2. *Helvetica Chimica Acta* and Coordination Chemistry

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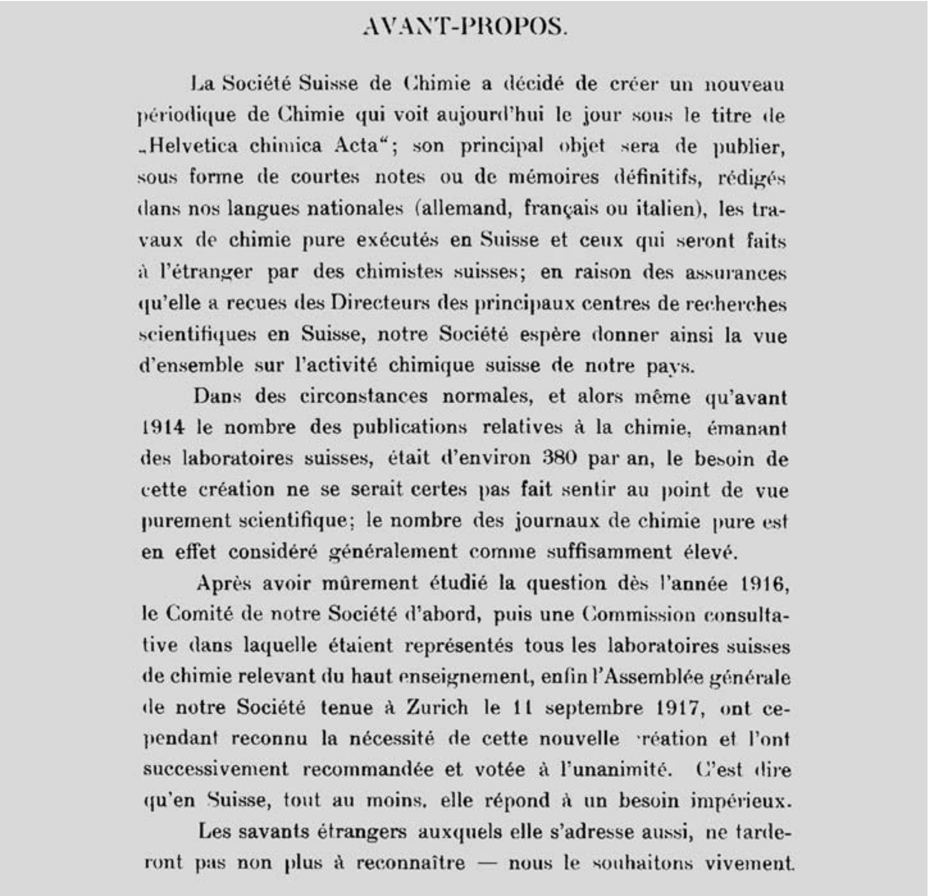
This year, *Helvetica Chimica Acta* (*HCA*) celebrates its 75th year of publication. Its volumes contain many papers of fundamental importance in the field of coordination chemistry. Thus, this is an appropriate time to assess their impact.

The significance of these contributions should be judged within the well-defined historical framework outlined by *Ph.-A. Guye* in the 'Avant-propos' which appeared on the first issue [1]:



AVANT-PROPOS.

La Société Suisse de Chimie a décidé de créer un nouveau périodique de Chimie qui voit aujourd'hui le jour sous le titre de „Helvetica chimica Acta"; son principal objet sera de publier, sous forme de courtes notes ou de mémoires définitifs, rédigés dans nos langues nationales (allemand, français ou italien), les travaux de chimie pure exécutés en Suisse et ceux qui seront faits à l'étranger par des chimistes suisses; en raison des assurances qu'elle a recues des Directeurs des principaux centres de recherches scientifiques en Suisse, notre Société espère donner ainsi la vue d'ensemble sur l'activité chimique suisse de notre pays.

Dans des circonstances normales, et alors même qu'avant 1914 le nombre des publications relatives à la chimie, émanant des laboratoires suisses, était d'environ 380 par an, le besoin de cette création ne se serait certes pas fait sentir au point de vue purement scientifique; le nombre des journaux de chimie pure est en effet considéré généralement comme suffisamment élevé.

Après avoir mûrement étudié la question dès l'année 1916, le Comité de notre Société d'abord, puis une Commission consultative dans laquelle étaient représentés tous les laboratoires suisses de chimie relevant du haut enseignement, enfin l'Assemblée générale de notre Société tenue à Zurich le 11 septembre 1917, ont cependant reconnu la nécessité de cette nouvelle création et l'ont successivement recommandée et votée à l'unanimité. C'est dire qu'en Suisse, tout au moins, elle répond à un besoin impérieux.

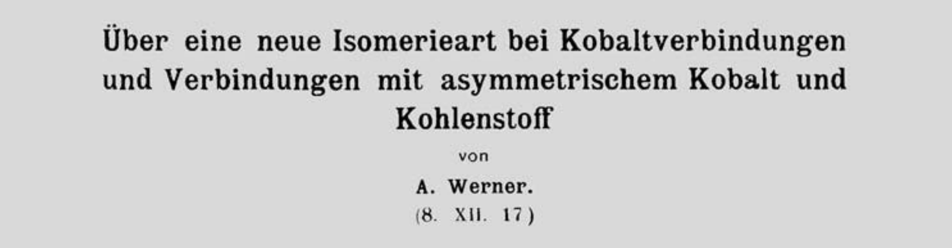
Les savants étrangers auxquels elle s'adresse aussi, ne tarderont pas non plus à reconnaître — nous le souhaitons vivement.

It should also be remembered that, until recent times, there were few specialist journals (a notable exception being the *Zeitschrift für anorganische Chemie*), and inorganic and coordination chemists outside Germany generally published their work in the journal of their national Chemical Society. Thus, Swiss coordination chemists used mainly *HCA* for their publications, at least until the appearance of specialist journals in English such as the *Journal of Inorganic and Nuclear Chemistry* (1955) and *Inorganic Chemistry* (1962). In other words, this account can be regarded as a summary of the highlights in Coordination Chemistry in Switzerland, 'seen through the eyes' of the papers published in *HCA*.

A few words about the contents of this article. Its author deliberately restricted himself to contributions in the field of coordination chemistry, having been an active participant in this area for more than half of the period in question. Some aspects of coordination chemistry not mentioned here and the wider field of inorganic chemistry will be included in other contributions. Last, but not least, no attempt has been made to give a comprehensive review; a personal choice was made, and if serious omissions have occured, an apology in advance is offered.

The choice of coordination chemistry as the subject of the first 'review' was not accidental but connected with the fact that the first article published in the first issue of *HCA* was a contribution from *Alfred Werner* [2]. However, soon after his *Nobel Prize* award in 1913, ill health forced him to reduce his activities in the 'Chemisches Laboratorium der Universität Zürich', and thus only six of his papers were published in *HCA*, three of them after his death in 1919.

It is worth dwelling a little on this first paper. Not surprisingly, it is on the subject of chirality in transition metal complexes, in this case, those of the isomeric forms of *cis*-[$Co(NO_2)_2(en)(pn)$]X (en = ethylenediamine; pn = 1,2-propanediamine; X = counterion), a family of compounds denoted at that time as the *flavo*-series. As can be seen from the original drawing reproduced below, there is a chiral metal center and a chiral C-atom on the organic ligand pn as well as two possible orientations of the Me



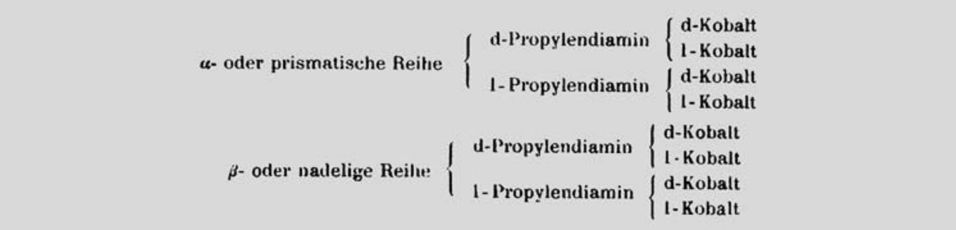
Über eine neue Isomerieart bei Kobaltverbindungen und Verbindungen mit asymmetrischem Kobalt und Kohlenstoff

von

A. Werner.

(8. XII. 17)

group relative to the anionic ligands. As shown in this publication, eight different isomeric forms are possible. *Werner*'s co-worker, *A. Smirnoff*, was able to isolate all of them. They were characterized by optical rotatory dispersion, and the spectra of the four



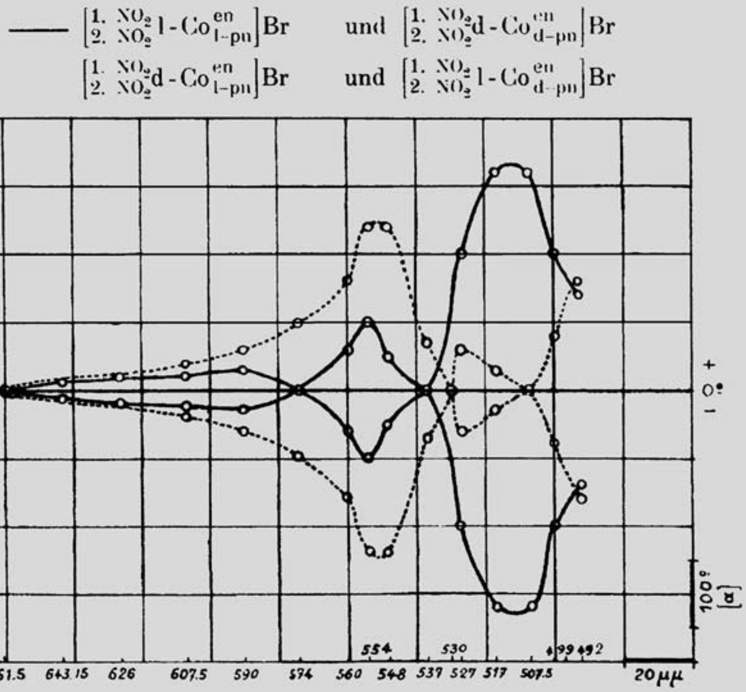
α- oder prismatische Reihe
- d-Propylendiamin
  - d-Kobalt
  - l-Kobalt
- l-Propylendiamin
  - d-Kobalt
  - l-Kobalt

β- oder nadelige Reihe
- d-Propylendiamin
  - d-Kobalt
  - l-Kobalt
- l-Propylendiamin
  - d-Kobalt
  - l-Kobalt

compounds of the so-called α-series are reproduced below. Note should be made here that, even at that time, such measurements were routinely carried out for the characterization of optically active coordination compounds.

