbamylpyrazole (**34**).[72] Substitution of a thiol at the imidazole 2-position yields complexes which exhibit N,S four-membered ring chelation, as in (**35**) and (**36**).[73,74]

Some of the most popular N,X (X = O, S, Se) bidentate chelating ligands are different carbazide derivatives (**37**; X = O), thiosemicarbazide (X = S), and selenosemicarbazide (X = Se). A comprehensive review of the thiosemicarbazides and thiosemicarbazones has appeared.[75] The interest in these ligands derives from their pharmacological activity related to metal chelation. The coordination properties of ligands with X = O, and especially when X = S, are extensive with a wide variety of structures beyond the scope of this review. Nevertheless, a typical example of N,S chelation is shown in Figure 14b.[61] Selenosemicarbazide (**37** X = Se, R = NH$_2$) has also received intensive study, generally in comparison with its thio analog.[76]

Dithizone (**38**), among other thiosemicarbazides, has been used as a versatile analytical reagent.[62] Complexes of alkyl- and arylmercury with dithizone have been examined because of their photochromism.[77]

2.1.5 Selenium Donor Ligands

Mixed donor bidentate ligands containing selenium are not as well known as their sulfur analogs. Typical examples are shown in Figure 15.[78–83] The stability constants of complexes with the 3d metals as well as with Pd^{II} have been determined for ligand (**39**), which coordinates in an Se,N bidentate fashion.[78] Generally, the aromatic character of a heterocycle increases when selenium is placed in a ring system. The mixed Se,N donor (**40**), which has aromatic properties, is a selective analytical reagent for platinum group metals.[79] Numerous complexes of the 3d metals, Pd^{II}, Hg^{II}, Pb^{II}, Cd^{II}, and trivalent Co^{III} and In^{III} can be formed with ligand (**41**).[80]

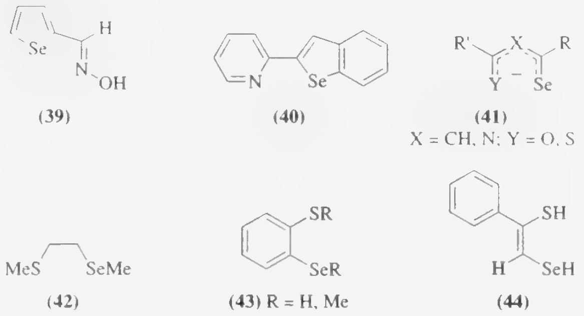


Figure 15 Selenium ligands

Complexes of the soft acids Pt^{II} and Pt^{IV} with the soft–soft Se,S bidentate ligands (**42**) and (**43**) are also known.[81,82] The ligand (**43**; R = H), when fully deprotonated, forms very stable complexes with Cu^{III} and Ni^{III} in the unusual trivalent oxidation states.[82] The Ni^{II} complex of another Se,S bidentate ligand (**44**) is product of the photochemical reaction between tetracarbonylnickel and different heterofulvalenes.[83]

2.1.6 Tellurium Donor Ligands

Compounds (**45**) and (**46**) are potential O,Te bidentate ligands (Figure 16). The chemistry of bivalent and tetravalent tellurium has been extensively developed by Sadekov.[84] Mixed donor bidentate behavior is seen for tellurium in (**45**; R = *o*-NH$_2$), with its hard–soft N,Te donor set, as shown in Figure 8b.[85]

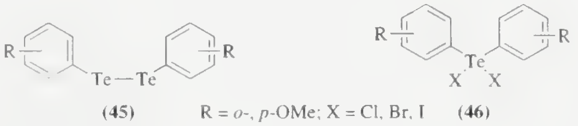


Figure 16 Tellurium ligands

2.2 Tridentate ligands

2.2.1 N$_2$O

1,2-Pyrazole derivatives of type (**48**) have been found to be very good ligands for first row transition metals (Figure 17).[86] They form two six-membered chelate rings with either N$_2$O (**48**) or N$_2$S (**56**) donor sets.

Ligand (**49**) acts as a bis tridentate chelating agent for Cu and forms dinuclear dicopper complexes.[87]

2.2.2 NO$_2$

The diethanol and dipropanol amines (**50**) and (**51**) are recognized for their strong complex-forming properties and as precursors to macrocyclic ligands.[1,2] The 2,6-pyridinedicarboxylic acid (**52**) has also received detailed study, and is a good chelating agent for determination of first row transition metals using ion chromatography.[88] 2,6-Picolinic acid has the ability to stabilize different peroxo compounds, for example vanadium(V).[89]

2.2.3 NO$_2$/NOS

Amino acid derivatives containing a methyl sulfoxide group (**54**) represent rare examples of ambidentate tridentate chelate ligands, having alternative donor sets NO$_2$ or NOS. The Pt^{II} dinuclear complex has NOS coordination with a monodeprotonated NH group.[90]

2.2.4 N$_2$S/NS$_2$

Ligands (**57**) and (**58**) have been found to be complexing agents for Cu^{II},[91] forming six- and five-membered chelating rings, respectively. The ligands (**59**) and (**60**) also have an NS$_2$ donor set. The first ligand of this series forms two six-membered chelate rings,[92] while (**60**) forms two five-membered metallocycles with copper(II), in which the Cu–N distance is significantly shorter than the Cu–S.[93]

The cyclic tetrasulfur tetranitride S$_4$N$_4$ has been found to be a good chelating agent for different transition metals.[94] Treatment of S$_4$N$_4$ with [PtCl$_2$(PR$_3$)$_2$]$_2$ or Ir(CO)Cl(PPh$_3$) leads to opening the S$_4$N$_4$ ring to yield (**61**), and complex formation with this tridentate ligand occurs. The complex of Pt^{IV} with (**61**) exists in both *mer* and *fac* isomeric forms.

2.2.5 P$_2$O/P$_2$As/PAs$_2$

The phosphorus-containing tridentate ligands (**62**)–(**64**) are excellent chelating agents for platinum group and other transition metals. In spite of the possibility of tetra or hexadentate coordination, (**62**) with its P$_2$O$_4$ donor set unexpectedly forms Pt complexes in which only P$_2$O coordination takes place.[95] The tridentate ligand (**63**) forms four-membered chelates in polynuclear complexes of monovalent Au and Ir.[96] As expected, the diarsine ligand (**64**) is a good stabilizer of low-valence states such as Ir^I;[97] the complex contains two six-membered chelating rings.

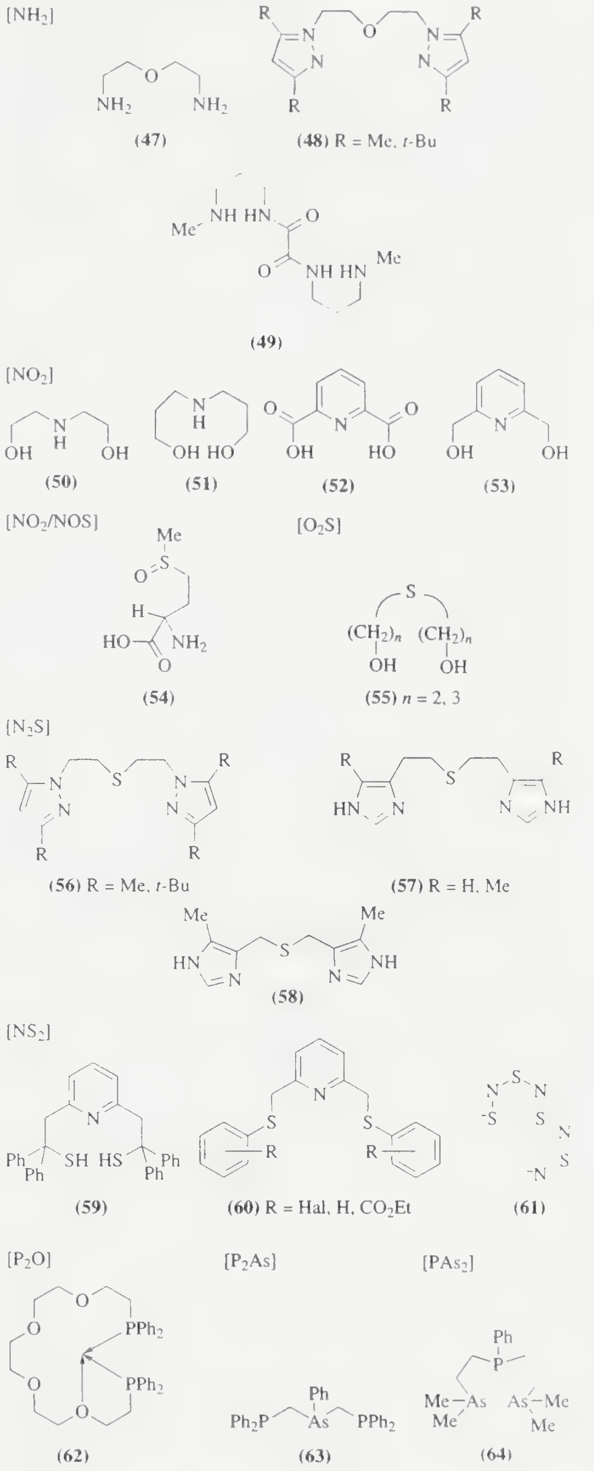


Figure 17 Tridentate ligands

2.3 Tetradentate Ligands

Figure 18 shows examples of tetradentate ligands.

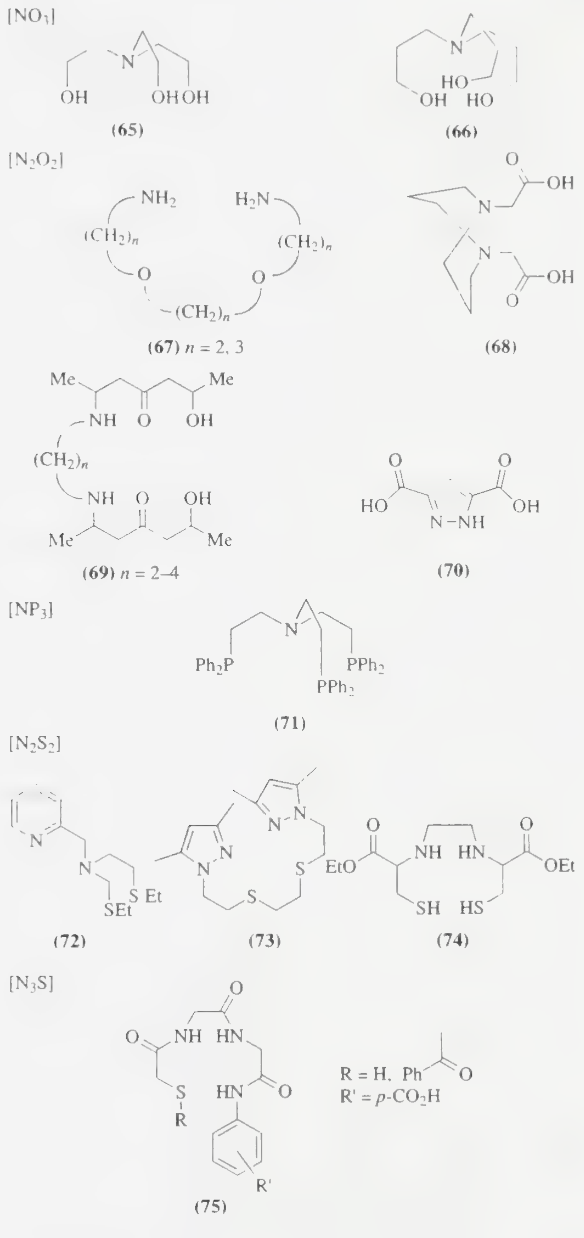


Figure 18 Tetradentate ligands

2.3.1 *NO$_3$*

The chemistry of atranes having different central atoms, e.g. (**65**) and (**66**), has received detailed study for applications in chelation.[98,99] For example, interesting pentacoordinated Ti^{IV} complexes have been obtained and characterized.[100]

2.3.2 *N$_2$O$_2$*

Ligands with terminal amino groups in different oxo ethers have been studied extensively. Ligands such as (**67**) usually exhibit N$_2$O$_2$ donor behavior. The synthesis and properties of these important precursors for synthetic macrocycles have been reviewed in detail.[1,2] The dicarboxylate (**68**) acts as a tetradentate chelating agent with the formation of one six- and two five-membered chelate rings.[101] Compound (**69**) represents a large series of ligands known as 'compartmental' ligands because they can in principle house two different metal ions. The chemistry of these interesting compounds has been reviewed.[102] 1,2-Pyrazole-3,5-dicarboxylic acid (**70**) is also capable of forming dinuclear complexes, for example in the NO bischelate complex with VO^{2+}.[103]

2.3.3 *NP$_3$*

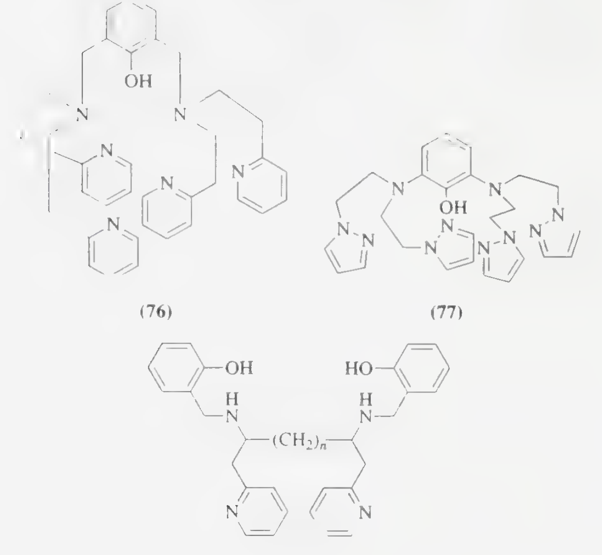
The NP$_3$ ligand (**71**) is of interest in organometallic chemistry because of its propensity to stabilize low-valence oxidation states of Rh, Ni, Co, and Ir.[104] Especially significant progress has been achieved in complexes with metal–metal bonds.