Tabelle 1.

Doppeltaktive Bromide der α-Reihe (Prismen).

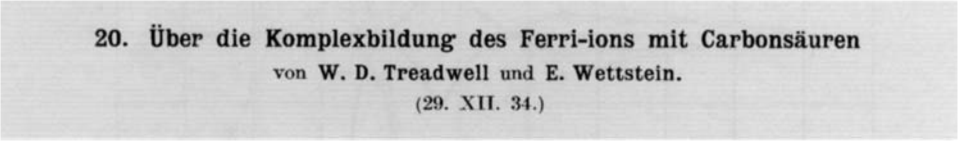


An extensive obituary of *Alfred Werner*, written by his former pupil *Paul Karrer*, was published in 1920 [3], and the very good photograph which appeared there is reproduced below.

The course of history is such that *Alfred Werner*'s coordination chemistry school disappeared practically without trace in Switzerland, but it would certainly be inappropriate to speculate here why this occurred.

Alfred Werner

Only very sporadic publications dealing with what we would now consider as coordination chemistry were published in *HCA* between 1920 and 1935, when there appeared an article by *W. D. Treadwell*, professor of General and Analytical Chemistry at the ETH in Zurich with the title shown below [4]:



20. Über die Komplexbildung des Ferri-ions mit Carbonsäuren
von **W. D. Treadwell** und **E. Wettstein.**
(29. XII. 34.)

The reader will clearly recognize that the type of curves shown in the figure shown on p. 25 can be considered as being direct fore-runners of those which became very familiar later in connection with *complexometric titrations*.

The pioneering work of *W. D. Treadwell* was not limited to that mentioned above: a number of publications appeared in *HCA* between 1941 and 1943, describing the characterization of cyano complexes of Mn, Fe, Co, and Ni in very low oxidation states [5].

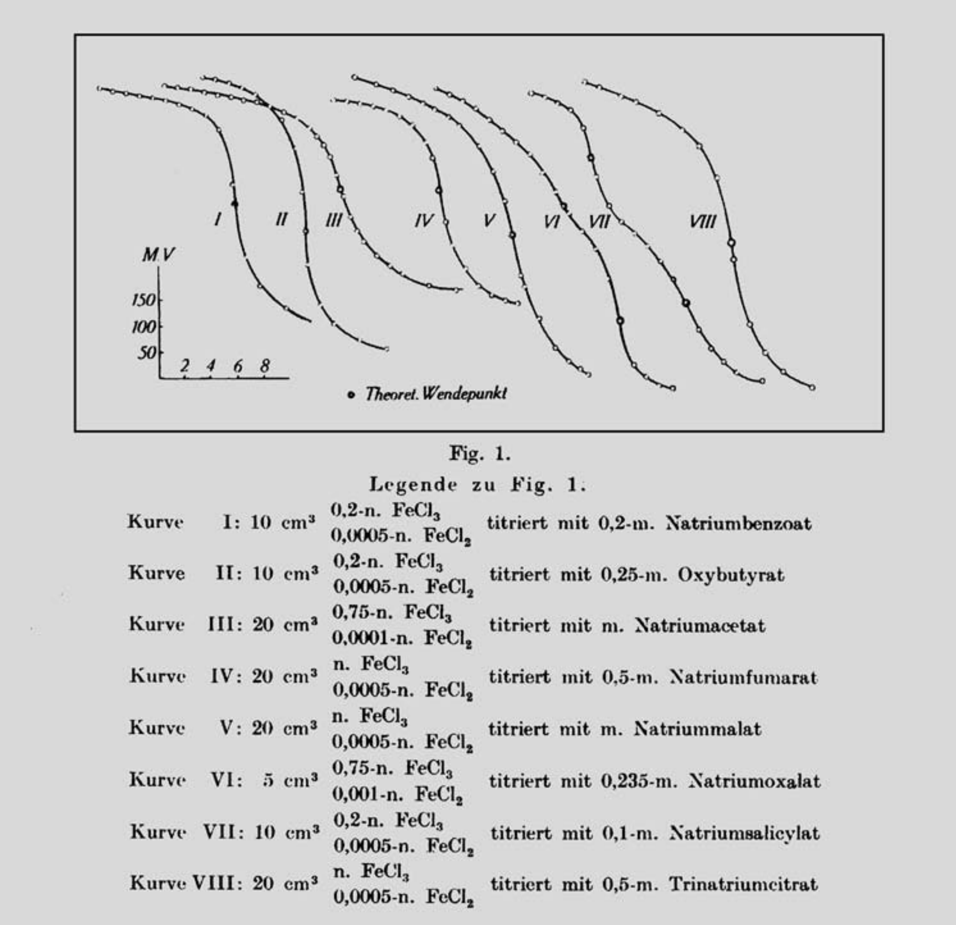


Fig. 1.

Legende zu Fig. 1.

Kurve I:	10 cm³	0,2-n. $FeCl_3$ 0,0005-n. $FeCl_2$	titriert mit 0,2-m. Natriumbenzoat
Kurve II:	10 cm³	0,2-n. $FeCl_3$ 0,0005-n. $FeCl_2$	titriert mit 0,25-m. Oxybutyrat
Kurve III:	20 cm³	0,75-n. $FeCl_3$ 0,0001-n. $FeCl_2$	titriert mit m. Natriumacetat
Kurve IV:	20 cm³	n. $FeCl_3$ 0,0005-n. $FeCl_2$	titriert mit 0,5-m. Natriumfumarat
Kurve V:	20 cm³	n. $FeCl_3$ 0,0005-n. $FeCl_2$	titriert mit m. Natriummalat
Kurve VI:	5 cm³	0,75-n. $FeCl_3$ 0,001-n. $FeCl_2$	titriert mit 0,235-m. Natriumoxalat
Kurve VII:	10 cm³	0,2-n. $FeCl_3$ 0,0005-n. $FeCl_2$	titriert mit 0,1-m. Natriumsalicylat
Kurve VIII:	20 cm³	n. $FeCl_3$ 0,0005-n. $FeCl_2$	titriert mit 0,5-m. Trinatriumcitrat

However, another ten years had to lapse, before the significance of complexes of this type was fully recognised.

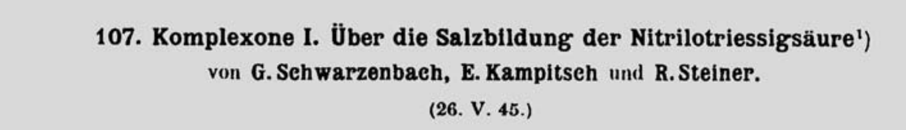
Regrettably, there was no obituary notice of *W. D. Treadwell* in *HCA*. May his photograph shown on p. 26, made available by the *Hauptbibliothek der ETH*, serve as a tardy amend for this omission.

The next development in Swiss coordination chemistry was of truly international dimensions. It was the work of a former research student of *W. D. Treadwell*: *Gerold Schwarzenbach*. He started his academic career as an analytical chemist in the Chemisches Laboratorium der Universität Zürich under the direction of *Paul Karrer* who, by the mid-twenties had become a fully fledged organic chemist.

Schwarzenbach published many papers on acid dissociation, indicators, and related topics between 1930 and 1955. However, it was his 1945 publication [6], whose title appears on p. 26, which added a new dimension to the field of coordination chemistry.

W. D. Treadwell

Schwarzenbach himself liked to call these studies 'messende Komplexchemie'. Figures such as that shown on p. 27 [6] soon became classics in the chemical literature.



107. Komplexone I. Über die Salzbildung der Nitrilotriessigsäure¹)
von **G. Schwarzenbach, E. Kampitsch** und **R. Steiner.**
(26. V. 45.)

As mentioned earlier, *Schwarzenbach* was Professor of Analytical Chemistry, and naturally, the analytical applications of the aminopolycarboxylic acids were developed at a very early stage. It is interesting to note that he chose to publish a short summary of the full scope of what became known as complexometric titrations. This article [7] is reproduced on p. 27.

While the analytical chemistry aspects of *Schwarzenbach*'s work were later made widely available to the chemical community through a book translated in many languages, more than 50 papers on the coordination chemistry of polydentate ligands were published over many years, mostly in *HCA*. These were subdivided into groups, mainly the *Komplexone*, the *Metallindikatoren*, and the *Metallkomplexe mit Polyaminen*.

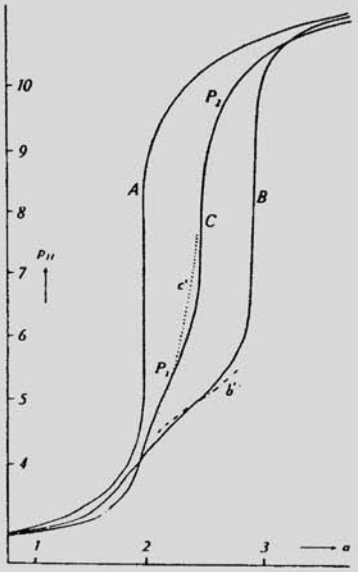


Fig. 1.

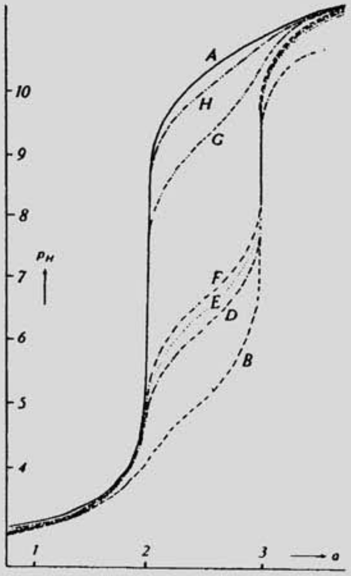


Fig. 2.