2.3.4 *N$_2$S$_2$/N$_3$S*

IR, Raman, and EXAFS studies have been used for investigation of the copper complex of ligand (**72**), with applications as a model for copper proteins.[105] Complexes of divalent copper also were also characterized with the pyrazole derivative (**73**).[106] In this complex there are two six-membered and one five-membered chelate rings, and the tertiary nitrogen atoms are not involved in coordination. These ligands also have applications in nuclear medicine, as exemplified by (**74**), which forms very stable oxo-technetium complexes.[107] Similar properties are demonstrated by (**75**) in the case of rhenium.[108]

2.4 Polydentate Ligands

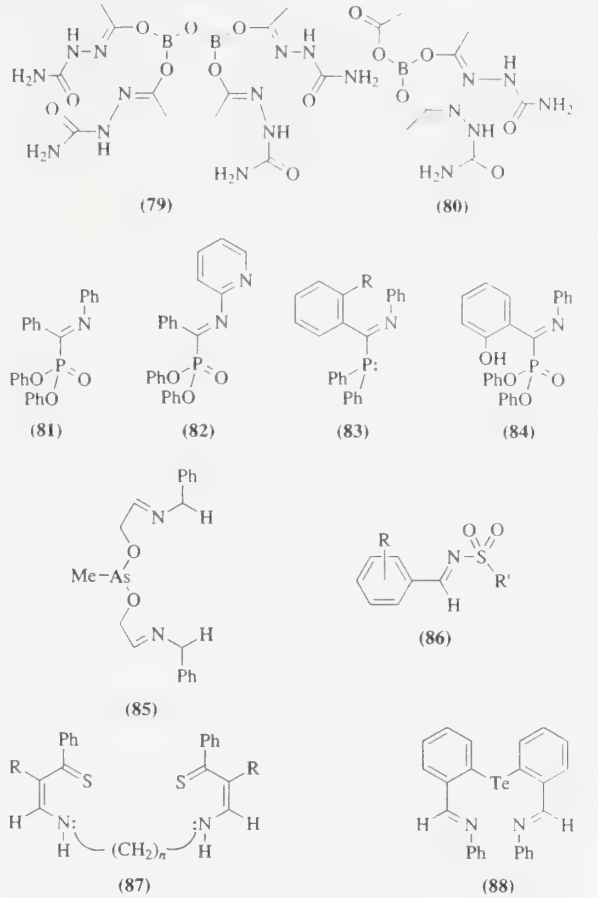
Increasing the number of donor atoms (Figure 19) does not necessarily increase the denticity of the ligand. Thus in many cases even tri- and tetradentate ligands actually form di- or polynuclear complexes. Ligands (**76**) and (**77**) are bis tetradentate ligands when they coordinate to two Cu^{II} ions via the bridging deprotonated phenol and the double set of three nitrogen atoms on each side of the molecules.[109,110] These ligands have found extremely important applications as models for some of the dinuclear copper proteins. On the other hand, in a complex of trivalent manganese [MnL](PF$_6$), (**78**) behaves in a hexadentate fashion, coordinating to just one metal ion.[111] Usually in complexes of Fe^{III}, and Mn^{II} and Mn^{III} with flexible ligands such as (**78**) the occupation of all coordination sites of one polydentate ligand is observed.



(76) **(77)**

(78) $n = 2, 3$

Figure 19 Polydentate ligands



(79) **(80)** **(81)** **(82)** **(83)** **(84)** **(85)** **(86)** **(87)** **(88)**

Figure 20 Schiff bases

3 SCHIFF BASES

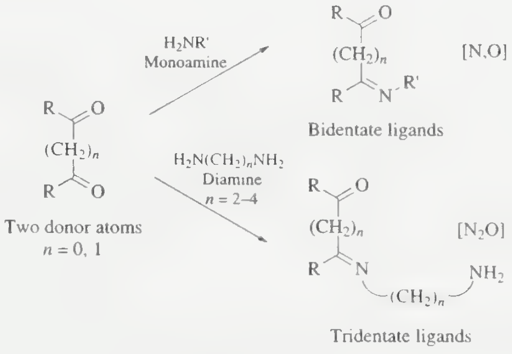
This is one of the most prevalent and important of the mixed donor systems in coordination chemistry. They result from the condensation of primary amines with ketones to give imines containing a C=N bond. An aryl group bonded to the nitrogen or carbon stabilizes the compounds, which are then known as Schiff bases.[112] The complexes are usually synthesized by carrying out the condensation reaction in the presence of a metal ion and, because the free ligands are not always stable, the template effect can be very important. An extensive review of the chemistry of mixed donor Schiff base ligands has appeared, including their synthesis, and spectroscopic and structural properties.[113] Hence this section will be limited to some of the many synthetic possibilities.

Complexes of Schiff bases have been obtained with almost all of the elements of the Periodic Table. Some of the commonly occurring mixed donor ligands are shown in Figure 20 and include heteroatoms such as B (**79**[114] and **80**[115]), P (**81–84**),[116] As (**85**),[117] and Group 16 elements (**86**,[118] **87**,[119] and **88**[120]).

It should be noted that Schiff bases with more than four donor atoms often act as tri- or tetradentate ligands, in which one or two donor atoms act as bridges. Thus many potentially penta- or hexadentate Schiff bases actually form bis-tridentate dinuclear or polynuclear complexes.[121]

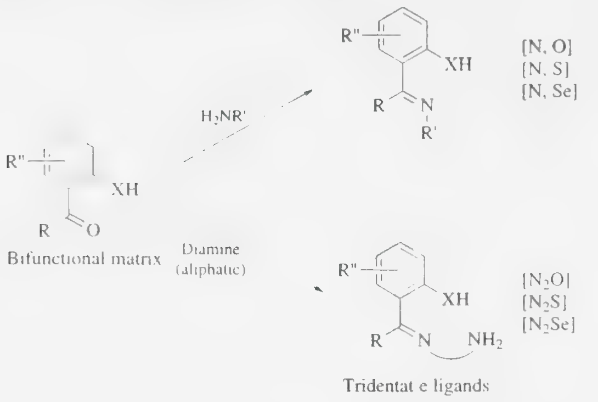
A relatively new group Schiff bases derived from salicylaldehyde, 2-hydroxynaphthaldehyde, or their respective ketones with α-amino acids has been prepared and studied.[122] Chirality in Schiff base ligands has also been treated.[123]

Although a number of the Schiff bases have primarily nitrogen donor atoms, many can display bi-, tri-, tetra-, or polydentate mixed donor capabilities. In general, the donor nature of the ligands depends both on the type of aldehyde or ketone used and the nature of primary amine or diamine. Schemes 1–3 demonstrate ways of obtaining Schiff bases of different denticities via 1:1 reactions of aldehydes with ketones to yield N,O, N,S, or N,Se donor sets.



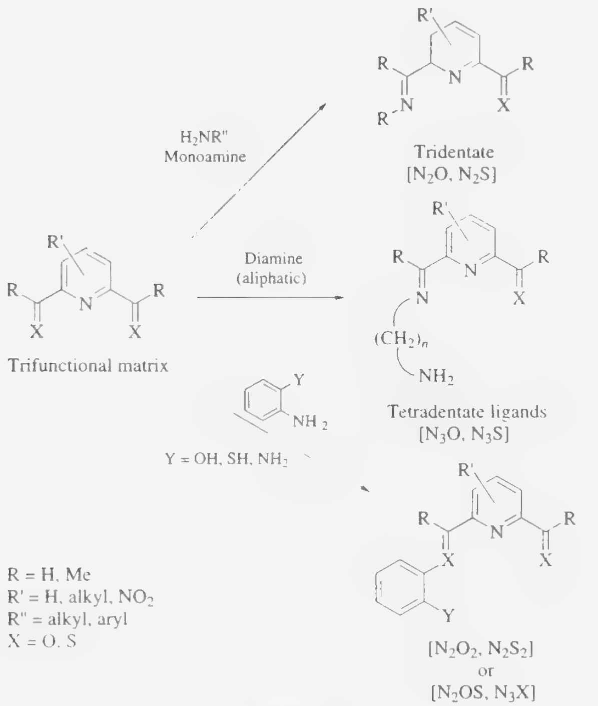
R = alkyl; R' = alkyl, aryl

Scheme 1



R = H, alkyl, aryl; R" = NO_2, Hal, alkyl; X = O, S, Se

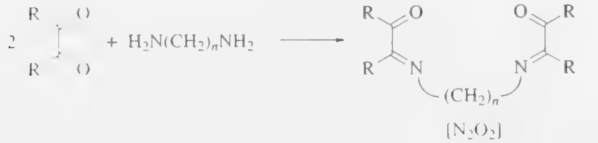
Scheme 2



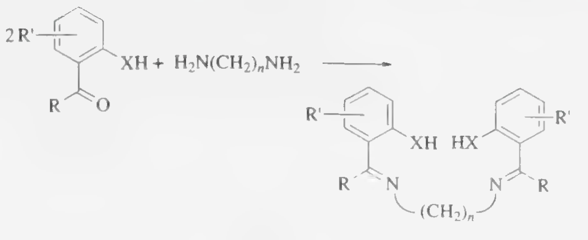
R = H, Me
R' = H, alkyl, NO_2
R" = alkyl, aryl
X = O, S

Scheme 3

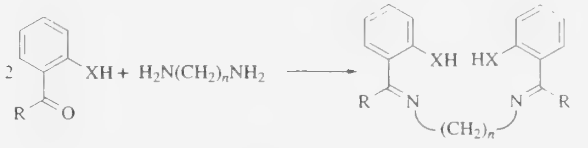
Reactions between two moles of carbonyl containing compounds and one mole of diamine lead to more complicated Schiff bases with higher denticity, as shown in Schemes 4–6.



Scheme 4



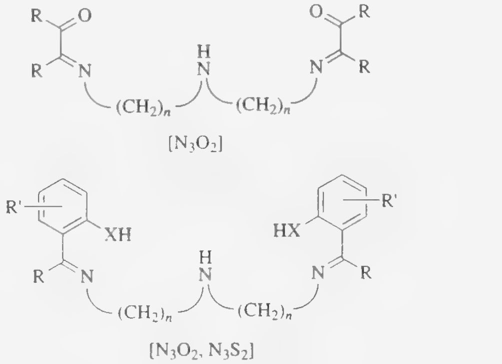
Scheme 5



R = H, alkyl; X = O, S, Se
Tetradentate ligands [N_2X_2]

Scheme 6

The use of aliphatic triamines, such as $NH_2–(CH_2)_n–NH–(CH_2)_n–NH_2$ (n = 2–4) yields a series of pentadentate ligands as shown in Scheme 7.



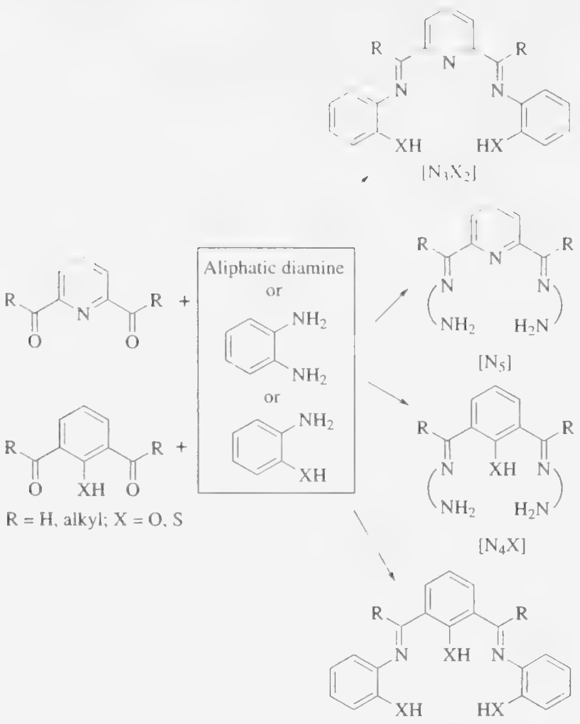
R = H, alkyl, aryl; R' = NO_2, Hal, alkyl; X = O, S

Scheme 7

The reaction of two moles of different diamines with trifunctional compounds, such as 2,6-diacetylpyridine derivatives or substituted 2,6-phenols, leads to pentadentate ligands as shown in Scheme 8.

Schiff bases are capable of demonstrating tautomerism, especially for the numerous derivatives of β-diketones or salicylaldehydes and naphthaldehydes (Figure 21). Investigations of this phenomenon have been carried out using IR, UV, and NMR spectroscopy.[113] The extensive photo- and thermochromic properties observed for different aryl-containing Schiff bases are based upon changing the degree of conjugation between functional groups as a result of conformational rearrangements.[113]

The Schiff base from benzophenone and *S*-methyl thiocarbazate shows N,S chelation. With oxotechnetium(V) (Figure 22) the result is a monoanionic Schiff base having two five-membered rings.[124]



Scheme 8

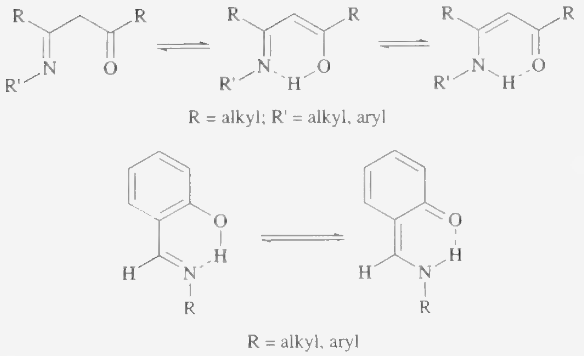


Figure 21 Tautomerism in Schiff bases

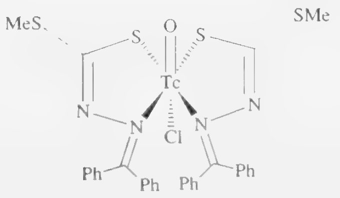
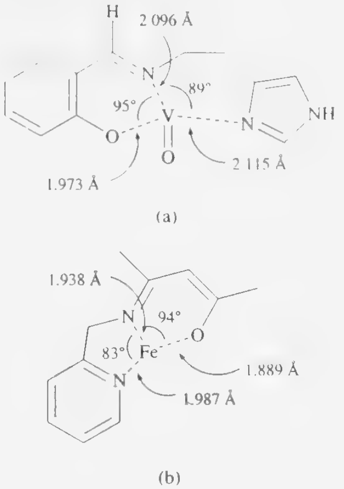


Figure 22 Structure of an oxo-Tc^V complex with a bidentate Schiff base

Tridentate Schiff bases with N_2O donor sets, which can be made from salicylaldehyde (Figure 23a)[125] or from a β-diketone (Figure 23b)[126] form stable complexes with transition metals; some of the Fe^{III} complexes exhibit spin cross-over (see *Coupling*).



(a)

(b)

Figure 23 Tridentate N_2O Schiff base complexes

In coordination compounds tetradentate Schiff bases can usually exist in different isomeric forms, and a detailed analysis of this problem has been made.[127] Figure 24 shows the structure of the Co^{III} complex in which the N_2O_2 ligand acts as doubly deprotonated anion and forms two six- and one five-membered chelates.