Neutralisationskurven der Nitrilo-triessigsäure, aufgenommen mit 0,1-n.Tetramethylammoniumhydroxyd als Titrationsflüssigkeit. a = Anzahl Äquivalente Base pro Formelgewicht Nitrilo-triessigsäure. Säurekonzentration $c_s = 2{,}1 \times 10^{-3}$. Kurve A: ohne Zusatz. Kurven B, D, E, F, G, H: unter Zusatz von Ca-, Mg-, Sr-, Ba-, Li-, Na-Chlorid in einer Konzentration von $c = 1{,}7 \times 10^{-2}$. Kurve C: unter Zusatz von $CaCl_2$ $c = 1{,}05 \times 10^{-3}$.

173. Nouvelles méthodes de dosage de certains cations métalliques

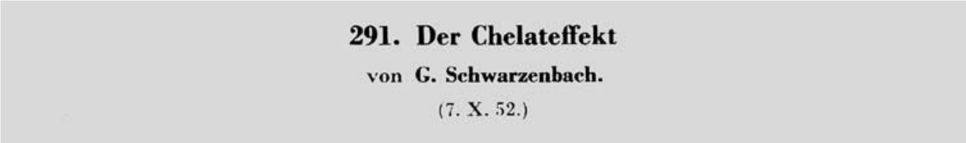
par **G. Schwarzenbach**.

(15 VI 46)

Ces méthodes¹) sont fondées sur les propriétés de quelques acides amino-polycarboxyliques, spécialement de l'acide nitrilo-triacétique $N(CH_2COOH)_3$, de l'acide uramile-diacétique $C_4H_3O_3N_2$–$N(CH_2COOH)_2$ et de l'acide éthylènediamine-tétracétique $(HOOCCH_2)_2N$—CH_2CH_2—$N(CH_2COOH)_2$. Les anions de ces acides forment des complexes stables avec la plupart des cations métalliques, même avec les alcalino-terreux, le lithium et le sodium. Cette formation de complexes peut être utilisée pour le dosage volumétrique de ces métaux. Nous avons mis au point trois modes d'emploi. La fin du titrage des deux premières méthodes est marquée par un effet de p_H utilisant le virage d'un indicateur coloré. Pour la troisième méthode, on utilise un indicateur donnant un composé coloré avec le cation à doser. Les cations suivants: Li, Mg, Ca, Sr, Ba, Zn, Hg, Cd, Cu, Fe, Co, Ni, Mn et Ce peuvent être dosés à l'aide de ces méthodes. Certains complexes du Co(III) avec l'acide éthylènediamine-tétracétique forment des précipités insolubles avec l'ion potassium. Cette propriété peut être utilisée pour effectuer un dosage gravimétrique, volumétrique ou colorimétrique du potassium.

Zurich, Institut de Chimie de l'Université.

What must be *Schwarzenbach*'s best known paper was published in 1952 [8]:

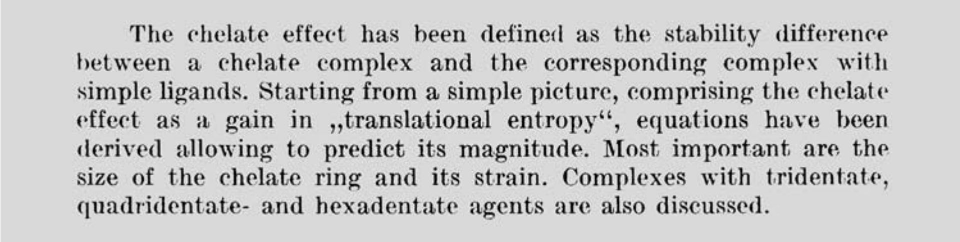


291. Der Chelateffekt

von **G. Schwarzenbach.**

(7. X. 52.)

The significance of this paper is best expressed using the summary he wrote:



The chelate effect has been defined as the stability difference between a chelate complex and the corresponding complex with simple ligands. Starting from a simple picture, comprising the chelate effect as a gain in „translational entropy", equations have been derived allowing to predict its magnitude. Most important are the size of the chelate ring and its strain. Complexes with tridentate, quadridentate- and hexadentate agents are also discussed.

Much discussion on the thermodynamic nature of the *chelate effect* followed this publication, but its essence was and remains that outlined by *Schwarzenbach* in his original publication which is given in the figure reproduced below.

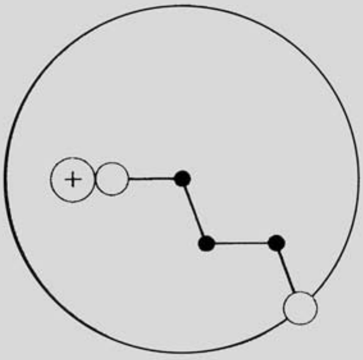
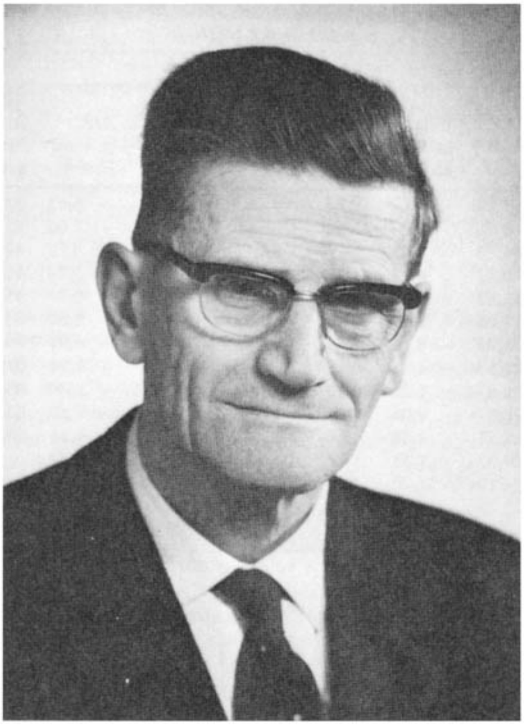


Fig. 1.
Der Zwischenkomplex MZ* mit Enklave. Die leeren Kreise sind die Ligandatome.

Schwarzenbach's move to the Laboratorium für anorganische Chemie of the ETH in 1955 saw a change in his research interests: oxygen and nitrogen were replaced by sulphur and phosphorus as donors. While a significant part of the work on sulfur ligands was published, mostly in *HCA*, his latter interest in the coordination chemistry of mercapto-

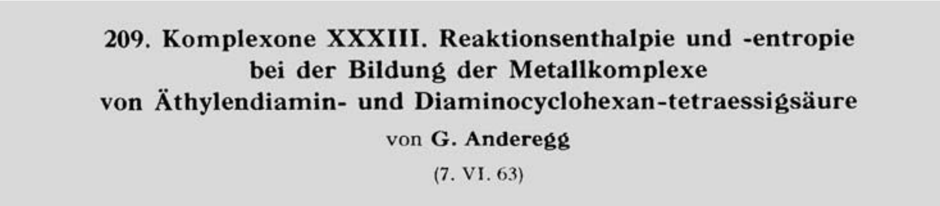


G. Schwarzenbach

phosphines is available only in the form of Ph. D. theses. Finally, it must be emphasized that *Schwarzenbach*'s work in the field of coordination chemistry published in *HCA* is not limited to that mentioned above, and for a full appreciation of his scientific contributions, the reader is referred to his Obituary, written by *Walter Schneider*, which was published in *HCA* in 1978 [9] where there also appears *Schwarzenbach*'s photograph shown above.

At this point a more readable account will result, if one proceeds along 'geographical' as apposed to 'chronological' lines and, therefore, one continues with the ETH.

Under *Schwarzenbach*'s leadership coordination chemistry at the Laboratorium für anorganische Chemie experienced a significant growth as equilibrium studies were com-



209. Komplexone XXXIII. Reaktionsenthalpie und -entropie bei der Bildung der Metallkomplexe von Äthylendiamin- und Diaminocyclohexan-tetraessigsäure

von **G. Anderegg**

(7. VI. 63)

Tabelle 3 *Thermodynamische Daten der Reaktion* $M^{\nu+} + L^{4-} \rightarrow ML^{\nu-4}$ *bei 20° und der ionalen Stärke 0,1* (KNO_3)

	EDTA				DCTA				
	log *K*	ΔG in Kcal Mol^{-1}	ΔH in Kcal Mol^{-1}	ΔS in cal Mol^{-1} $grad^{-1}$	log *K*	ΔG in Kcal Mol^{-1}	ΔH in Kcal Mol^{-1}	ΔS in cal Mol^{-1} $grad^{-1}$	$\Delta S_{MZ}-\Delta S_{MY}$
HL^{3-}	10,26	−13,76	− 5,67	27,6	12,35	−16,55	− 6,65	33,9	6,3
H_2L^{2-}	6,16	− 8,26	− 4,34	13,4	6,12	− 8,21	− 2,06	21,1	7,7
CaL^{2-}	10,7	−14,35	− 6,55	26,6	13,15	−17,63	− 3,70	47,5	20,9
BaL^{2-}	7,76	−10,41	− 4,93	18,7	8,64	−11,59	+ 0,33	40,9	22,2
SrL^{2-}	8,63	−11,57	− 4,08	25,6	10,54	−14,13	− 0,74	45,7	20,1
MgL^{2-}	8,69	−11,65	+ 3,49	51,0	10,97	−14,71	+ 3,80	63,1	12,1
CuL^{2-}	18,80	−25,21	− 8,15	58,2	21,95	−29,13	− 6,07	79,7	21,5
ZnL^{2-}	16,50	−22,13	− 4,85	59,0	19,32	−25,91	− 1,94	81,8	22,8
CoL^{2-}	16,31	−21,87	− 4,20	60,3	19,57	−26,24	− 2,80	80,0	19,7
CdL^{2-}	16,46	−22,07	− 9,05	44,4	19,88	−26,66	− 7,40	65,7	21,3
MnL^{2-}	13,80	−18,51	− 4,56	47,6	17,43	−23,37	− 4,14	65,60	18,0
NiL^{2-}	18,62	−24,97	− 7,55	59,4	–	–	− 5,37	–	–
PbL^{2-}	18,04	−24,19	−13,20	37,5	20,33	−27,26	−11,36	54,2	16,7
HgL^{2-}	21,80	−29,23	−18,90	35,5	24,95	−33,46	−16,60	59,0	23,5
LaL^{-}	15,50	−20,79	− 2,80	61,4	16,91	−22,68	+ 1,60	82,8	21,4

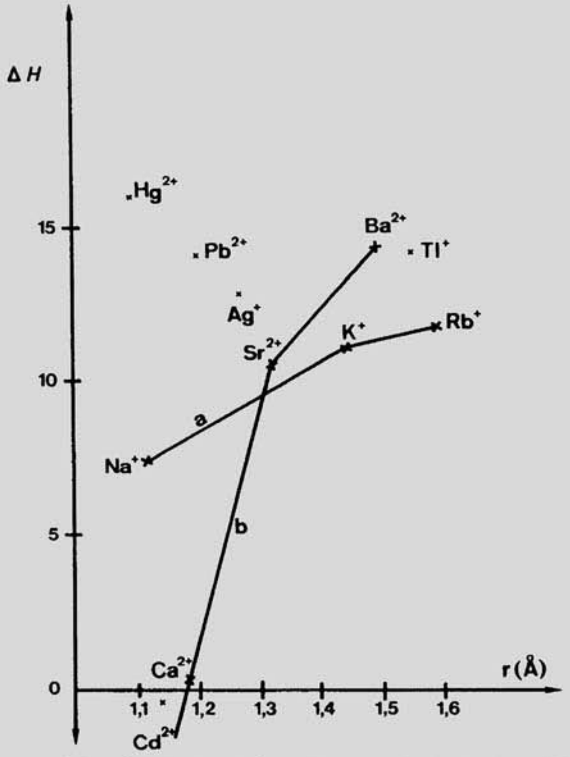


Fig. 2. *Die Bildungsenthalpie* ΔH [kcal mol^{-1}] *der Komplexe der Verbindung III als Funktion des Radius des entsprechenden Metallions*

plemented by studies of the thermodynamics and kinetics of complex formation. Thus, entropy and enthalpy data were regularly obtained by *Giorgio Anderegg* and his coworkers and appeared in print in *HCA*, as shown by the data published in the first paper of this series [10], reproduced on p. 30, dealing, not unexpectedly, with the aminopolycarboxylic acids.

Mention should also be made of the studies of the thermodynamics of the complexes formed by metal ions with *Jean-Marie Lehn*'s 'cryptands', more of whom will be said later in this account. A figure taken from *Anderegg*'s original publication [11], showing the enthalpies of complex formation of a variety of metal ions with the ligand $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$, is also reproduced on p. 30.

While most of the work done in the USA and in England on the kinetics of substitution reactions was carried out on robust complexes, *Gerard Geier* studied fast reaction systems, particularly those which had to be followed by T-jump techniques. The table shown below, taken from the paper with the title *'Die Kinetik der Murexid-Komplexbildung mit Kationen verschiedenen Koordinationscharakters. Eine Untersuchung mittels der Temperatursprung-Relaxationsmethode'*, which appeared in *HCA* [12], is a pioneering contribution in the area of coordination kinetics as it gives rates for the water-exchange reaction for 27 metal cations. This was the first report on substitution lability in aqueous solution for most of them.

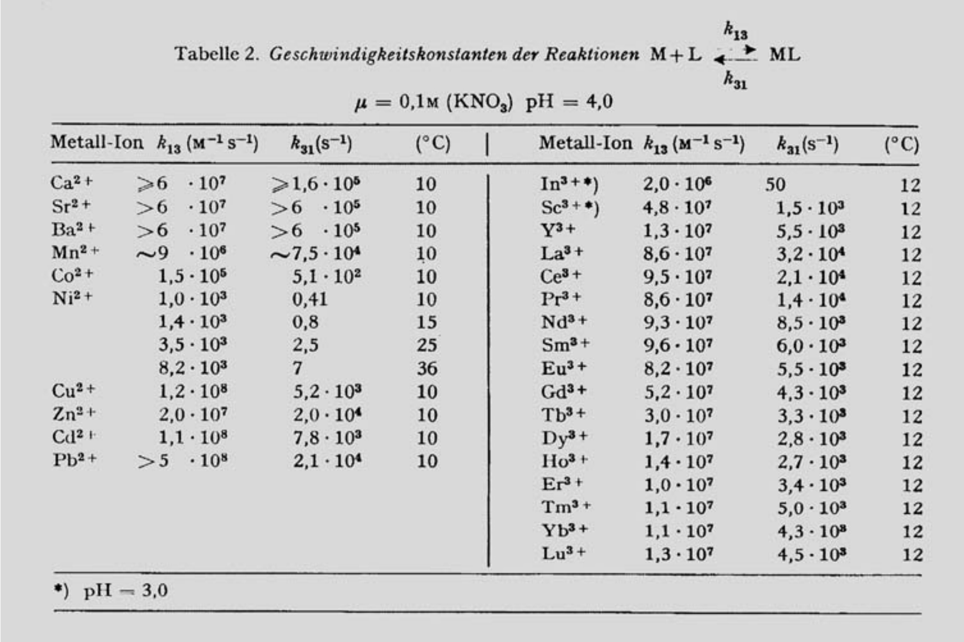


Tabelle 2. *Geschwindigkeitskonstanten der Reaktionen* $M + L \underset{k_{31}}{\overset{k_{13}}{\rightleftarrows}} ML$

$\mu = 0{,}1\,\text{M}\ (KNO_3)\ \ pH = 4{,}0$

Metall-Ion	$k_{13}\ (M^{-1}\,s^{-1})$	$k_{31}(s^{-1})$	(°C)	Metall-Ion	$k_{13}\ (M^{-1}\,s^{-1})$	$k_{31}(s^{-1})$	(°C)
Ca^{2+}	$\geqslant 6 \cdot 10^7$	$\geqslant 1{,}6 \cdot 10^5$	10	In^{3+}*)	$2{,}0 \cdot 10^6$	50	12
Sr^{2+}	$> 6 \cdot 10^7$	$> 6 \cdot 10^5$	10	Sc^{3+}*)	$4{,}8 \cdot 10^7$	$1{,}5 \cdot 10^3$	12
Ba^{2+}	$> 6 \cdot 10^7$	$> 6 \cdot 10^5$	10	Y^{3+}	$1{,}3 \cdot 10^7$	$5{,}5 \cdot 10^3$	12
Mn^{2+}	$\sim 9 \cdot 10^6$	$\sim 7{,}5 \cdot 10^4$	10	La^{3+}	$8{,}6 \cdot 10^7$	$3{,}2 \cdot 10^4$	12
Co^{2+}	$1{,}5 \cdot 10^5$	$5{,}1 \cdot 10^2$	10	Ce^{3+}	$9{,}5 \cdot 10^7$	$2{,}1 \cdot 10^4$	12
Ni^{2+}	$1{,}0 \cdot 10^3$	0,41	10	Pr^{3+}	$8{,}6 \cdot 10^7$	$1{,}4 \cdot 10^4$	12
	$1{,}4 \cdot 10^3$	0,8	15	Nd^{3+}	$9{,}3 \cdot 10^7$	$8{,}5 \cdot 10^3$	12
	$3{,}5 \cdot 10^3$	2,5	25	Sm^{3+}	$9{,}6 \cdot 10^7$	$6{,}0 \cdot 10^3$	12
	$8{,}2 \cdot 10^3$	7	36	Eu^{3+}	$8{,}2 \cdot 10^7$	$5{,}5 \cdot 10^3$	12
Cu^{2+}	$1{,}2 \cdot 10^8$	$5{,}2 \cdot 10^3$	10	Gd^{3+}	$5{,}2 \cdot 10^7$	$4{,}3 \cdot 10^3$	12
Zn^{2+}	$2{,}0 \cdot 10^7$	$2{,}0 \cdot 10^4$	10	Tb^{3+}	$3{,}0 \cdot 10^7$	$3{,}3 \cdot 10^3$	12
Cd^{2+}	$1{,}1 \cdot 10^8$	$7{,}8 \cdot 10^3$	10	Dy^{3+}	$1{,}7 \cdot 10^7$	$2{,}8 \cdot 10^3$	12
Pb^{2+}	$> 5 \cdot 10^8$	$2{,}1 \cdot 10^4$	10	Ho^{3+}	$1{,}4 \cdot 10^7$	$2{,}7 \cdot 10^3$	12
				Er^{3+}	$1{,}0 \cdot 10^7$	$3{,}4 \cdot 10^3$	12
				Tm^{3+}	$1{,}1 \cdot 10^7$	$5{,}0 \cdot 10^3$	12
				Yb^{3+}	$1{,}1 \cdot 10^7$	$4{,}3 \cdot 10^3$	12
				Lu^{3+}	$1{,}3 \cdot 10^7$	$4{,}5 \cdot 10^3$	12

*) pH = 3,0

The more theoretical and physico-chemical aspects of coordination chemistry at the ETH were pursued by *Walter Schneider*. Two aspects of this activity, which were published in *HCA*, deserve mention here. The first [13] describes an investigation of the thermal decomposition of $[Cr(Ox)_3]^{3-}$ (Ox = oxalate) catalysed by a variety of metal cations and the second an ESR spectral study of square planar Cu^{II} complexes [14].