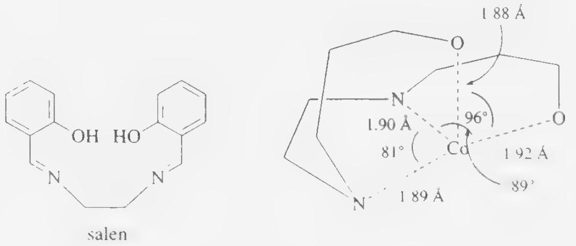


Figure 24 Tetradentate N_2O_2 Schiff base complex

Pentadentate ligands also give coordination compounds which can exist as different geometric isomers, depending on the flexibility of the overall ligand geometry. A nice example of a practically planar neutral pentadentate ligand is shown in Figure 25a for a complex of Mn^{II}.[128] The opposite possibility, a completely nonplanar, twisted, triply deprotonated pentadentate Schiff base, is found in the oxotechnetium(V) complex of Figure 25b.[129]

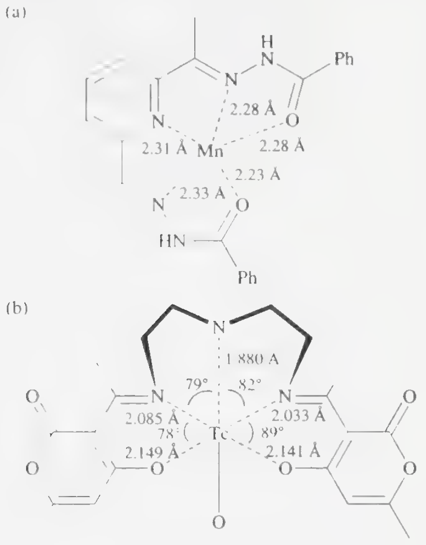


Figure 25 Pentadentate N_3O_2 Schiff base complex

A rare example of a hexadentate Schiff base complex of Ni^{II} is shown in Figure 26. Here, an N_4S_2 donor atom set is present, including two imine and two oxime nitrogen atoms.[130]

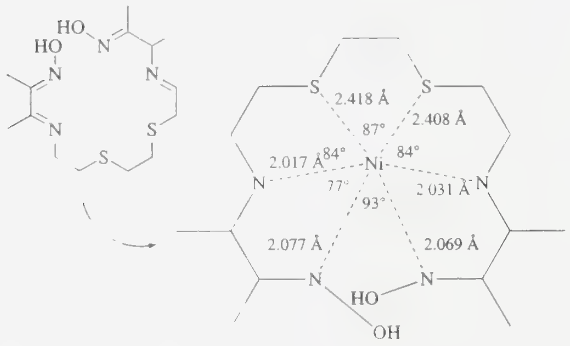
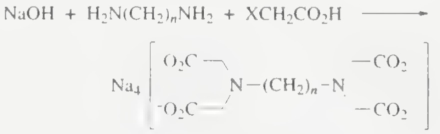


Figure 26 Hexadentate N_4S_2 Schiff base complex

4 COMPLEXONES

This large class of ligands for coordination and analytical chemistry occupies an intermediate position between amino acids and mixed donor chelating ligands. The name complexone first appeared in publications of Schwarzenbach,[131] who named this series of organic ligands containing the iminodiacetic fragment, $-N(CH_2CO_2H)_2$. Complexones form very stable complexes with almost all metal ions. These ligands will be briefly described here only from the point of view of structural chemistry as mixed donor chelating agents. More detailed information about the chemistry of complexones in solution and the stability constants of their complexes is available.[132]

The usual method of preparation of these ligands is the reaction between the respective diamine and the α-halo-substituted acetic acid in the presence of NaOH (Scheme 9). The water-insoluble free acid can be precipitated by adding HCl or H_2SO_4. Other synthetic procedures for obtaining complexones have been described.[132]

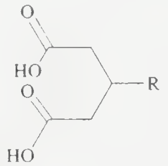


X = Br, Cl; n = 2–8

Scheme 9

Usually the formation of five- or six-membered chelates occurs both in solution and in the solid state. The strong polychelating effect is responsible for the high stability of the complexes formed, and the common M:L ratio is usually 1:1. The unusual stability and high coordination numbers (6 and 7) of the central atom can be explained in terms of the flexibility of the carbon–carbon and carbon–nitrogen chains due to the presence of sp^3 carbon atoms in most complexones.

A list of the most interesting ligands and their denticity is given in Figure 27. EDTA (Figure 28), a tetraprotic acid, has pK_i values (pK_1 = 1.99, pK_2 = 2.67, pK_3 = 6.16, pK_4 = 10.26) similar to those for other substituted EDTA derivatives, some of which are also shown in Figure 28. A number of variations are possible; for example, different chain lengths between the amine and carboxylate (**90**), phosphate substitution for the carboxylates (**91**), cyclic linkers between the two amines (**92**), substitution on both the carbon and nitrogen atoms (**93**)–(**96**),[132,133] and interspersion of different heteroatoms between the two amines.[134] A direct correlation between the pK_i values and complex stability has been found.



	Donor set
R = Me, Pr, *t*-Bu, Ph or R = NH_2, NO, NO_2, CH_2CN	O_2N
R = PhCO, $HX(CH_2)_2$, $MeX(CH_2)_2$ (X = O, S)	O_3N, O_2SN
R = $CH_2P(O)(OH)_2$ (PhDA), CH_2CO_2H (NTA)	O_3N
R = $H_2N(CH_2)_2$	O_2N_2

Figure 27 Tri- and tetradentate complexone ligands

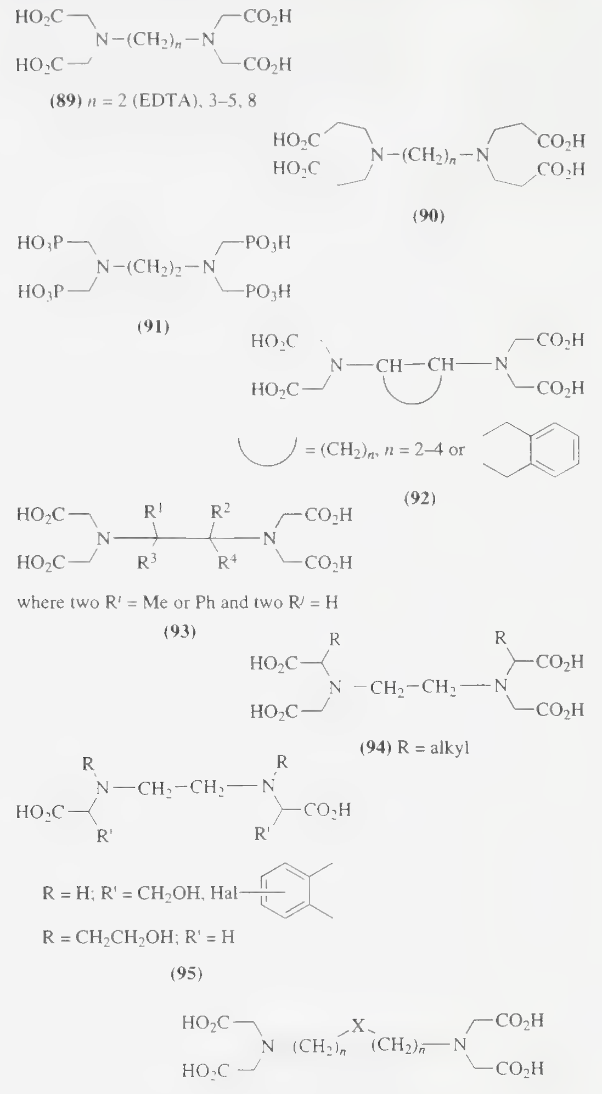


Figure 28 Hexa- and heptadentate complexone ligands

Typical structures of selected coordination compounds with complexones of different denticity are shown in Figure 29 for an NO_3 chelate of the vanadyl ion,[135] in Figure 30 for an N_2O_3 coordinated ruthenium(III) EDTA complex,[136] and in Figure 31 for two Fe^{III} chelates, one with an N_2O_4 complexone,[133] and the second with a complexone with an extended amine linkage and N_3O_4 chelation.[134]

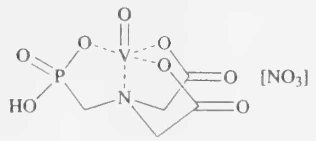


Figure 29 Structure of an NO_3 complexone with vanadyl ion

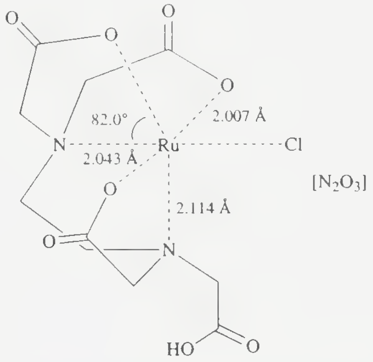


Figure 30 Structure of an N_2O_3 Ru^{III} EDTA complex

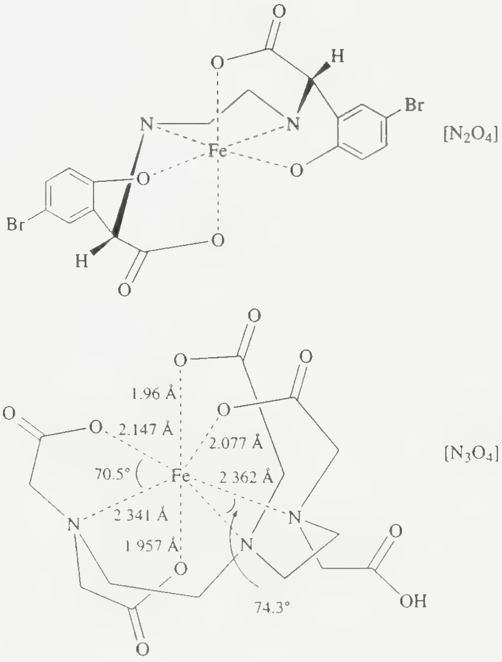
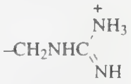
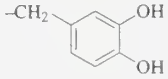
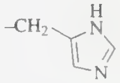
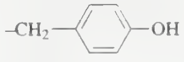
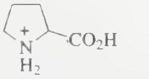
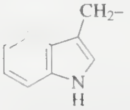


Figure 31 Structures of two Fe^{III} chelates with N_2O_4 and N_3O_4 donor complexones

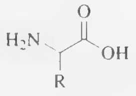
5 AMINO ACIDS

Amino acids have been of particular interest as ligands because of their importance in Nature. This area of coordination chemistry has expanded tremendously in the last 30 years, especially owing to the numerous biological applications. A list of the 24 most important and widely studied α-amino acids together with their abbreviation and potential donor atoms is given in Table 1. An in-depth treatment of the wide variety of amino acids, peptides, and their complexes is well beyond the scope of this review. Hence, only a few of the more salient points will be noted. A number of very comprehensive reviews exist.[137–141]

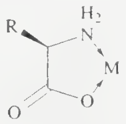
Table 1 Commonly Occurring α-Amino Acids, $RCH(NH_2)CO_2H$

Name	Common abbreviation	R	Donor atoms set
Alanine	Ala	–Me	N,O
Arginine	Arg	 $-CH_2NHC(\overset{+}{N}H_3)(=NH)$	N,O
Asparagine	Asn	$-CH_2CONH_2$	N,O; O,O
Aspartic acid	Asp	$-CH_2CO_2H$	
Cysteine	Cys	$-CH_2SH$	N,O; N,S
Dihydroxy-phenylalanine	Dopa		N,O; O,O
Histidine	His		N,N; N,O
Serine	Ser	$-CH_2OH$	N,O; O,O
Valine	Val	–*i*-Pr	N,O
Leucine	Leu	–*i*-Bu	N,O
Isoleucine	Ile	–*s*-Bu	N,O
Glycine	Gly	–H	N,O
Glutamine	Gln	$-CH_2CH_2CONH_2$	N,O; O,O
Glutamic acid	Glu	$-CH_2CH_2CO_2H$	N,O; O,O
Methionine	Met	$-CH_2CH_2SMe$	O,S; N,O
Lysine	Lys	$-CH_2CH_2NH_3^+$	N,O; N,N
Penicillamine	Pen	$-CMe_2SH$	O,S; N,O
Phenylalanine	Phe	$-CH_2Ph$	N,O
Threonine	Thr	$-CH(OH)Me$	N,O; O,O
Tyrosine	Tyr		N,O
Proline	Pro		N,O
β-Alanine	β-Ala	$H_3\overset{+}{N}(CH_2)_2CO_2H$	N,O
Tryptophan	Trp		N,O

The most significant are the α-amino acids, which have the general formula of type (**97**), where the side chain R can either participate or not in coordination, depending in part on whether it contains a coordinating heteroatom. These compounds all undergo at least two reversible deprotonation steps from the singly positively charged ammonium species to the monoanion that coordinates. The pK_a for the first ionization of the carboxylate is 2–3, while the ammonium group is deprotonated at about pH 9 to give the amino form necessary for coordination.



(97)



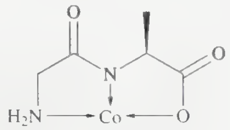
(98)

While monodentate coordination is observed through the amino group, and less commonly through the carboxyl group, the more common mode of coordination is bidentate through both the N and O atoms (**98**). The list of complexes resulting from this type of coordination is extensive. The numerous examples have a rich stereochemistry, which includes both optical (*R*, *S*) and geometrical (*cis*, *trans*, *mer*, and *fac*) isomers. When coordinating side chains are present, the situation is even more complex and higher dentate complexes can readily be obtained. Amino acids which accomplish this are histidine, cysteine, methionine, asparagine, glutamine, arginine, lysine, serine, and threonine.

Amino acids can eliminate water to form di-, tri-, and higher peptides (Scheme 10) having one or more peptide bonds, –C(O)–NH–C–. The R groups in the peptide may be the same or different and the product may not only have a linear chain, but may also be cyclic in nature. Di- and tripeptides also form stable five-membered chelates with metal ions. The denticity of the ligands usually increases due to the increased possibilities for chelate formation. At high pH the peptide nitrogen atom often loses its proton during complexation. In this case the peptide can act as a tridentate chelating dianion, such as in the complex $[Co^{III}(GlyAlaO)_2]$ (**99**).[142]

$$H_3\overset{+}{N}\text{–CHR–}CO_2^- + H_3\overset{+}{N}\text{–CHR–}CO_2^- \xrightarrow{-H_2O} H_3\overset{+}{N}\text{–CHR–}CO_2\text{–NH–CHR–}CO_2^-$$

Scheme 10



(99)

6 RELATED ARTICLES

Ammonia & N-Donor Ligands; Macrocyclic Ligands; P-Donor Ligands; S-Donor Ligands; Water & O-Donor Ligands.

7 REFERENCES

1. R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875.
2. K. E. Krakowiak, J. S. Bradshaw, and D. J. Zameska-Krakowiak, *Chem. Rev.*, 1989, **89**, 929.
3. R. S. Vagg, in 'Comprehensive Coordination Chemistry', eds. G Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, Vol. 2, Chap. 20.4, p. 793.
4. J. A. Bertrand and P. G. Eller, *Prog. Inorg. Chem.*, 1976, **21**, 29.
5. V. N. Kokozey, V. R. Polyakov, and Yu. A. Simonov, *Zh. Neorg. Khim.*, 1992, **37**, 74.
6. G. Nieuwpeert and G. C. Verschoor, *Inorg. Chem.*, 1981, **20**, 4079.
7. K. G. Orrell, *Coord. Chem. Rev.*, 1989, **96**, 1.
8. E. W. Abel, D. Ellis, K. G. Orrell, and V. Sik, *J. Chem. Res. (S)*, 1991, 222.
9. D. C. Jicha and D. H. Busch, *Inorg. Chem.*, 1962, **1**, 884.
10. D. Carrillo, P. Gourzerh, and Y. Jeannin, *Polyhedron*, 1989, **8**, 2837.
11. C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1970, **9**, 1878.
12. J. E. Anderson, S. M. Sawtelle, J. S. Thompson, S. A. K. Nguyen, and J. Calabrese, *Inorg. Chem.*, 1992, **31**, 2778.
13. Y. Sugiura, T. Kikuchi, and H. Tanaka, *Adv. Chem. Ser.*, 1980, **191**, 393.
14. A. Bader and E. Linder, *Coord. Chem. Rev.*, 1991, **108**, 46.
15. P. D. W. Boyd, J. Hope, C. L. Raston, and A. H. White, *Aust. J. Chem.*, 1990, **43**, 601.
16. E. I. Sinyavskaya, *Koord. Khim.*, 1991, **17**, 1599, (*Chem. Abstr.*, 1992, **116**, 68457).
17. P. H. Leung, A. C. Wills, and S. B. Wild, *Inorg. Chem.*, 1992, **31**, 1406.
18. S. Chooi, A. Hor, P.-H. Leung, and K. F. Mok, *Inorg. Chem.*, 1992, **31**, 1494.
19. W. Clegg, C. D. Garner, and M. H. Al-Samman, *Inorg. Chem.*, 1983, **22**, 1534.
20. E. Block, G. Ofori-Okai, H. Kang, J. Wu, and J. Zubieta, *Inorg. Chem.*, 1991, **30**, 4784.
21. D. M. Stearns and W. H. Armstrong, *Inorg. Chem.*, 1992, **31**, 5178
22. K. A. Jorgensen, *Chem. Rev.*, 1989, **89**, 438.
23. F. Charbonier and R. Faure, *Cryst. Str. Commun.*, 1981, **10**, 1129.
24. G. F. de Sousa, C. A. L. Filgueiras, M. Y. Darensbourg, et al., *Inorg. Chem.*, 1992, **31**, 3040
25. S. F. Pavkovic and J. N. Brown, *Acta Crystallogr., Sect. B*, 1982, **38**, 274
26. D. A. d'Avignon and T. L. Brown, *Inorg. Chem.*, 1982, **21**, 3041.
27. E. Bouwnan, M. A. Bolcar, E. Libby, J. Huffman, K. Folting, and G. Christou, *Inorg. Chem.*, 1992, **31**, 5185.
28. G. Schneewriss and K. H. Koenig, *Z. Anal. Chem.*, 1983, **316**, 16.
29. D. Le Flock, D. Carmichael, and L. Richard, *J. Am. Chem. Soc.*, 1991, **113**, 667.
30. B. Schmid, L. M. Venanzi, T. Gerfin, V. Gramlich, and F. Mathey, *Inorg. Chem.*, 1992, **31**, 5117
31. C. L. Klein, R. J. Majeste, L. M. Trefonas, and C. J. O'Connor, *Inorg. Chem.*, 1982, **21**, 1891.
32. G. A. Foulds, *Coord. Chem. Rev.*, 1990, **98**, 45
33. H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385.
34. K. Wieghardt, E. Hofer, W. Holbach, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1980, **19**, 2927
35. H. W. W. Adrian and A. Van Tets, *Acta Crystallogr., Sect. B*, 1978, **34**, 88.
36. M. H. Dickman and R. J. Doedens, *Inorg. Chem.*, 1982, **21**, 682
37. P. Basu and A. Chakrovorty, *Inorg. Chem.*, 1992, **31**, 4980.
38. R. Graziani, U. Casselato, P. A. Vigato et al. *J. Chem. Soc., Dalton Trans.*, 1983, 697.
39. A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1.
40. G. Rindorf, *Acta Chem. Scand.*, 1971, **25**, 774.
41. P. Couzerh, Y. Jeannin, and C. Rocchicioli-Deltcheff, *J. Coord. Chem.*, 1979, **6**, 221.
42. A. A. Dvorkin, I. O. Fritskiy, Yu. A. Simonov, et al., *Dokl. Akad. Nauk USSR*, 1990, **310**, 87, (*Chem. Abstr.*, 1990, **113**, 106821).
43. D. A. White, *J. Am. Chem. Soc.*, 1971, **10**, 233.
44. A. Sreekantan, C. C. Patal, H. Manohar, *Transition Met. Chem.*, 1981, **6**, 214.
45. S. I. Tyukhtenko, A. T. Pilipenko, N. N. Gerasimchuk, et al., *Dokl. Acad. Nauk Ukr. RSR, Ser. B*, 1987, 60, (*Chem. Abstr.*, 1989, **111**, 38645).
46. S. I. Tyukhtenko, A. T. Pilipenko, N. N. Gerasimchuk, et al., *Dokl. Acad. Nauk Ukr. RSR, Ser. B*, 1988, 57, (*Chem. Abstr.*, 1989, **111**, 69783).
47. N. N. Gerasimchuk, E. Kuzmann, A. Buki, A. Vertes, L. Nagy and K. Burger, *J. Inorg. Chim. Acta*, 1991, **188**, 45.
48. N. N. Gerasimchuk and K. V. Komasevitch, *Zh. Neorg. Khim.*, 1992, **37**, 3207.
49. V. V. Skopenko and R. D. Lampeka, *Zh. Neorg. Khim.*, 1982, **27**, 3117, (*Chem. Abstr.*, 1983, **98**, 134485).
50. K. V. Domasevitch, V. V. Skopenko, and N. N. Gerasimchuk, *Dokl. Acad. Nauk Ukr. RSR, Ser. B* 1989, 26.
51. N. N. Gerasimchuk, Y. A. Simonov, A. A. Dvorkin, and O. N. Rebrova, *Zh. Neorg. Khim..*, 1993, **38**, 266.
52. O. A. Domashevskaya, V. V. Skopenko, N. N. Gerasimchuk, G. A. Zvereva, and G. M. Larin, *Koord. Khim.*, 1990, **16**, 630.
53. K. V. Domasevitch and N. N. Gerasimchuk, *Ukr. Khim. Zh.*, 1992, **58**, 603.
54. A. G. Jones, B. V. DePamphilis, and A. Davison, *Inorg. Chem.*, 1981, **20**, 1617.
55. M. M. Borel and M. Ledesert, *Acta Crystallogr., Sect. B*, 1977, **33**, 2993.
56. T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, 1982, **21**, 2860
57. R. D. Bereman, D. M. Baird, J. D. Dorfman, and J. Bordner, *Inorg. Chem.*, 1982, **21**, 2365.
58. A. Ouchi, M. Shimoi, T. Takeuchi, and H. Saito, *Bull. Chem. Soc Jpn.*, 1981, **54**, 2290.
59. P. L. Watson, J. A. Albanese, J. C. Calabrese, et al., *Inorg. Chem.*, 1991, **30**, 4638.
60. R. Hirschon, W. K. Musker, M. M. Olmstead, and J. L. Dallas, *Inorg. Chem.*, 1981, **20**, 1701.

61. M. Lanfranchi, A. M. M. Lanfredi, A. Tiripicchio et al., *Acta Crystallogr., Sect. B*, 1978, **34**, 95.

62. R. Meij, D. L. Stufkens, and K. Vrieze, *J. Organomet. Chem.*, 1978, **155**, 324

63 K. Weighardt, E. Hofer, W. Holzbach, B. Nuber, and J. Weiss, *Inorg Chem.*, 1980, **19**, 2927.

64 J. D. Lyndon, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, 1982, **21**, 3186.

65 F. Feigi and V. Anger, in 'Spot Tests in Inorganic Analysis', 6th edn, Elsevier, London, 1972

66. W. Dietzschetal, P. Strauch, and E. Hoyer, *Coord. Chem. Rev.*, 1992, **121**, 68

67 T. Chivers, M. Edwards, A. Meestma, J. C. Van de Grampel, and A. van der Lee, *Inorg. Chem.*, 1992, **31**, 2156.

68 S. K. Mondal, R. Roy, and K. Nag, *J. Indian. Chem., Sect. A*, 1981, **20**, 982

69. Gideon J. J. Steyn, A. Roodt, and J. G. Leipoldt, *Inorg. Chem.*, 1992, **31**, 3477

70. F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 115.

71. D. M. Knotter, G. Blasser, J. P. M. Van Vilet, and G. Van Koten, *Inorg. Chem.*, 1992, **31**, 2196.

72. S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.

73. E. S. Raper and P. H. Crackett, *Inorg. Chim. Acta*, 1981, **47**, 159.

74. W. O. Foye and J. R. Lo, *J. Pharm. Sci.*, 1972, **61**, 1209.

75. M. J. M. Campbell, *Coord. Chem. Rev.*, 1975, **15**, 279.

76. A. T. Hutton, H. M. N. H. Irving, and L. P. Nassimbeni, *Acta Crystallogr., Sect. B*, 1980, **36**, 2064.

77 D. R. Goddard and S. O. Ajayi, *J. Chem. Soc. (A)*, 1971, 2673.

78. L. S. Bark and D. Griffin, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3811.

79. L. S. Bark and D. Brandon, *Talanta*, 1967, **14**, 759.

80. E. Uhleman, E. Ludwig, W. Huebner, and R. Szargan, *Z. Chem.*, 1983, **23**, 32.

81. E. W. Abel, K. S. Bhargava, K. Kite, K. G. Orrell, V. Sik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1982, 583.

82. C. G. Pierpont, B. J. Gorden, and R. Eisenberg, *Chem. Commun.*, 1969, 401.

83. E. Fanghaenel and H. Poleschner, *Z. Chem.*, 1979, **19**, 192.

84 I. D. Sadekov, *Usp. Khim.*, 1987, **56**, 343, (*Chem. Abstr.*, 1987, **106**, 60224); *Sulfur Rep.*, 1990, **5**, 359.

85. R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie, and F. H. Musa, *J. Chem. Res. (S)*, 1979, **145**, 1901.

86 C. Kutal, *Coord. Chem. Rev.*, 1990, **99**, 218.

87. F. Lloret, M. Julk, J. A. Real, et al., *Inorg. Chem.*, 1992, **31**, 2956.

88. J. T. Tarter, 'Ion Chromatography', Dekker, New York, 1987.

89. K. A. Jorgensen, *Chem. Rev.*, 1989, **89**, 438.

90. W. A. Freeman, *J. Chem. Soc., Chem. Commun.*, 1977, 607.

91. F. Mani, *Coord. Chem. Rev.*, 1992, **000**, 342.

92. R. H. Holm, *Chem. Rev.*, 1987, **87**, 1421.

93. F. Teixidor, G. Sanchez-Castello, N. Lucena, L. Escriche, R. Kiverkas, M. Sundberg, and J. Casalo, *Inorg. Chem.*, 1991, **30**, 4931.

94 M. G. Barker, *Coord. Chem. Rev.*, 1990, **103**, 184.

95. V. Ashima, M. L. Webster, and G. M. Gray, *Inorg. Chem.*, 1992, **31**, 2580.

96. A. L. Balch and J. V. Catalano, *Inorg. Chem.*, 1991, **30**, 1302.

97 N. M. Doherty and N. W. Hoffman, *Chem. Rev.*, 1991, **91**, 553.

98. J. Woning and J. G. Verkade, *J. Am. Chem. Soc.*, 1991, **113**, 944.

99. M. A. Laraway and J. G. Verkade, *J. Am. Chem. Soc.*, 1990, **112**, 9421.

100. W. M. P. B. Menge and J. G. Verkade, *Inorg. Chem.*, 1991, **30**, 4628.

101 W. E. Broderick, K. Kanamori, R.D. Willet, and J. I. Legg, *Inorg Chem.*, 1991, **30**, 3875

102. H. Adams, N. A. Bailey, D. E. Fenton, M. S. Gonzalez, and C. A. Phillips, *J. Chem. Soc., Dalton Trans.*, 1983, 371

103 C. W. Hahn, P. G. Ramusen, and J. C. Bayon, *Inorg. Chem.*, 1992, **31**, 1963.

104. C. Mealli, C. Ghilardi, and A. Orlandini, *Coord. Chem. Rev.*, 1992, **120**, 361.

105. J. Han, N. J. Blackburn and T. M. Loehr, *Inorg. Chem.*, 1992, **31**, 3223.

106. W. G. Haanstra, M. Fernaucta, and J. de O. Cabral, *Inorg. Chem.*, 1992, **31**, 3150.

107. D. S. Edwards, E. H. Cheeseman, and M. W. Watson, *Technetium Rhenium Chem. Nucl. Med.*, 1990, **3**, 433

108. L. Hansen, R. Cini, A. Taylor, et al., *Inorg. Chem.*, 1992, **31**, 2801.

109. M. Mahroof-Tahir, N. N. Murty, K. D. Karlin, N. J. Blackburn, S. N. Shaikh, and J. Zubieta, *Inorg. Chem.*, 1992, **31**, 3001.

110. S. Schindler, D. J. Szalda, and C. Creutz, *Inorg. Chem.*, 1992, **31**, 2255.

111. A. Neves, S. M. D. Erthal, I. Veneato, A. Ceccato, Y. P. Mascarenhas, O. R. Nasimento, M. Horner, and A. A. Batista, *Inorg. Chem.*, 1992, **31**, 4749.