212. Trioxalatokobaltat(III)-Ion in wässeriger Lösung: Thermischer Zerfall und Elektronaustausch mit Dioxalatokobaltat(II)-Ion[1])

von **W. Schneider**

(7. VI. 63)

$$\mathrm{CoOx}_3^{3-} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} \mathrm{CoOx}_2^{2-} + \mathrm{Ox} \qquad (4)$$

$$\mathrm{CoOx}_3^{3-} + \mathrm{Ox}^{-} \xrightarrow{k_3'} \mathrm{Co^{II}} + 3\,\mathrm{Ox}^{2-} + 2\,\mathrm{CO_2} \qquad (5)$$

k_1', k_2', k_3': Geschwindigkeitskonstanten

197. ESR-Spektren von $\mathrm{CuN_4}$-Chromophoren II[1]): Komplexe mit Ammoniak, Äthylendiamin, Biguanid, N-Trifluoracetimidoyl-trifluoracetamidin, N-Trichloracetimidoyl-trichloracetamidin, Tetraaza-undecan, Hexamethyl-tetraaza-cyclotetradecan und -cyclotetra decadien[2]) in Einkristallen

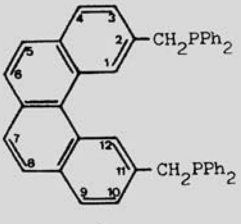
von **W. Schneider** und **P. Baccini**

Laboratorium für Anorganische Chemie der ETH, Zürich

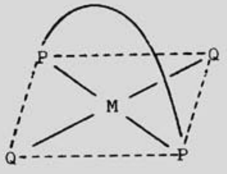
Herrn Prof. Dr. W. FEITKNECHT zum 70. Geburtstag gewidmet.

(28. VIII. 69)

The active pursuit of *Schwarzenbach*'s interests in the coordination chemistry of 'soft donors' was left to an 'outsider', the author of this article, who regretfully admits that he published only a fraction of the work done during his Zurich years in *HCA*. Reserved for this journal, however, have been the coordination chemistry of special ligands, *i.e.*, *trans*-spanning chelating diphosphine as shown below [15]:



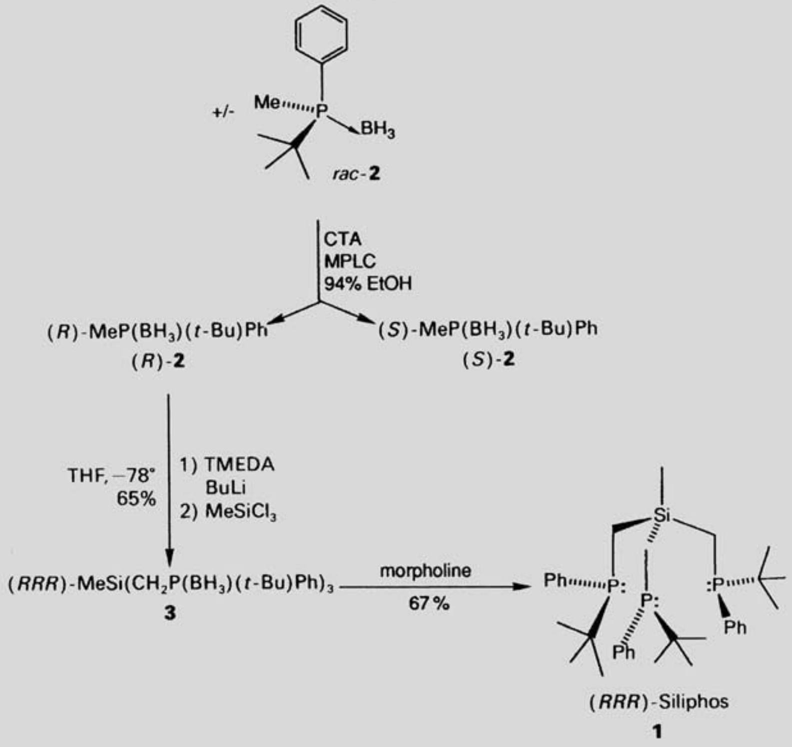
1



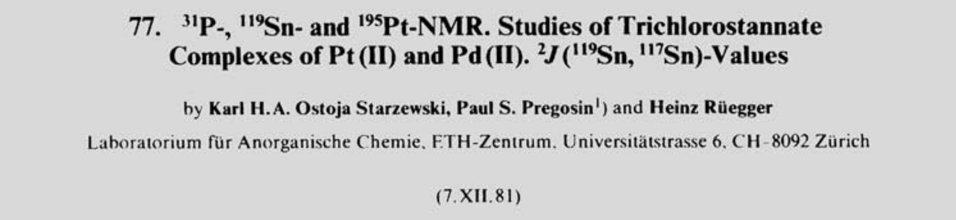
2

and the first optically pure C_3-symmetric tritertiary phosphine ligand bearing chirality on the P-atom prepared as shown in the scheme reproduced on p. 33 [16].

Scheme



Finally, the application of NMR techniques to coordination chemistry has not been neglected, and *Paul S. Pregosin* has been the prime motor behind these developments.



77. ^{31}P-, ^{119}Sn- and ^{195}Pt-NMR. Studies of Trichlorostannate Complexes of Pt(II) and Pd(II). $^2J(^{119}\mathrm{Sn}, ^{117}\mathrm{Sn})$-Values

by **Karl H. A. Ostoja Starzewski, Paul S. Pregosin**[1]) and **Heinz Rüegger**

Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 6, CH-8092 Zürich

(7.XII.81)

The most characteristic aspect of these studies has been the 'multinuclearity' of the approach, as can be seen from the title of the paper shown above and one of the figures contained there [17] shown on p. 34.

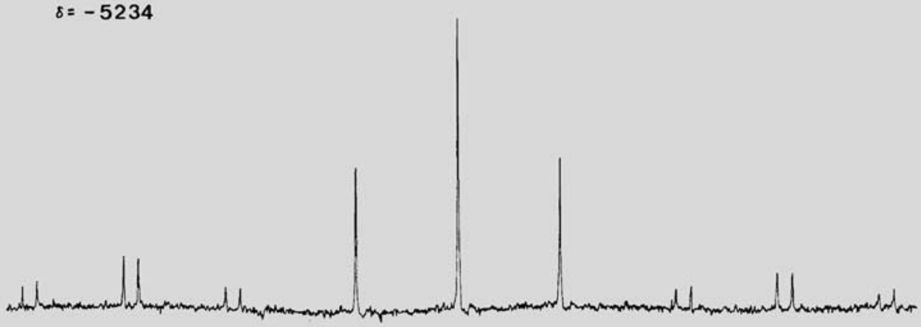


Fig. 2. *^{195}Pt-NMR. spectrum of [$Pt(SnCl_3)_3(P(OEt)_3)_2$]$^-$* (The intense triplet in the center of the spectrum stems from the two equivalent $^1J(^{195}Pt,^{31}P)$-values. The smaller, symmetrically placed signals result from the coupling constants $^1J(^{195}Pt,^{119}Sn)$ and $^1J(^{195}Pt,^{117}Sn)$)

An account of the work done at the ETH, involving coordination compounds, published in *HCA*, would be woefully incomplete, if mention were not made of the fascinating studies carried out in the Laboratorium für organische Chemie on the ferrioxamines by *Vladimir Prelog* and on the chemistry associated with Vitamin B_{12} by *Albert Eschenmoser*. However, both of these topics will be discussed elsewhere.

Mention should also be made here of the publication by *Jack D. Dunitz* in *HCA* of the X-ray crystal structure of the first cyclobutadiene complex [18]. The figure which appeared in that paper is shown below.

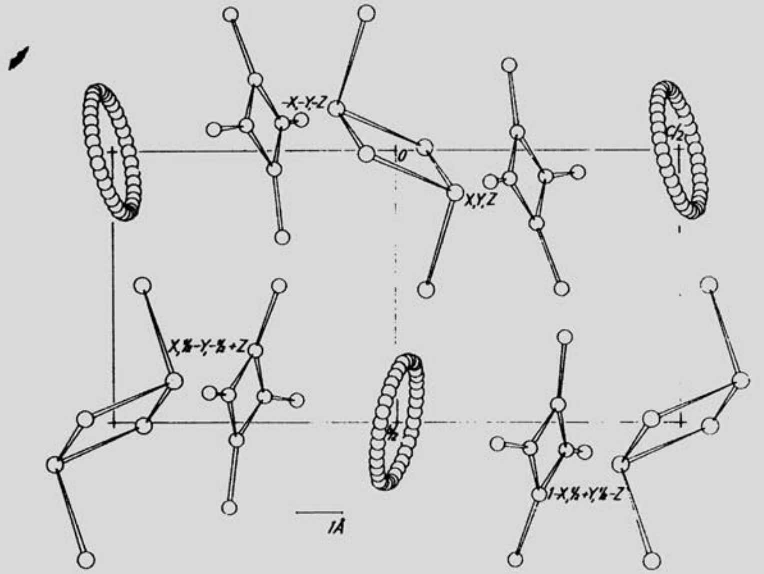
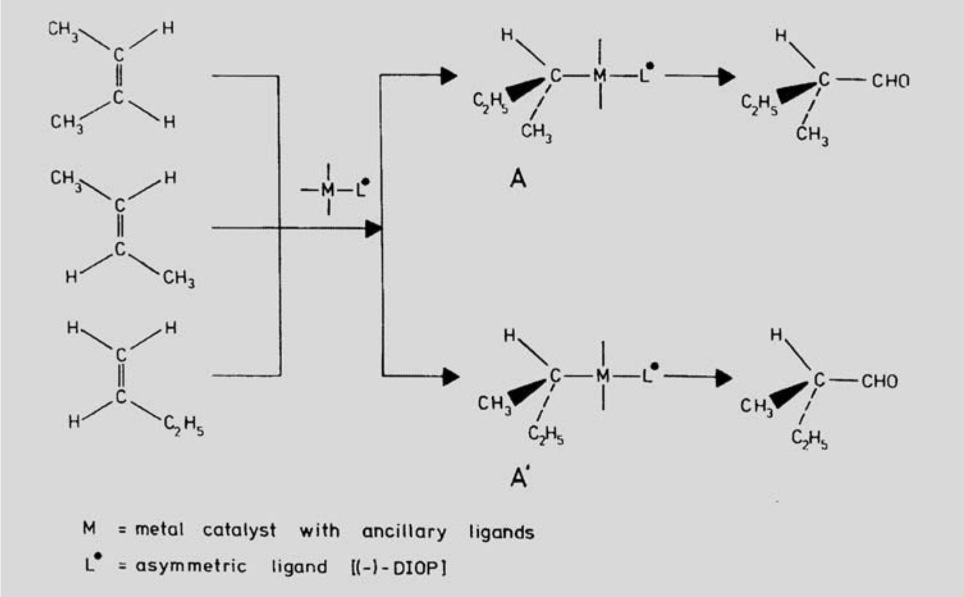
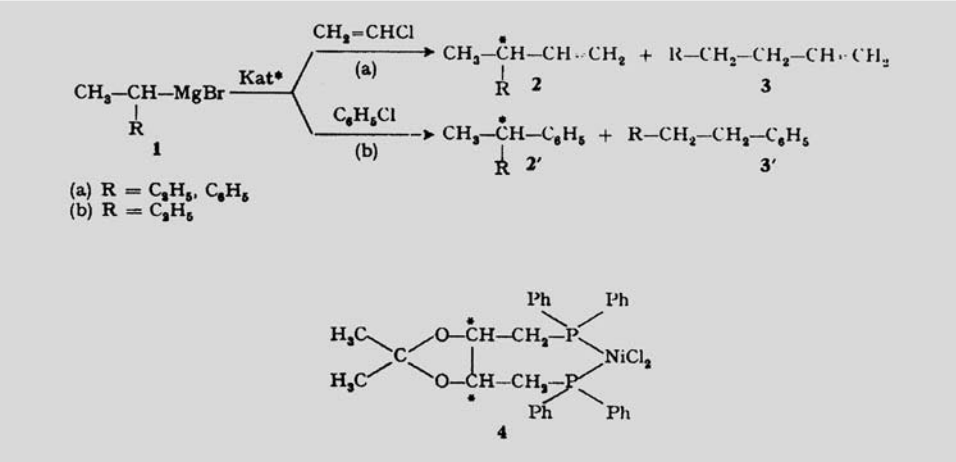