112. H. Schiff, *Ann. Chim. (Paris)*, 1864, **131**, 118.

113. M. Calligaris and L. Randaccio, in 'Comprehensive Coordination Chemistry', eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, Vol. 2, Chap. 20.1, p. 715.

114. J. P. Tandon, *J. Indian Chem. Soc.*, 1986, **63**, 451.

115. V. P. Singh, R. V. Singh, and J. P. Tandon, *Synth. React. Inorg. Metal-Org. Chem.*, 1989, **19**, 669.

116. A-E. Ibragim, E. Ibrahim, and R. Farag, *Gazz. Chim. Ital.*, 1988, **118**, 141.

117. P. Aslamidis and K. Friedhelm, *Chem.-Ztg.*, 1987, **111**, 273.

118. A. K. Varshney and P. S. Verma, *Synth. React. Inorg. Metal-Org. Chem.*, 1989, **19**, 75.

119. M. S. Korobov, Yu. Olehnovich, and M. Konstantinovski, *Koord. Khim.*, 1989, **15**, 1622, (*Chem. Abstr.*, 1990, **113**, 16852).

120. V. I. Minkin, I. D. Sadekov, and A. A. Makarenko, *Zh. Oshch. Khim.*, 1988, **58**, 1684, (*Chem. Abstr.*, 1989, **110**, 212694).

121. B. F. Hoskins, R. Robson, G. A. Williams, and J. C. Wilson, *Inorg. Chem.*, 1991, **30**, 4160.

122. L. Casella, M. Gubotti, A. Pintar, L. Messoori, A. Rockenbauer, and M. Gyor, *Inorg. Chem.*, 1987, **26**, 1031.

123. M. Tabcheh, A. El-Achbar, L. Pappalardo, M.-L. Roumestant, and P. Viallefont, *Tetrahedron*, 1991, **47**, 4611.

124. J. G. H. Du Preez, T. T. A. Gerber, and O. Knoesen, *J. Coord. Chem.*, 1987, **16**, 285.

125. Ch. R. Cornman, J. Kampf, M. S. Lah, and V. L. Pecoraro, *Inorg Chem.*, 1992, **31**, 2035.

126. H. Oshio, K. Toriumi, Y. Maeda, and Y. Takashima, *Inorg Chem.*, 1991, **30**, 4252.

127. M. Caligaris, G. Manzini, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1972, 543.

128. C. Lorenzini, C. Pelizzi, G. Pelizzi, and G. Pradieri, *J. Chem. Soc., Dalton Trans.*, 1983, 721

129. S. Liu, S. J. Rettig, and C. Orvig, *Inorg. Chem.*, 1991, **30**, 4915.

130. S. B. Choudhury, D. Ray, A. Chakravorty, *Inorg. Chem.*, 1991, **30**, 4354.

131. G. Schwarzenbach, E. Kampitsch, and R. Steiner, *Helv. Chim. Acta*, 1945, **28**, 1133.

132. G. Anderegg, in 'Comprehensive Coordination Chemistry', eds. G. Wilkinson, R.D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, Vol. 2, Chap. 20.3, p. 777.

133. R. B. Lauffer, A. C. Vincent, and S. Padmanabhan, *J. Am. Chem. Soc.*, 1987, **109**, 2216.

134. D. C. Finnen, A. A. Pinkerton, W. R. Dunham, R. H. Sands, and M. O. Funk, Jr., *Inorg. Chem.*, 1991, **30**, 3960.

135. D. P. Riley, D. L. Fields, and W. Rivers, *Inorg. Chem.*, 1991, **30**, 4191.

136. M. M. Taqui Khan, D. Chatterjee, R. R. Merchant, P. Paul, S. H. R. Abdi, D. Srinivas, M. R. H. Siddiqui, M. A. Moiz, M. M. Bhadbhade, and K. Venkatasubramarian, *Inorg. Chem.*, 1992, **31**, 2711.

137. 'Metal Ions in Biological Systems', ed. H. Sigel, Dekker, New York, 1974, Vol. 1.

138. 'Aminoacids, Peptides, and Proteins', ed. R. C. Sheppard, Royal Society of Chemistry, London, 1985, Vol. 16.

139. S. H. Laurie, in 'Comprehensive Coordination Chemistry', eds. G. Wilkinson, R.D. Gillard, and J.A. McCleverty, Pergamon, Oxford, 1987, Vol. 2, Chap. 20.2, p. 739.

140. P. A. Manoric, 'Mixed Ligand Metallocomplexes in Chemistry, Biology and Medicine', Naukova Dumka, Kiev, 1991.

141. G. G. Smith, A. Khatib, and G. S. Reddy, *J. Am. Chem. Soc.*, 1983, **105**, 293.

142. G. G. Smith, A. Khatib, and G. S. Reddy, *J. Am. Chem. Soc.*, 1983, **105**, 293; M. T. Barnet, H. C. Freeman, D. A. Buckingham, I.-N. Hsu, and D. Van der Helm, *Chem. Commun.*, 1970, 367.

Mixed Oxidation States

A substance in which the same element, commonly a metal, has two different oxidation states; for example, Prussian Blue, $KFe^{II}[Fe^{III}(CN)_6]$. Such a compounds is often highly colored because of an *Intervalence Transfer Transition*.

Mixed Valence Compounds

John P. Fackler, Jr.
Texas A&M University, College Station, TX, USA

Glossary

Delocalized valency: valency not confined to single atomic center
Fourfold symmetry: rotation by 90° produces an identical arrangement
Ligand fields: the perturbation of the electronic structure of an ion or atom by the surrounding ligands
Superconductivity: electrical conductance without energy loss
Valency: the electronic structure of a compound or metal ion

Abbreviations

Ln = a general abbreviation for lanthanide elements; PKS model = the model developed by Piepho, Krausz, and Schatz for treating the electronic structure of mixed valence compounds.

1 INTRODUCTION

A survey of the literature[1] from 1980 to 1993 shows that over 2500 articles have been published during this period which contain 'mixed valence' or 'mixed valent' in the title. Thus the 1967 statement of Robin and Day[2] that stated mixed valence chemistry represented a 'neglected class of inorganic compounds' is no longer valid. Mixed valency, the name used to describe compounds containing ions of the same element in two different oxidation states, has come of age.[3,41]

Mixed valence compounds have been used since antiquity as components in pigments such as the oxides of Fe, compounds which can produce red to black colorations in *Ceramics*. Today, biologists, as well as chemists, physicists, and geologists, study mixed valence materials. Biological systems have given us an opportunity to explore the ways in which mixed valency is used to store and transfer energy, convert light to chemical reactivity in photosynthesis, and in general utilize mixed valency in redox reactions. Physicists and chemists have been particularly

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

January 6, 1995

Dr. Nick Gerasimchuk
Meadowbrook Apartment
Bristol Terrace, DD317
Lawrence, Kansas 66049

Dear Nick,

A long trip to Europe has delayed my responding to your most interesting letter of November 19th, and thanking you for that chapter in the Encyclopedia of Inorganic Chemistry.

I don't think that you should have any difficulties getting a green card, and I enclose my letter of recommendation.

All good wishes for 1995.

Sincerely,

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

January 6, 1994

TO WHOM IT MAY CONCERN:

I have known Dr. Nick Gerasimchuk, now living in Lawrence, Kansas, for the last six years.

When I first met him, he was professor of inorganic chemistry at Kiev State University. At that time, I was chairman of Sigma-Aldrich Corporation, a publicly owned chemical company headquartered in St. Louis.

I met Dr. Gerasimchuk in Budapest to discuss collaboration between him and his group in Kiev and Sigma-Aldrich. That collaboration developed very fruitfully.

I am convinced that Dr. Gerasimchuk is a very able chemist and a straightforward and responsible man whose work in inorganic chemistry in the Department of Chemistry at Kansas University in Lawrence has been very productive. For instance, he has recently contributed a chapter on his research for the Encyclopedia of Inorganic Chemistry. I can recommend him highly, both professionally and as a person.

Alfred Bader

Dr. Nick Gerasimchuk
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November, 19 /1994

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin; 53211

Dear Alfred and Isabel Bader,

Almost one month past since Andrew and Taras visited us. Enclosed please find some photos about their visit, and which show nice warm October days in Lawrence.

We had a lot of discussions about everything, including our business with ALDRICH. I'm very glad that our joint efforts several years ago produced so nice results now. We have got recently from our friends new set of 120 new compounds for ABC library and I'll proceed them to Bob Wandler soon.

In the meantime we are doing well in the lab, past all cumes with an excellent scores and in a very short time. We both work for Prof. Kristin Bowman-James (Mertes) at the Inorganic Chemistry Division of the University of Kansas. Professor Leo Ohrimovich should know our advisor very well because they work in the same field of Chemistry - *Macrocyclic Ligands and their Complexes.*

In the nearest future I'm going to apply for the permanent resident status (Green Card), and I need your advice in this question. May I ask you to be so kind to step forward as my referee? In this case we will need your recommendation letter. According to existing regulations I need to meet certain criteria, and with my background, Russian Ph.D., list of publications, participation in different conferences and 8 years teaching experience there will be no problem to meet them. My *Personal and Professional Data* are enclosed. At the same time probably the most important thing is letters from American professional people who know me.

I do not have any experience in such questions, and your advice is very valuable for me.

Thanks for your attention and I'm sorry for giving you troubles.
With the best wishes, yours sincerely
Nick Gerasimchuk.

Personal and Professional Data

Name: **Nikolay N. Gerasimchuk**

Born: August 26, 1959

Education:

1976: High school graduation (Vinnitsa, Ukraine)

1976-1981: Studies, and graduation with MS degree from the Shevchenko State University in Kiev, majoring in Inorganic Chemistry

02/18/1980: Getting *Gold Medal Award* of Ukrainian Academy of Sciences for the best student research "Investigation of salts of nitrosodiamidocyanmethanid-ion and its sulphur analog"

1981-1984: Post-graduate studies under the direction of Prof. V.V.Skopenko (Department Head). The dissertation, entitled "Synthesis and Investigation of Iron(II) Complexes which Include Non-linear Acidoligands of the Methanide- and Amide- types", dealt with anaerobic preparation of unstable Fe(II) complexes with the anions of C-H, and N-H acids, and with neutral heterocyclic amines. Compounds obtained were studied by means of IR, NMR, Mossbauer, UV-Vis spectroscopy Thermogravimetry and Magnetochemistry.

03/25/1985: Defense of the above dissertation, and obtaining the "Candidate of Science" degree (the Soviet equivalent of Ph.D.)

Working Experience:

1985-1986: Research Associate at the Inorganic Chemistry Division of Chemistry Department.

1986-1989: Assistant Professor in the Department of Inorganic Chemistry at the Kiev State University, organizing there in 1987 a laboratory for Mossbauer spectroscopy and magnetochemistry.

1989-1990: Visiting Researcher at the University of Szeged (Hungary), under the direction of Prof., Dr. K.Burger.

1990: Teaching, and doing research back in Kiev, supervising graduate and three undergraduate students, who are working on problems of complexation of p-, d-, f-

metals with cyanoxime anions.

1991: Getting of the Associate Professor position at Kiev University, Chemistry Department.

1991-1992: Continue teaching and doing research at the above university and laboratory.

1993: Joining the research program at the Chemistry Department of Kansas University in Lawrence.

Publications:

Authored or co-authored 46 articles since 1982, and presented 13 posters.
Participated in writing with Prof. K.Bowman-James and contributed a chapter into *Encyclopedia of Inorganic Chemistry* (v.5. John Wiley & Sons, 1994)

Applications of Research :

The five former USSR patents about antimicrobial activity of cyanoximes and their complexes have been registered.

Areas of Interest:

Coordination chemistry of ambidentate ligands with p-, d- metal ions, macrocyclic ligands and their complexes. Physical methods.

Courses taught:

General Chemistry. Chemistry of elements. Introduction course of Coordination Chemistry. Physical methods of investigation of inorganic and complex compounds (Chapters: Magnetochemistry, Mossbauer spectroscopy, NMR)

Conferences and Meetings attended, Lecturing:

1981: Annual Ukrainian Conference on Inorganic Chemistry. Simferopol. September, 28-October,5. Ukrainian Academy of Sciences, Simferopol State University.

1982: Ukrainian Conference of Young Scientists. Odessa, May 12-14. Odessa State University, Ukraine.

1983: All-Union (USSR) Conference on Physical Methods in Inorganic and Coordination Chemistry. October 26-November 2. Kishineu, Institute of Chemistry of Academy of Sciences. Moldova.

1985: All-Union (USSR) Tchugaev's Conference on Inorganic Chemistry. September 8-12, Kiev University, Ukrainian Academy of Sciences. Kiev.

1986: All-Union (USSR) IV Simposium on Spectroscopy of Coordination Compounds. October 21-26. Rostov-on-Don; USSR Academy of Sciences, Rostov State University.

1987: November 18: Invited Lecturer for a talk at the Chemistry Department of Leningrad State University on *Application of the NMR 14-N spectroscopy in Organic and Inorganic Chemistry.*

1988: All-Union (USSR) IV Simposium on Spectroscopy of Coordination Compounds. October 23-29. Rostov-on-Don; USSR Academy of Sciences, Rostov State University.

1992: VI Conference (with International participation) on Crystallochemistry of Inorganic and Complex Compounds. Lvov, September 21-25. Ukraine.
Invited Lecturer at the Laboratory of Nuclear Chemistry of Lorand Etvos University; December, 6. Budapest, Hungary.

1993: Invited Lecturer at the Chemistry Department of BYU; January,7. Provo, Utah. USA.
Chemistry Department of KU; January, 26. Lawrence, Kansas. USA.
Chemistry Department of University of Utah; June, 3. Salt-Lake City. USA.

1994: 2nd KAN-SYN/EPSCOR Workshop. Manhattan, May 23-25. Kansas State University. USA.
XIX International Simposium on Macrocyclic Chemistry. Lawrence, June 12-17. The University of Kansas, USA.
Midwest Regional Meeting of the American Chemical Society. Kansas-City, November, 3.

Practical skills:

11 years experience in the field of anaerobic synthesis of inorganic and coordination compounds. Complicated experiments, vacuum technique, cryostates. Knowledge and interpretation of results of physical methods such as IR, NMR, UV-Vis, Mossbauer spectroscopy, magnetochemistry, thermal analysis, x-ray diffraction. Work on PC with different software, including Windows, Lotus, CW, ChemWindow, *etc.*

March 20, 1995

Dr. Nick Gerasimchuk
Meadowbrook Apts.
Bristol Terrace DD317
Lawrence, KS 66049

Dear Nick:

Thank you for your letter of March 15th.

Isabel and I plan to drive down to Chicago this Thursday to pick up Andy and his friend and then bring them back to Milwaukee. Isabel and I will be visiting our first granddaughter in Pennsylvania this weekend; we have not seen her since she was born in October. We will then be back on Monday and hope to have a good deal of time to chat with Andy about his efforts.

Best regards,

AB/cw

Dr. Nick Gerasimchuk
chemist
Meadowbrook Apt.,
Bristol Ter., DD317
Lawrence, KS, 66049.
phone home (913) 842-0711

March, 15 /1995

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin; 53211

Dear Alfred and Isabel Bader,

Thank you very much for you letter of March, 2. I have received the respective letter from ALDRICH concerning my questions about a week later than your letter came. Thanks again. It seems to me that things may go pretty well.

Probably you already know that Andrew and Igor Miroshnichenko arrive in Chicago O'Hare airport on March 23. I have direct flight from Kansas City to Milwaukee by *Midwest Express* at 8:40 a.m. on Friday, March 24. Also, I have a reservation for a car rent at Hertz in Milwaukee. Thus, in the best case I will be able to get ALDRICH main office at 11 a.m. for the meeting and discussion. My flight back to Kansas will be Sunday, March 26 at 3:25 p.m.

I hope very much that we can meet during these days.

I look forward to see both of you soon.

With the best wishes, yours sincerely
Nick Gerasimchuk.

Nick Gerasimchuk

Dr. Nick Gerasimchuk
chemist
Meadowbrook Apt.,
Bristol Ter., DD317
Lawrence, KS, 66049.
phone home (913) 8420411

September,29 /1994

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin; 53211

Dear Dr. Bader,

Thank you for your letter from September 26, which I just received.

Of course I had and will have several more conversations with Andrew by phone and fax. In most cases my attempts to send a fax message were successful after 20-30 min. trying. However, couple of weeks ago I was not able to send him fax also. It took me two days, before I could get through. Why it became a problem I have no idea.

In the meantime I wait from them more detailed information about their visit. As far as I concern Andrew and Taras have got some problems with visas and tickets. Hope that they overcome these temporary problems and we can see them soon.

My next set of samples for ABC collection is about to be ready, and I hope to send it to Bob Wandler next week. There are more than 40 excellent amino- and amidoshugars, esters which play an essential role in non-enzymatic hydrolysis of several types of important proteins.

Sorry, please, for my previous sending of letters without a phone number. We can be reached by this number at home from 8 a.m. to 10 a.m. or after 10 p.m. The rest of the time we are in the lab, which phone number is (913) 864-42-78.

With the best wishes to Isabel and Bob Wandler.
Sincerely yours,

Nick Gerasimchuk

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

September 26, 1994

Dr. Nick Gerasimchuk
Meadowbrook Apartment
Bristol Terrace, DD317
Lawrence, Kansas 66049

Dear Nick,

Thank you for your long letter, sent without your telephone number.

We so look forward to seeing Andy in Milwaukee next month. Isabel, Bob Wandler and I plan to drive to O'Hare to pick them up, and then have many good discussions about their efforts.

I have had a terrible time trying to contact Andy. He has sent me several faxes which I have received safely, but when I try to fax him at each of the two fax numbers he has, I simply cannot get through. I have tried at least a dozen times, always to no avail.

It has occurred to me that you might be speaking to him by telephone, in which case I would like to ask you to let him know how welcome he will be.

All good wishes.

Sincerely,

Dr. Nick Gerasimchuk
chemist
Meadowbrook Apt.,
Bristol Ter., DD317
Lawrence, KS, 66049.

September,2 /1994

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin; 53211

Dear Dr. Bader,

Time is running very fast. I'm sorry again for a long silence. A lot of things happened last 6 month.

Our study is going well. We have got an "A" grades for the spring semester. Summer semester was very short, and besides we had a real "nightmare" with the XIX International Symposium on Macrocyclic Chemistry which took place in Lawrence June 12-17 this year. I mean that we were overloaded with different things to do for this very representative meeting. This is typical problems and hot times of all hosts of conferences all over the world. Anyway, this conference was a great event in this field of chemistry. There were almost 200 participants from 18 countries, including Ukraine and Russia. We presented two posters, which abstracts are enclosed. So, it was incredibly interesting and at the same time very difficult to serve as a guide, driver, receptionist etc. But we have got new, unknown before, experience and new scientific contacts.

Our research also going into the right direction. Two big papers already have been prepared, but not sent yet to editors of *J.A.C.S.* and *Inclusion Phenomena*. Our supervisor probably will work on it later this year, which very surprised me. Being in Kiev and working at the Chemistry Department I have published 46 good quality papers. We thought that new interesting results should be published quickly, but here scientists, probably, have different attitude to publications.

Crystal and molecular structures of two compounds are enclosed too. There is a rare example of coexistence in one crystal two different conformers, significantly different by torsion angles. Thus, two independent molecules of an interesting dialdehyde set two crystallographically non-equivalent positions. This compound is a very important precursor for the new series of macrocyclic expanded porphyrins. Another picture describes molecular structure of our first well characterized new bimetallic complex of Mn(II) on a base of mentioned above dialdehyde and propylendiamine as starting substances for the template Schiff-base condensation. Our research is devoted to the modeling of Mn- and Ni-containing enzymes. At least this is a good coordination

chemistry if not exactly structural or functional models.

During current year I have learned how to operate professionally with E.P.R. and N.M.R spectrometers, which now became "my best silent friends" (my wife says that).

Also a book, namely **"Encyclopedia of Inorganic Chemistry"**, was published recently in *John Wiley* (London) and contains my contribution as a chapter which titled as **Mixed Donor Ligands**. I send a copy of this paper as soon as I receive my personal reprints.

Our vacation was an interesting two weeks trip to Colorado, Utah and Arizona, as usually. Prof. Andor and his wife Iren visited us this summer and we made our journey together. Enclosed find please some our recent photos.

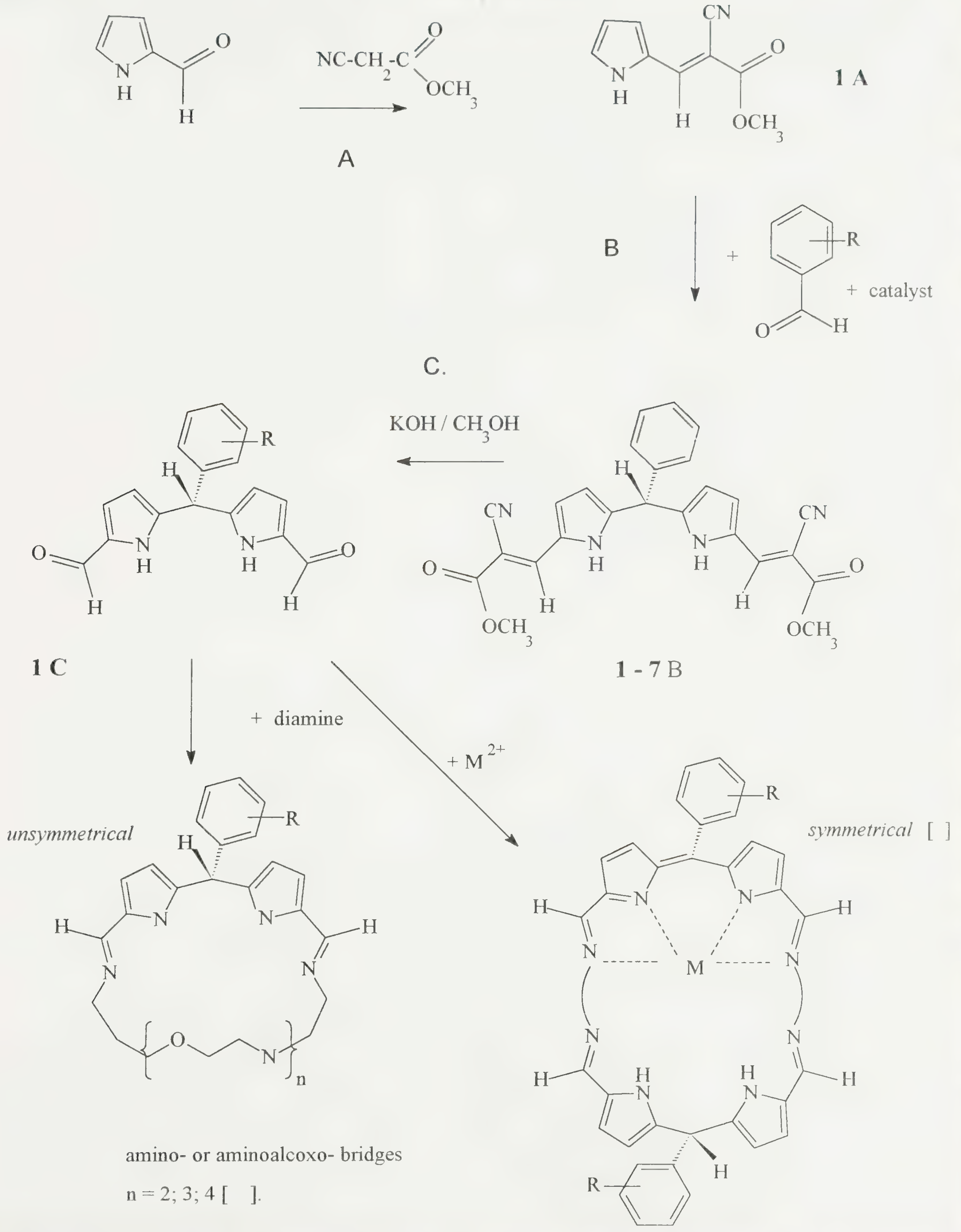
Next week, probably, Andrew Esaulenko and Taras Ilcoon will visit Milwaukee again. I'm sure that they will have a great time visiting **Aldrich** and your family. I remember very well and with pleasure January 1993, when I was happy to feel what it is difficult to explain. Thank you once more for what you have done for all of us.

I will be very glad to know what interesting happened in your life during last time.

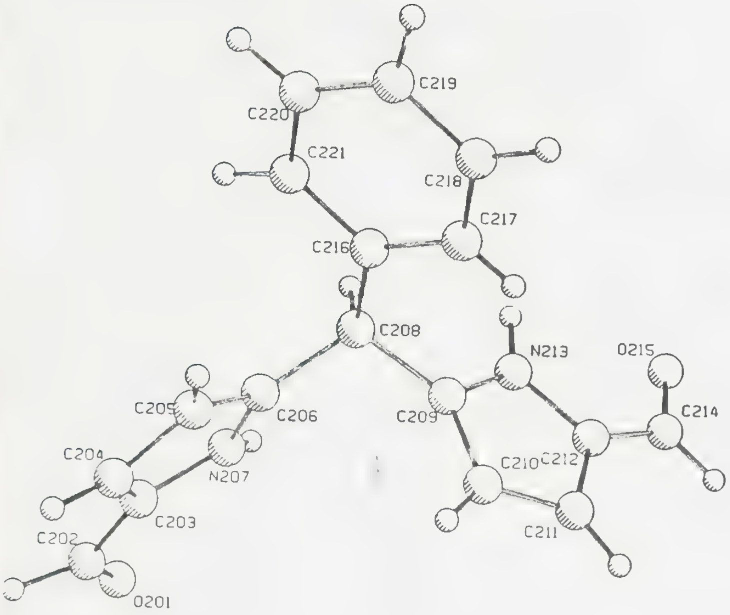
The best wishes to Isabel Bader,
yours sincerely, Nick.

Nick Gerasimchuk

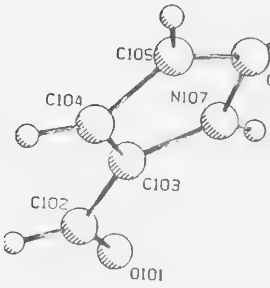
Fig.1.


NC-CH$_2$-C(=O)OCH$_3$
A
1 A
B
+ catalyst
C.
KOH / CH$_3$OH
1 C
1 - 7 B
+ diamine
+ M^{2+}
unsymmetrical
symmetrical [ ]
amino- or aminoalcoxo- bridges
n = 2; 3; 4 [ ].

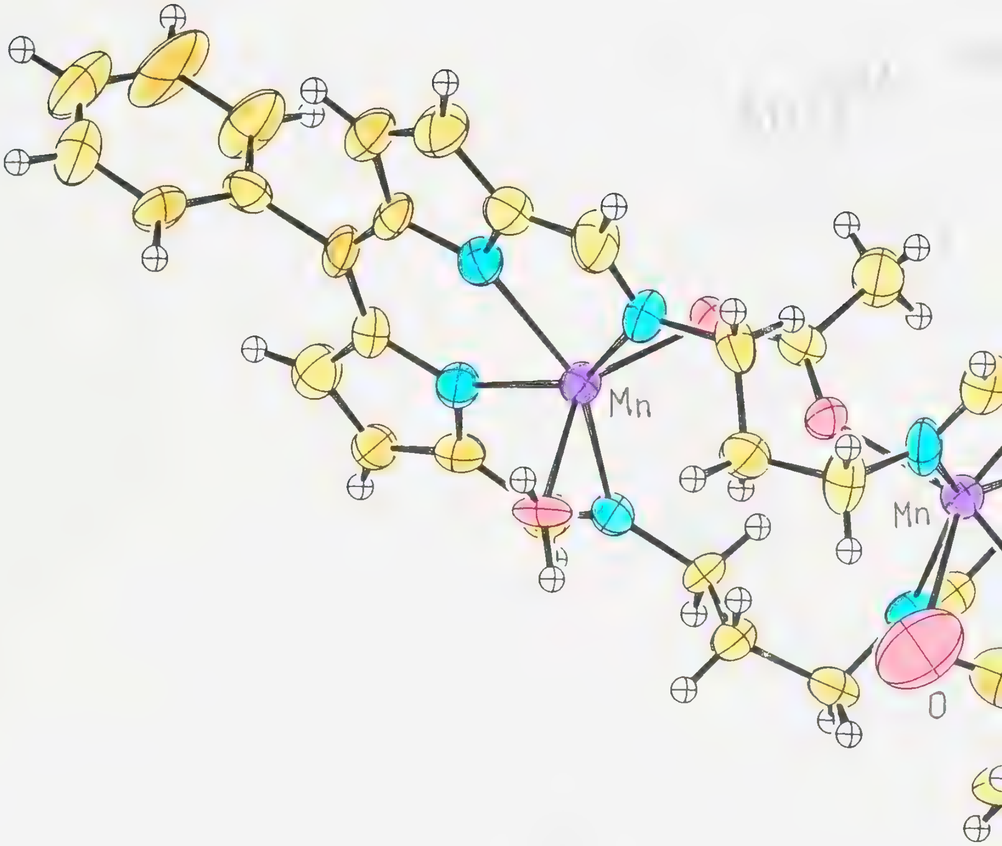
149 [illegible]