Fig. 7. ***1,2,3,4-Tetramethyl-cyclobutadien-nickel(II)-chlorid, Benzol-Addukt. Darstellung der räumlichen Packung in der Projektion entlang [100]***

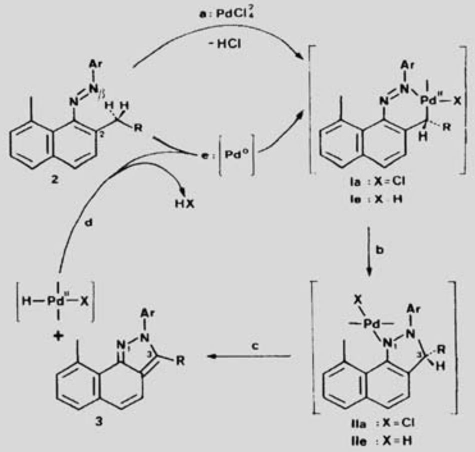
Furthermore, research work in the field of organometallic coordination chemistry and homogeneous catalysis has been carried out for a number of years in the Technisch-chemisches Laboratorium by *Piero Pino* and *Giambattista Consiglio*. Noteworthy among their contributions published in *HCA* are the first example of the asymmetric hydroformylation of alkenes using Pt catalysts [19]:



and the first example of the stereospecific Ni-catalysed cross-coupling reaction [20]:

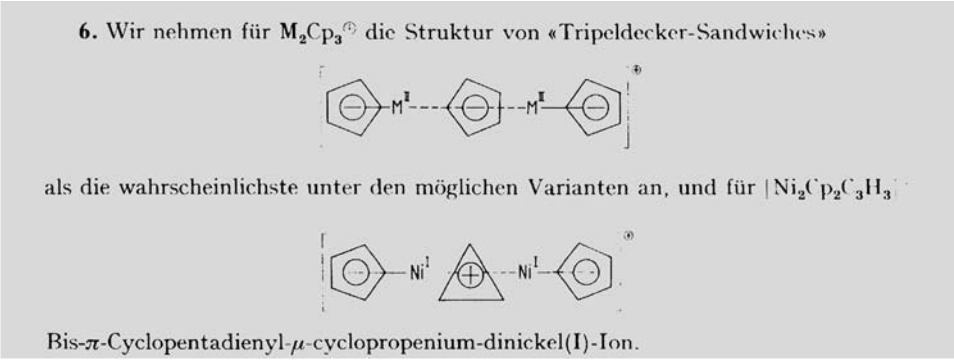


Numerous papers on the formation and reactivity of cyclometallated compounds, mostly of palladium with naphthalene derivatives, by *Paul Rys* at the Technisch-chemisches Laboratorium, were published in HCA. A particularly interesting contribution describes the formation of 2-arylbenzo[*g*]indazoles *via* cyclometallated 1-arylnaphthalenes [21]:



a: Cyclopalladation
b: Insertion (addition of Pd–C to N=N bond)
c: δ-Hydride elimination
d: Reductive elimination
e: Oxidative addition

Regular activity in the field of coordination chemistry at the University of Zurich resumed only after the arrival of *Helmut Werner* in 1967. However, it is worth recalling that there is an earlier *HCA* article by *Ernst Schumacher* (then Professor of Inorganic Chemistry there) [22] giving mass-spectrometric evidence for the existence of the triple-decker sandwiches shown below. The isolation of compounds of this type, however, was first reported in 1972.



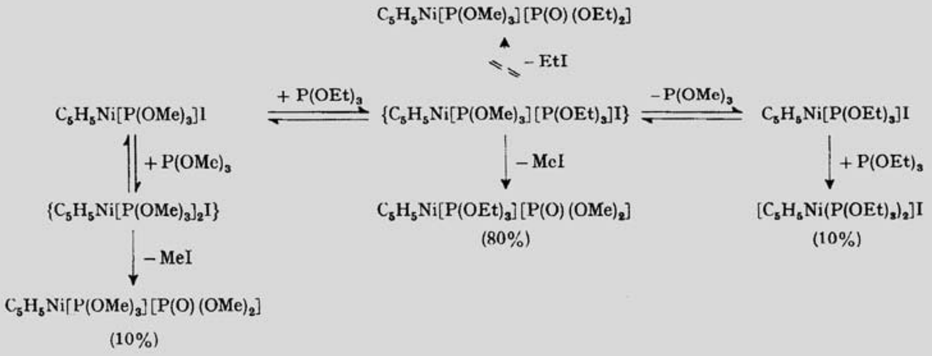
6. Wir nehmen für $M_2Cp_3^{\oplus}$ die Struktur von «Tripeldecker-Sandwiches»

als die wahrscheinlichste unter den möglichen Varianten an, und für $|Ni_2Cp_2C_3H_3|$

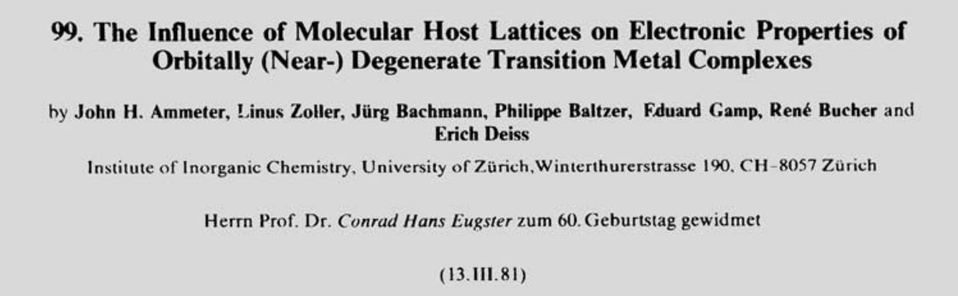
Bis-π-Cyclopentadienyl-μ-cyclopropenium-dinickel(I)-Ion.

Helmut Werner's earlier publications in HCA [23] described kinetic investigations of substitution reactions at organometallic complexes by phosphines and phosphites. Later, his studies acquired a more preparative interest and led to the dicovery of the coordination chemistry equivalent of the *Arbuzov* rearrangement in metallocene-Ni complexes [24]. The first reaction of this type reported by *Werner* is shown below.

Schema 1. *Verlauf der Reaktion von* $C_5H_5Ni[P(OMe)_3]I$ *und* $P(OEt)_3$ (in Klammern: NMR.-spektroskopisch bestimmte Ausbeute. Bedingungen: 15°, Aceton, Molverhältnis $C_5H_5Ni[P(OMe)_3]I : P(OEt)_3 = 1:1$)



The interest in organometallic chemistry at the Anorganisch-chemisches Institut of the University of Zurich continued even after *Helmut Werner* moved to Wurzburg. His



99. The Influence of Molecular Host Lattices on Electronic Properties of Orbitally (Near-) Degenerate Transition Metal Complexes

by **John H. Ammeter, Linus Zoller, Jürg Bachmann, Philippe Baltzer, Eduard Gamp, René Bucher** and **Erich Deiss**

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Herrn Prof. Dr. *Conrad Hans Eugster* zum 60. Geburtstag gewidmet

(13.III.81)

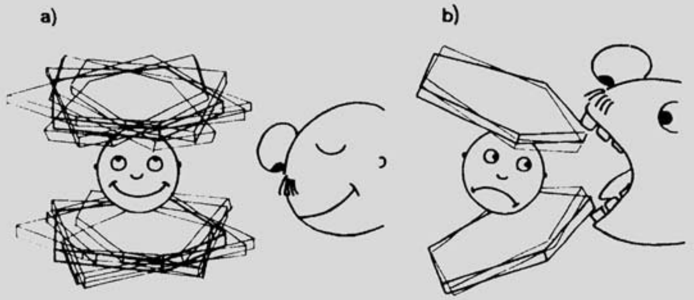
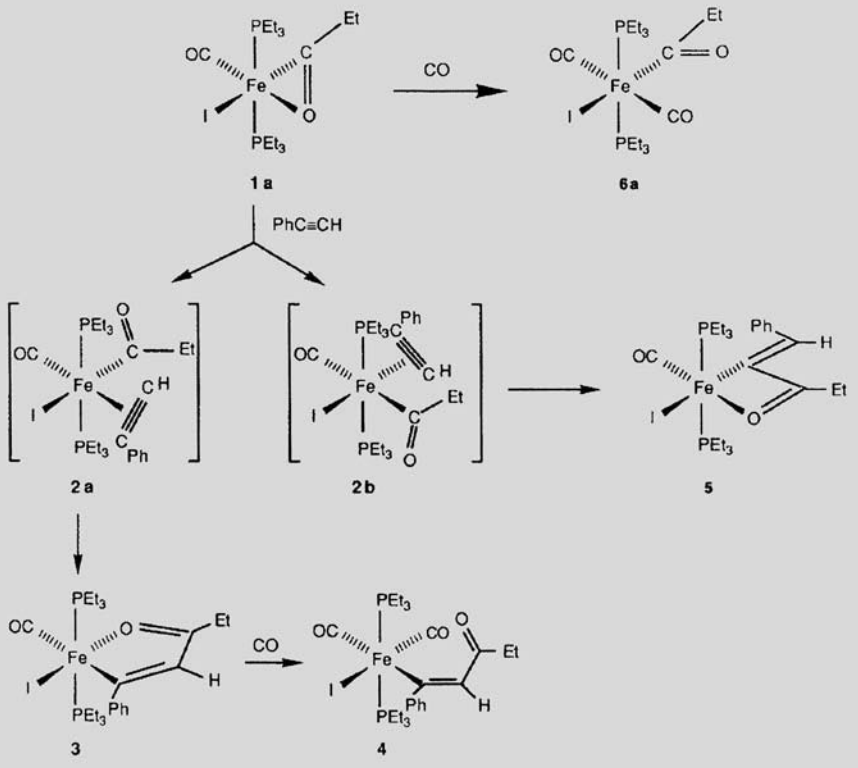


Fig. 14. *Illustration of the matrix effect explained* in Figures 11–13: *suppression of the dynamic* Jahn-Teller *ring tilt motion* (Fig. 9) *of free gaseous* d^5*-metallocenes* (a) *by an asymmetric molecular environment in a host lattice* (b).

successor, *John Ammeter*, continued to pursue there his theoretical and physico-chemical studies, particularly of the *Jahn-Teller* effects in metallocenes. An attractive illustration of this type of work, which appeared in *HCA* [25], is shown on p. 37.

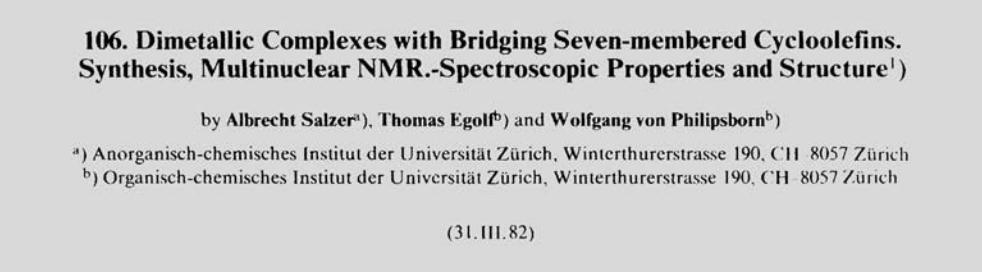
Organometallic chemistry is also being pursued by *Ammeter*'s successor *Heinz Berke*. A recent publication [26] describes the reaction of an η^2-acyl complex with phenylacetylene which gives, among other products, one containing a 'metallafuran' unit.

Scheme 1



1a 6a 2a 2b 5 3 4

Noteworthy are also the bimetallic complexes containing a bridging π-atomic system prepared by *Albrecht Salzer*. One example of a compound of this type [27] is shown on p. 39.



106. Dimetallic Complexes with Bridging Seven-membered Cycloolefins. Synthesis, Multinuclear NMR.-Spectroscopic Properties and Structure[1])

by **Albrecht Salzer**[a]), **Thomas Egolf**[b]) and **Wolfgang von Philipsborn**[b])

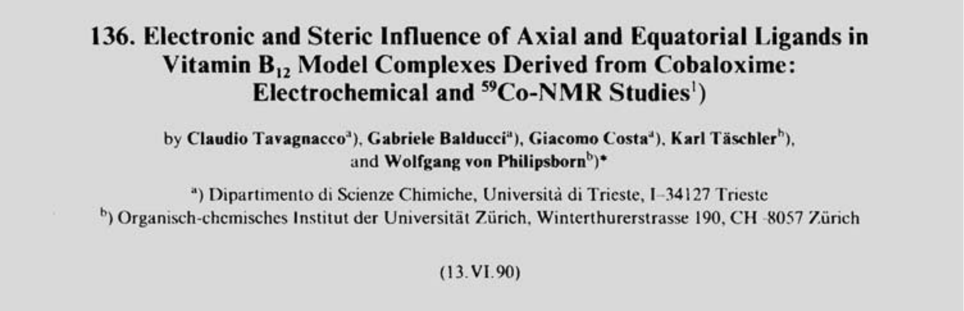
[a]) Anorganisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
[b]) Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(31.III.82)

Scheme 1[a])

[a]) The drawing of the bridging ring in this and subsequent *Schemes* does not imply a planar structure of the C_7H_7-unit *(cf. Scheme 2)*.

Much interesting coordination chemistry, albeit of spectroscopic nature, has been carried out in the Organisch-chemisches Institut der Universität Zürich by *Wolfgang von Philipsborn*. He has made many contributions to transition-metal NMR. In the fascinating recent example [28]:



136. Electronic and Steric Influence of Axial and Equatorial Ligands in Vitamin B_{12} Model Complexes Derived from Cobaloxime: Electrochemical and ^{59}Co-NMR Studies[1])

by **Claudio Tavagnacco**[a]), **Gabriele Balducci**[a]), **Giacomo Costa**[a]), **Karl Täschler**[b]), and **Wolfgang von Philipsborn**[b])*

[a]) Dipartimento di Scienze Chimiche, Università di Trieste, I-34127 Trieste
[b]) Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(13.VI.90)

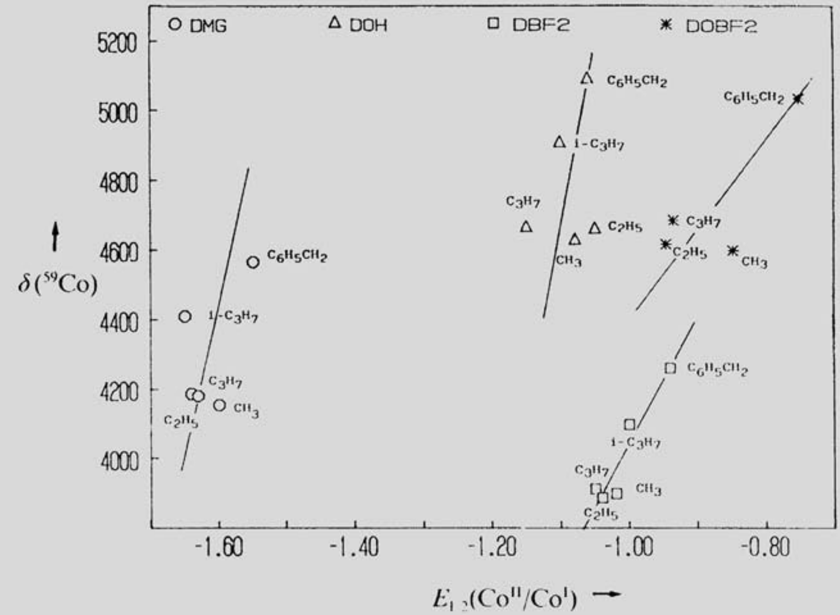
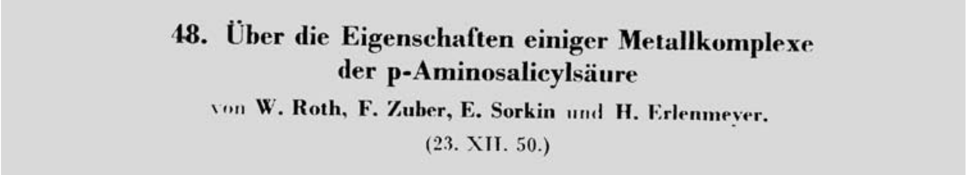


Fig. 7. $E_{1/2}$*(II) Values of the four alkyl-cobalamin model series* (see the *Scheme*) vs. δ(^{59}Co) *values*

one observes a good correlation between the $E_{1/2}(Co^{II}/Co^{I})$ values and the ^{59}Co-NMR chemical shifts for alkyl-cobalamine model compounds.

From the early fifties another significant development took place in Switzerland, this time in the area now known as Bioinorganic Chemistry. This development was started by *Hans Erlenmeyer* at what was then known as the Anstalt für anorganische Chemie der Universität Basel. The series of nearly forty papers, published under the heading 'Metallionen und biologische Wirkung', must surely be the earliest major contribution to this area.

The first paper to appear in HCA [29] shows that there exists a correlation between

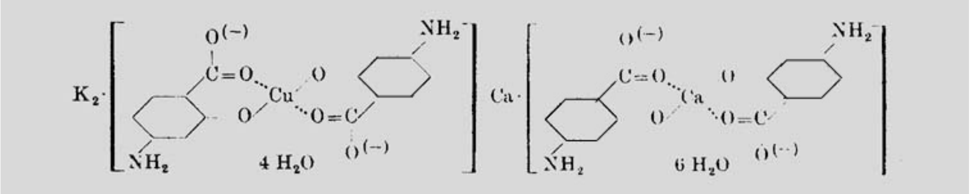


48. Über die Eigenschaften einiger Metallkomplexe der p-Aminosalicylsäure

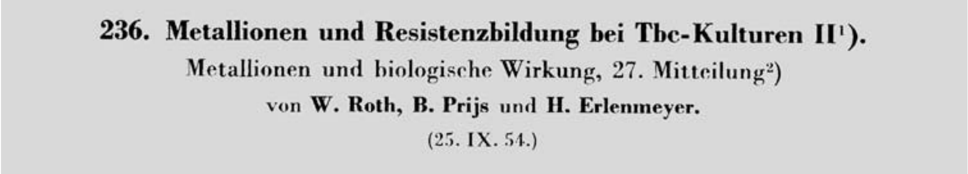
von **W. Roth, F. Zuber, E. Sorkin** und **H. Erlenmeyer.**

(23. XII. 50.)

tubercolostatic activity and the formation of the Cu^{II} complexes of ligands such as salicylic acid.