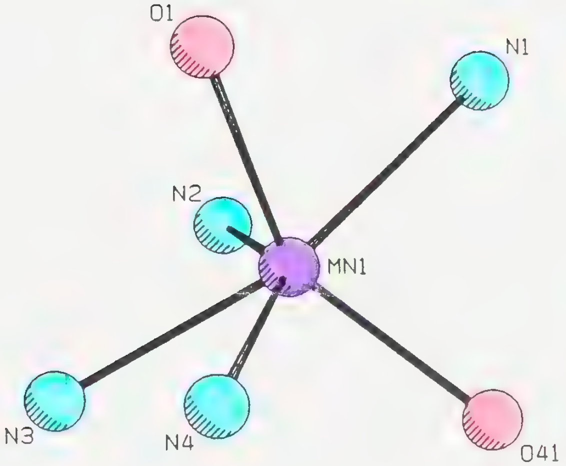


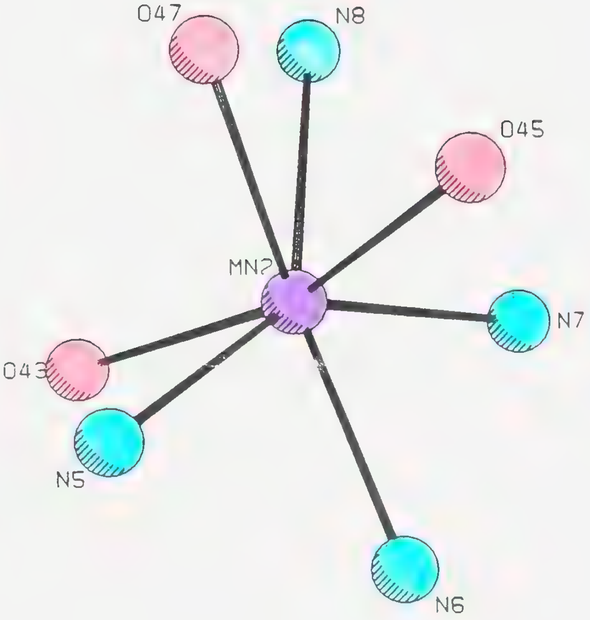
149 (M[illegible]



Comparison of two molecu

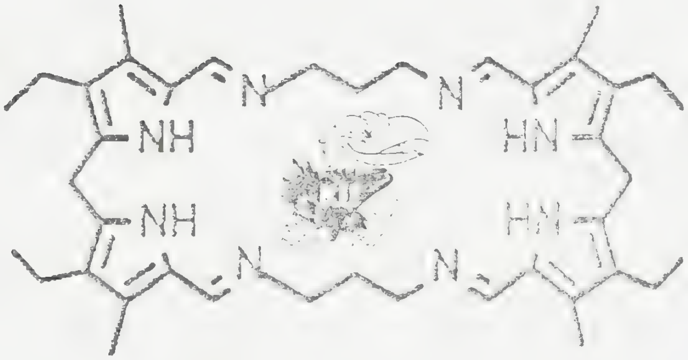

Mn
Mn
O
H


O1
N1
N2
MN1
N3
N4
O41


O47
N8
O45
MN2
N7
O43
N5
N6

XIX International Symposium on Macrocyclic Chemistry

June 12–17, 1994
The University of Kansas
Lawrence, Kansas, USA



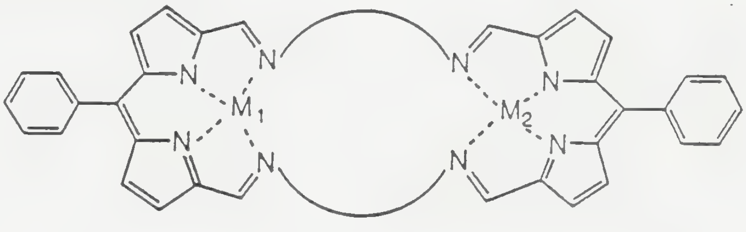
Program and Abstracts

A22

SYNTHETIC AND STRUCTURAL ASPECTS OF PRECURSORS FOR EXPANDED PORPHYRINS

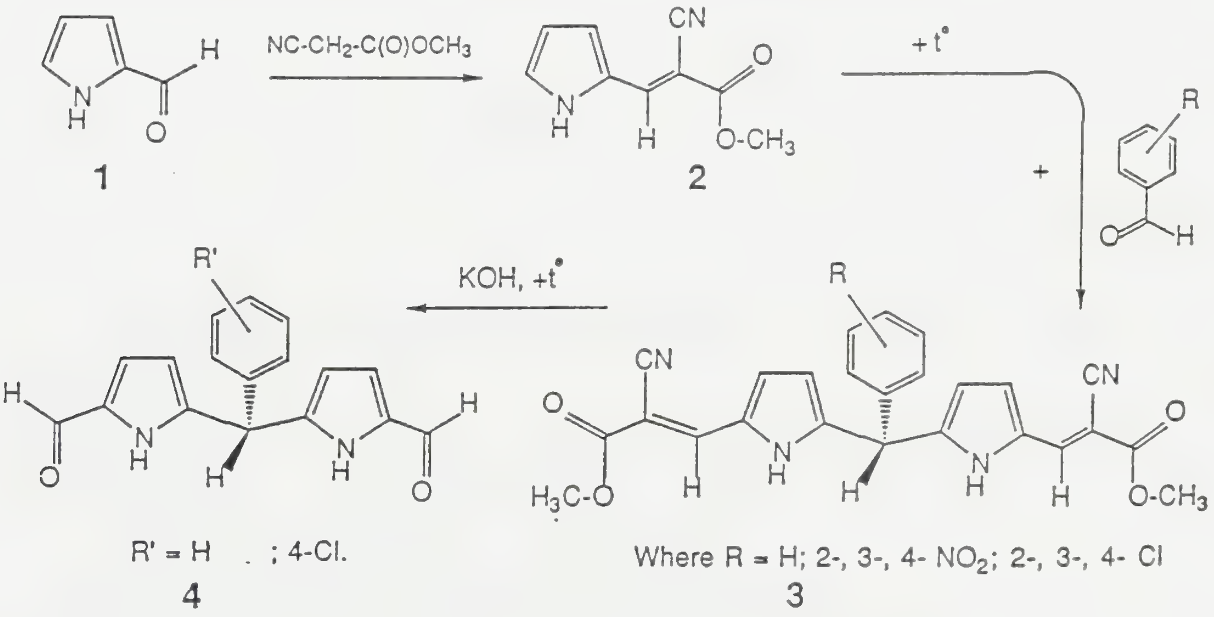
N. N. Gerasimchuk, K. Gu, O. A. Gerasimchuk, A. Reiter, and K. Bowman-James
Department of Chemistry, University of Kansas, Lawrence, Kansas

The catalytic potential of a series of binucleating expanded porphyrins has led to an examination of strategies to simplify the multistep synthetic procedure. The use of the commercially available starting reagent pyrrole-2-carboxaldehyde can greatly reduce the number of steps in the procedure to obtain 5,5'-diformyldipyrromethanes, key reagents used in Schiff base condensations to obtain expanded porphyrins such as **1**.



1

The use of the cyanovinyl protective group as shown in Scheme 1 has allowed for this new route to be pursued. This particular method allows for the isolation of the desired dipyrromethanes in a three-step procedure.



Scheme 1

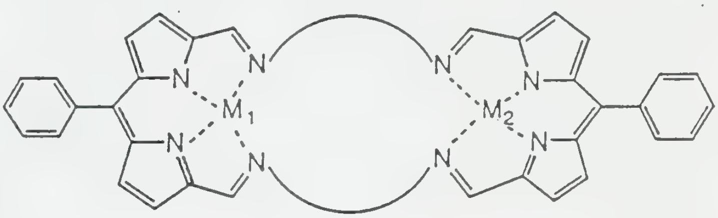
The crystal structures of **2** and **4** have been determined by X-ray crystallographic techniques. Compound **2** is planar, while **4** has a *cis-syn* nonplanar geometry with significant distortion at the bridgehead carbon.

ST39

SMALL MOLECULE ACTIVATION BY EXPANDED PORPHYRINS

K. Bowman-James, A. Gerges, K. Gu, O. A. Gerasimchuk, and N. N. Gerasimchuk
Department of Chemistry, Unversity of Kansas, Lawrence, Kansas

The reaction between 2,2'-diformyldipyrromethanes and diamines in the presence of divalent metal ions gives a variety of macrocyclic ligands which are known as expanded porphyrins. When short chain diamines are used simple binucleating macrocycles such as 1 are formed.



1

The recent crystal structure of the dimanganese(II) complex of 1 shows one of the manganese ions to be six coordinate with a coordinated water molecule, while the other is seven coordinate with a weakly chelating acetate ion (Figure 1).

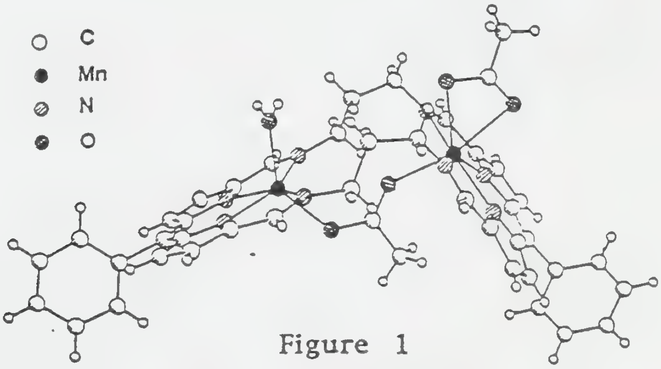
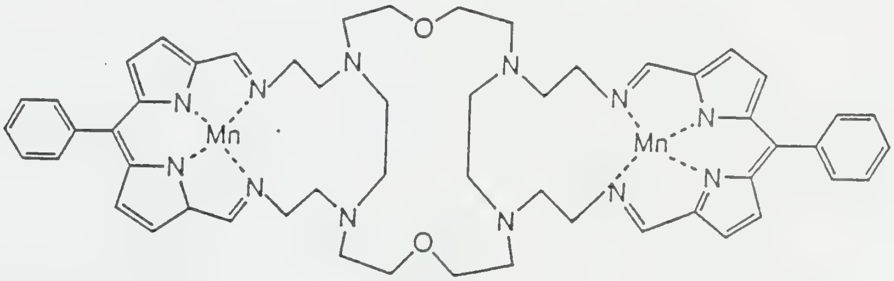


Figure 1

When polyamine macrocycles with pendant amine chains are reacted with 2,2'-diformyldipyrromethanes, multicyclic expanded porphyrin systems such as 2 are formed.



2

The manganese complexes exhibit cytochrome P450 reactivity and reversibly bind CO_2. The reactivity of the complexes with CO_2 and H_2O_2 will be described.

Topica, our local
capital

Pass in Colorado

The Delicate Arch, symbol of Utah

Utah; Arches Nat. Park.


INDEPENDENCE PASS
Elevation 12,095 feet
CONTINENTAL DIVIDE

Kansas City, Cultural center
PLAZA

The highest point I ever
stand on

Colorado

Chemistry Department
of KU.

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

February 15, 1994

Dr. Nick Gerasimchuk
Meadowbrook Apartment
Bristol Terrace, DD317
Lawrence, Kansas 66049

Dear Nick,

I am so happy to have your letter of February 4th.

Of course Isabel and I would love to see you in Milwaukee, but please remember that I travel a great deal and am away about half of the time.

Best wishes.

Sincerely,

c: Mr. Robert Wandler

Dr. Nick Gerasimchuk
chemist
Meadowbrook Apt.,
Bristol Ter., DD317
Lawrence, KS, 66049.

February,4 /1994

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin; 53211

Dear Dr. Bader,

Thank you very much for your letter from January 4th. I'm so glad receive letters from you.

We are working hard in the lab. Our first big article was written and given to our supervisor before the Christmas eve, and will be submitted to the "Journal Org. Chem." soon. Nevertheless, some very important organic compounds we can prepare after months struggle for yield, purity and so on. This substances are exclusively good for the preparation of the three-dimensional macrocycles, which is new idea in this field of chemistry. Those macrocycles promise to have nice practical applications.

Our classes are going well too, and the midterm session also will be soon.

In my spare time I try to collect as much compounds for the Library as I can. From the last lot the 12 substances I made my own. Also it was successful to organize new contacts with people both in the US, and in former USSR.

We have an idea to visit Milwaukee this year probably during the spring brake in KU, if it will be possible and not very difficult for you.

With the best wishes from both of us,
yours sincerely,
Nick

Nick Gerasimchuk

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

January 4, 1994

Dr. Nick Gerasimchuk
Meadowbrook Apartment
Bristol Terrace, DD317
Lawrence, Kansas 66049

Dear Nick,

I am so happy to find your letter of November 24th with those beautiful photographs upon returning from a couple of months in England.

From there, I was in touch with Andy Esaulenko who is sending some very fine samples to Bob Wandler.

I am delighted to see that you have collected almost 300 good compounds for the Library. By all means send them directly to Bob Wandler, who will arrange for payment to you.

Do you and Olga have any plans to visit Aldrich and the Baders later this year?

All good wishes to you both.

Sincerely,

c: Mr. Robert Wandler

Dr. Nick Gerasimchuk
chemist
Meadowbrook Apt.,
Bristol Ter., DD317
Lawrence, KS, 66049.

November,24 /1993

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin; 53211

Dear Dr. Bader,

I'm sorry for a long silence. A lot of things happened during last half a year. We moved to Lawrence, Kansas, at the beginning of July. Olga and I were admitted to the University of Kansas for Graduate Study. Thus, I began work for my second Ph.D. This research project is devoted to the chemistry of new "expanded" metalloporphirines. This work seems to be interesting to me.

We rent nice comfortable one bedroom apartment and live very good. Now we can work together again like it was in Kiev.

Professor Andor visited us in August. We had traveled in Idaho, Wyoming (Yellow Stone Nat. Park), Arizona, and almost all canyons and national parks of Utah. These two weeks of our vacation were really wonderful. Enclosed please find several photos about this summer.

Three years ago we had only dreams to travel abroad, and particularly in the U.S.A.. Certainly, all these dreams come true only due to our hard work with you and "Aldrich". Thank you very much once more for all what you did for us.

I continue collection of the interesting samples for the ABC-library. Almost 300 new good compounds have been collected since this February. I made some of them myself. At least 100 more substances I'll be able to find or obtain during following year.

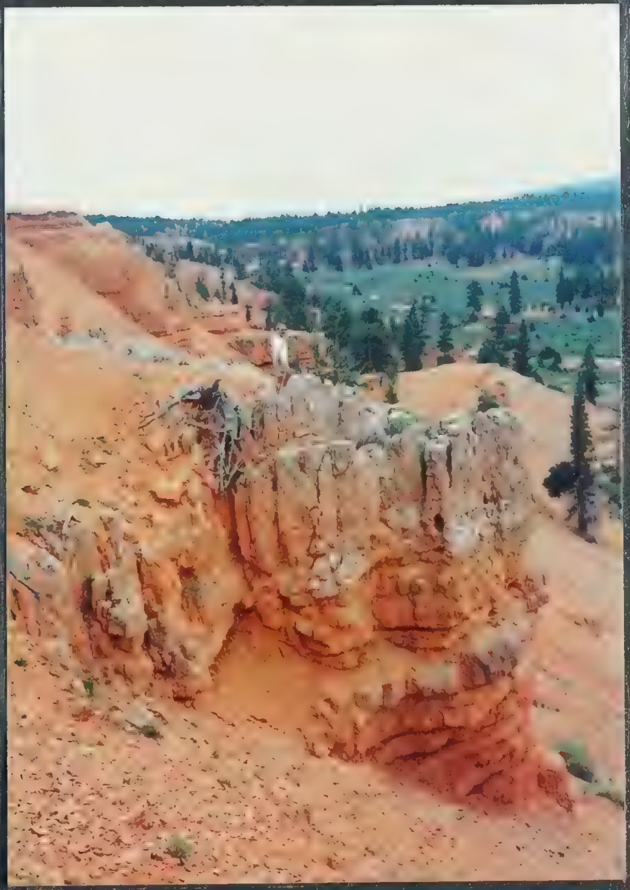
Dear Dr. Bader, let me wish Happy Thanksgiving to you and your family!

The best personal regards to Mrs. Isabel Bader.

Sincerely yours,

Nick Gerasimchuk

Nick Gerasimchuk



[illegible]

Wyoming, Jackson City
Small excursion and
amateur movie

South Table [illegible] and Thad

Prof. [illegible] in Red Canyon

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

February 28, 1994

Mr. Edward M. Giles
Chairman
The Vertical Group
61 Broadway, Suite 918
New York, New York 10006

Dear Ed:

Thank you for sending me the Metabolix information, which I return.

When I visited with the principals at M.I.T., I was well impressed with them personally, but I do feel that this is too speculative for me to be interested.

Best wishes.

Sincerely,

Enclosure

Boston

Ed Giles

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

April 27, 1994

Mr. Royce Gipson
2911 Senour Road
Indianapolis, Indiana 46239

Dear Royce,

As you know, I am just working on my autobiography which I hope will be completed this year.

Could you please look over the enclosed paragraph and tell me whether BEAM is an herbicide or a fungicide. Should I add anything else to this?

Fond regards from house to house.

As always,

Enclosure

GIPSON & GIPSON

Dear Alfred and Isabel,

The enclosure appeared a few weeks ago in our Sunday paper, and we were immediately reminded of you. Although I'm quite sure that this is not a "new" story to you, we thought to send the clipping for you to read what was being said in our paper about it. We're truly sorry that your recent foray into Tennessee didn't provide us with the opportunity for you to stop through Indianapolis. Perhaps such opportunity can still come to pass further into the year.

The house-building project has finally gotten to be full-steam, and it actually appears that the thing will eventually be finished and habitable. We would really like to look forward to welcoming you for a visit in it , once we're there. "There" will hopefully be accomplished by early July, unless other, un-planned situations intervene.

We hope all continues well with you both. I expect to be speaking with you soon, Alfred, about happenings here at Lilly/DowElanco.

With our best regards and affection.

Royce & Shirley

Robert P. Lattimer, *Chairman*
BF Goodrich R&D Center
9921 Brecksville Rd.
Brecksville, Ohio 44141
Phone 447-5369

Sibylle E. Walter, *Chairperson-Elect*
Goodyear Tire & Rubber Co.
142 Goodyear Blvd, D-415B
Akron, Ohio 44305
Phone 796-7457

George H. Kuhls Jr., *Secretary*
The Chemical Group of MONSANTO
260 Springside Dr.
Akron, Ohio 44333
Phone 668-8292

Harlan W. Frerking, *Treasurer*
Goodyear Tire & Rubber Co.
142 Goodyear Blvd D-410G
Akron, Ohio 44305
Phone 796-7358

Clifford L. Schrader, *Past Chairman*

COUNCILORS
James Visintainer
James Duddey

AKRON SECTION
1993

ALTERNATE COUNCILORS
James Beecher
Henry Stevens

AMERICAN CHEMICAL SOCIETY

April 23, 1993

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

Dear Dr. Bader:

Thank you so much for coming to northeast Ohio and speaking at the Akron Section meeting on April 15. Your presentation was simply outstanding, and I enjoyed very much the chance to talk with you and your wife. I was a little surprised to hear that *The Bible Through Dutch Eyes* subject had not been chosen before. This was strictly my choice, since I am a (rather amateur) Bible student and was interested in your perspective. I found your talk and slides to be fascinating, so I do not regret the choice!

Best wishes in your future endeavors.

Sincerely,

Bob Lattimer

Robert P. Lattimer, Ph. D.
Chairman

P.S.-- I have asked our Treasurer to send you a check for $50.

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

April 8, 1994

Dr. Morel Guyot
3585 Beverly Glen
Sherman Oaks, California 91423

Dear Dr. Guyot:

Please do not mind that I have taken so long to reply to your query of January 30th regarding Rylander's book on hydrogenation, but I had to take counsel about that book. It is really not very useful for asymmetric hydrogenation as this topic is covered only briefly in the text; whereas, in reality it is much more complicated. If you are really interested, please look at Volume V of Morrison's Asymmetric Synthesis published by Academic Press.

Best wishes.

Sincerely,

Alfred: 3/31

Rylander's book is not very useful for asymmetric hydrogenation as this topic is covered only briefly in the text but in reality is much more complicated. Suggest that Merrel read the appropriate chapters in vol 5 of Morrison's <u>Asymmetric Synthesis</u> (Academic Press). Really no easy answers to Merrel's questions.

Steve

I have a couple of chemistry questions that you may be able to answer:

① Can CaH_2 be used instead of $LiAlH_4$ to destroy peroxides in THF prior to distillation? It seems such a waste to use $LiAlH_4$ just to do that.

② I have done some reading in Rylanders book "Hydrogenation Methods" on asymmetric hydrogenation but something is confusing. Does it mean if you treat the catalyst with a d compound that it makes the product become d; or does it give l; or could it be either depending on other factors? Is there a good way to draw an example of the catalyst surface with the impregnation compound to show what it does to the substrate to make it optically pure? Are there any good literature references that delve into this?

Between the time I wrote you my letter and I received your letter we had the 6.6 earthquake. Forturately I had securely packed anything that could be dangerous in metal army cans and thus I only had to clean up less aggressive messes such as broken plate glass windows.

Best Wishes!

Mool

PS: I am sending a letter and pics to Professor Roald Hoffmann!

1/30/94

To: Dr. Alfred Bader

From: Morel Guyot
3585 Beverly Glen
Sherman Oaks, Calif. 91423
818-789-6009

Dear Alfred: I received your letter dated 1/26/94. I had no idea about all those terrible things at Aldrich until I got your Letter to Chemists. Those people are "false blamers" seeking their own greedy ends. They are so greedy that enough is never enough so they try to wring out the last drop of blood from their victims. In addition they are probably jealous of *your* *ability* to relate to other people that they lack. There are probably many other horror stories of how they have interacted with others.

You had asked "How do I sell them?" Well, I do a show at Jet Propulsion lab in Pasadena every year; my "booth" is the steps in front of the Space Museum. I have enclosed some photos of past displays there. My prices range from several hundred dollars up to \$6000.00 They are all originals made by myself only. At one JPL show I sold a broken one (small crack on its edge) for \$50.00, two for \$1000.00 each and one for \$2000.00 A year later I sold one for \$800.00 at JPL. I sell them occasionally during the year in between shows. So far I have never been involved with any galleries.

I also do some scientific glassblowing (I have a Litton F lathe with nice chucks) and have enclosed a photo of a Crookes Tube that I built.

I have a couple of chemistry questions that you may be able to answer:

① Can CaH_2 be used instead of $LiAlH_4$ to destroy peroxides in THF prior to distillation? It seems such a waste to use $LiAlH_4$ just to do that.

② I have done some reading in Rylanders book "Hydrogenation Methods" on asymmetric hydrogenation but something is confusing. Does it mean if you treat the catalyst with a d compound that it makes the product become d; or does it give l; or could it be either depending on other factors? Is there a good way to draw an example of the catalyst surface with the impregnating compound to show what it does to the substrate to make it optically pure? Are there any good literature references that delve into this?

Between the time I wrote you my letter and I received your letter we had the 6.6 earthquake. Fortunately I had securely packed anything that could be dangerous in metal army cans and thus I only had to clean up less aggressive messes such as broken plate glass windows.

Best Wishes!

Noel

PS: I am sending a letter and pics to Professor Roald Hoffmann!

JPL 'D'

GUYOT

JPL 'D'

25434
2,113m

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

April 19, 1993

Dr. Robert P. Lattimer
B. F. Goodrich R&D Center
9921 Brecksville Road
Brecksville, Ohio 44141

Dear Dr. Lattimer:

I so enjoyed my evening with you at the Tangier Restaurant, and want to thank you most sincerely for help.

I understand from you that Monsanto would pay the honorarium I charge to companies (although I do not charge honoraria to A.C.S. sections), and the car expenses.

The additional mileage between Cleveland, Painesville and Akron was 100 miles, and the meals for the three days on the road, $72.00, for a total cost to the <u>two</u> sections of $100.00. Hence, I would appreciate a check from your section in the sum of $50.00 and a check for $50.00 from the Painesville section.

I do hope you will find this arrangement fair.

All good wishes.

Sincerely,

c: Dr. Barry Jacobson

Edith Crim
611 First St.
La Porte, Ind.

[illegible]

[illegible] 611 [illegible]

5-10-41

[illegible]

FAX TRANSMITTAL SHEET

FROM: DR. ALFRED BADER

2961 North Shepard Ave.
Milwaukee, Wisconsin 53211

PHONE: (414) 962-5169

FAX: (414) 962-8322

TO: Dr. Robert P. Lattimer
B. F. Goodrich R&D Center
FAX 1 216 447 5249

DATE: April 8, 1993

Dear Dr. Lattimer:

I much look forward to being with you next Thursday, April 15th.

I have now heard from Ms. Sharen Carroll at Monsanto. She has scheduled my talk there at 3:15 p.m., and we will check into the Holiday Inn/Montrose before the talk at Monsanto. It is very close to Monsanto, and we will return to the motel after the talk.

Could you pick us up at the Holiday Inn after Professor Katritzky's talk, which I am sorry we will have to miss. I have never met Professor Katritzky but have read many of his papers and hope he might stay for the dinner.

Should picking us up be difficult for you, please fax a map how to get from the Holiday Inn to Tangier.

Many thanks.

Sincerely,

Alfred Bader

louis godschalk

Herzliya, January 17, 1993
Tevet 25, 5753.

Shaloom Isabel and Alfred,

Herewith I send you some information about your "Rembrand" deal.

To give you a clue, I also send you a copy from your letter dated February 11, 1987.

Best wishes for you both.

bader193

Louis

P O B 6024 HERZLIYA 46101 ISRAEL TEL [illegible]

ALFRED BADER FINE ARTS

DR. ALFRED BADER

ESTABLISHED 1961

February 10, 1993

Dr. Louis Godschalk
P.O.B. 6024
Herzliya
46101 Israel

Dear Louis:

Your thoughtful note and its enclosures reminded Isabel and me of our happy meeting with you. We very much hope to have another chance to get together when next we visit Israel.

Best wishes.

Sincerely,

By Appointment Only
ASTOR HOTEL SUITE 622
924 EAST JUNEAU AVENUE
MILWAUKEE WISCONSIN USA 53202
TEL 414 277-0730 FAX 414 277-0709

Isabel L. Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

Feb 11/87

Dear Louis,

Our thanks for your card and best wishes for the year. We were in England for four weeks and Holland for one week at the end of November & December, so we had a great pile of mail to enjoy when we returned.

The weather there was fine then, but poor souls, they have had extreme cold since, and a great deal of snow in many parts which they are not able to deal with. Hopefully their spring will not be long — a beautiful time of year in both countries. Here we have almost none — a few days at best, then the heat of summer.

We have not been back to Israel since our visit in 1985. The chemical results were not great: Too many people with vague ideas, but not enough practical application to the job of producing. Sad. However, we've expanded our own production, purchased a small chemical group, increased our number of employees and can say with some pride that they are doing very well.

We hope your life has continued to be interesting and challenging, and hope all goes well with you and your family.

Sincerely
Alfred & Isabel Bader

Czech trip file

Ivo Starý

Département de Chimie Organique
Section de Chimie
Université de Genève
30, quai Ernest-Ansermet
CH-1211 Genève 4
SWITZERLAND

Dr. Alfred Bader

2961 North Shepard Avenue
Milwaukee, Wisconsin 53211
U.S.A.

October 31, 1994

Dear Dr. Bader,

Thank you very much for your letter of 16th September, 1994.

My deepest apologies for not having replied to you at an earlier date. I have been away from my Prague laboratory during this year having one-year postdoctoral position at the University of Geneva in Professor E. P. Kündig group. That is why I obtained your nice congratulations with delay when I visited the Czech Republic to receive the A. Bader Award for 1994 several days ago.

I consider it a great honour to be the first recipient of the A. Bader Award. It stimulates me very much for my future scientific career in chemistry. I am going to continue my research at the Institute of Organic Chemistry and Biochemistry in Prague from the beginning of 1995. Although I do not know you personally I am familiar with the products of your Aldrich Company which have helped me very much to achieve the appreciated results of my research.

I should greatly enjoy meeting you in Prague next June and expressing my thanks personally.

Once more many thanks and best regards.

Yours sincerely,

Ivo Starý