Over many years *Erlenmeyer* and coworkers tested large numbers of compounds of different types for tubercolostatic activity. As the work developed, the group became also interested in the interaction of these compounds with bacteria, and this led to publications such as [30]:



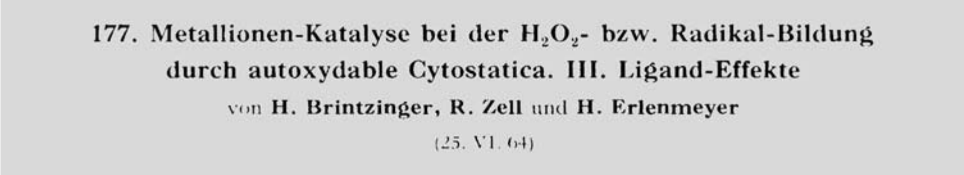
236. Metallionen und Resistenzbildung bei Tbc-Kulturen II[1]).

Metallionen und biologische Wirkung, 27. Mitteilung[2])

von **W. Roth, B. Prijs** und **H. Erlenmeyer.**

(25. IX. 54.)

In his latter years, *Erlenmeyer* became interested in metal ions and cytostatic activity. The title of what is probably his most significant contribution in this area [31] is shown below.



177. Metallionen-Katalyse bei der H_2O_2- bzw. Radikal-Bildung durch autoxydable Cytostatica. III. Ligand-Effekte

von **H. Brintzinger, R. Zell** und **H. Erlenmeyer**

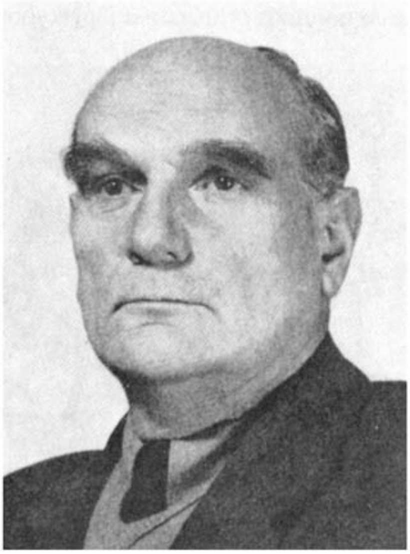
(25. VI. 64)

The reaction mechanism postulated at that time

$$\mathrm{Mn^{2+} + O_2 \rightarrow Mn^{3+} + {}^{\cdot}O\text{–}O^{-}} \tag{1}$$
$$\mathrm{Mn^{3+} + CH_3\text{–}NH\text{–}NH\text{–}CH_2R \rightarrow Mn^{2+} + CH_3\text{–}NH\text{–}N^{\cdot}\text{–}CH_2R + H^+} \tag{2a}$$
$$\mathrm{{}^{\cdot}O\text{–}O^{-} + H^+ + CH_3\text{–}NH\text{–}N^{\cdot}\text{–}CH_2R \rightarrow H_2O_2 + CH_3\text{–}N{=}N\text{–}CH_2R} \tag{3a}$$
$$\mathrm{{}^{\cdot}O\text{–}O^{-} + H^+ + CH_3\text{–}NH\text{–}NH\text{–}CH_2R \rightarrow H_2O_2 + CH_3\text{–}NH\text{–}N^{\cdot}\text{–}CH_2R} \tag{2b}$$
$$\mathrm{Mn^{3+} + CH_3\text{–}NH\text{–}N^{\cdot}\text{–}CH_2R \rightarrow Mn^{2+} + CH_3\text{–}N{=}N\text{–}CH_2R + H^+} \tag{3b}$$

is still worthy of serious consideration.

Erlenmeyer died not long after that publication, and his photograph, which appeared in an Obituary Notice [32], is reproduced below.



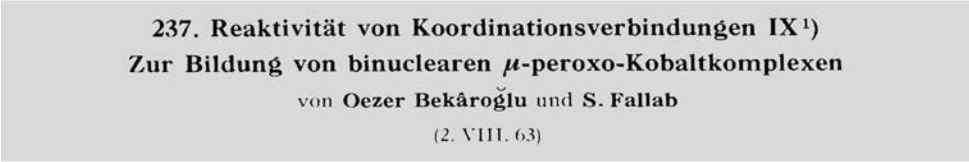
Hans Erlenmeyer

Finally, mention must be made of another of *Erlenmeyer*'s achievements: the establishment of a florishing school of coordination chemistry in the Institut für anorganische Chemie der Universität Basel with strong interests in the area of Bioinorganic Chemistry.

Silvio Fallab's collaboration with *Erlenmeyer*'s research programmes became first apparent, at least in *HCA*, with two publications which appeared in 1953 in connection with the topic *'Metallionen und biologische Wirkung'* [33]. Also *Hans Brintzinger*, *Klaus Bernauer*, *Thomas Kaden*, *Helmut Sigel*, and *Andreas Zuberbühler* came out of that school and made their international reputation through their publications in *HCA*.

Fallab's best known contributions on the reactivity of transition-metal complexes with molecular oxygen began to appear in *HCA* in 1959 [34] and became part of a series of papers with the general title *'Reaktivität von Koordinationsverbindungen'*.

The first paper on the formation of binuclear μ-peroxo-cobalt complexes appeared in *HCA* in 1963 [35].



237. Reaktivität von Koordinationsverbindungen IX 1)

Zur Bildung von binuclearen μ-peroxo-Kobaltkomplexen

von **Oezer Bekâroğlu** und **S. Fallab**

(2. VIII. 63)

Much of what is known about complexes of this type is due to his efforts in this area, and the results were also published in *HCA* as a series of papers under the heading *'Über Reaktionen oxygenierter Kobalt(II)-Chelate'*. Also much structural work on these complexes was done in collaboration with *Margaretha Zehnder*, and the X-ray structure of one of the more interesting compounds of this class [36] is shown below.

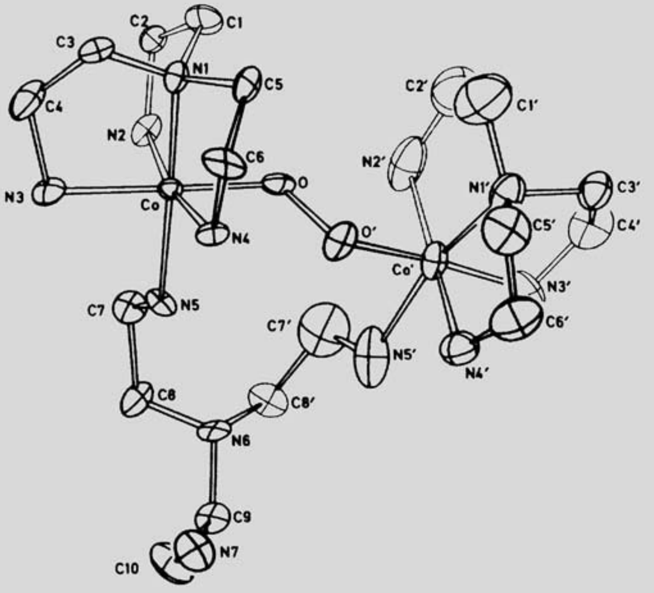
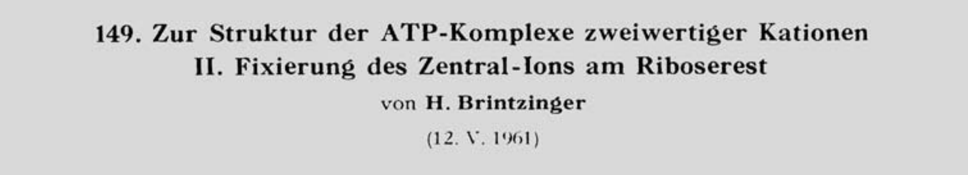


Fig. 1. *ORTEP des Kations* $[(\text{tren})\text{Co}(\text{O}_2,\text{tren})\text{Co}(\text{tren})]^{4+}$ **(Numerierung entsprechend Tabellen)**

Brintzinger's first publication in *HCA* appeared in 1955 and was on the topic *'Über Dipyridyl-Metallokomplexe'* [37]. However, from 1960 his main research interest centered around the interaction of cations with ATP.



149. Zur Struktur der ATP-Komplexe zweiwertiger Kationen
II. Fixierung des Zentral-Ions am Riboserest

von **H. Brintzinger**

(12. V. 1961)

An example of the information he was able to obtain from these studies is shown below [38].

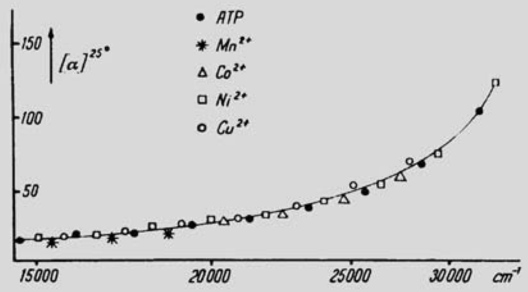
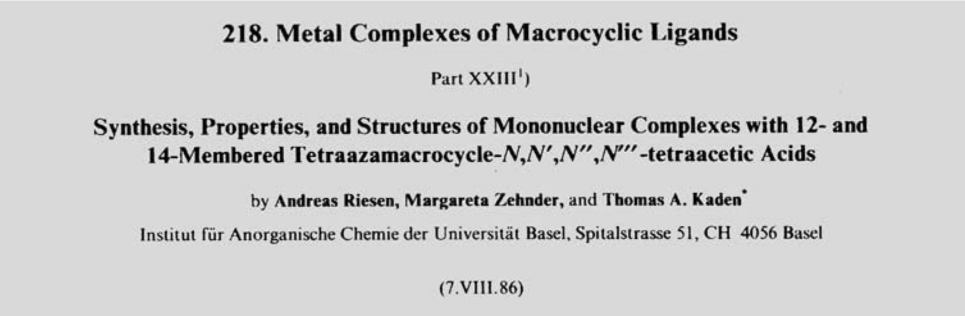


Fig. 3. *Rotationsdispersionskurven von ATP und deprotonisierten ATP-Komplexen verschiedener Metallionen, aufgenommen in 2 · 10^{-3}M-Lösungen*

A 1956 publication [39] introduced *Bernauer*'s name to the readers of *HCA*. This was part of the series *'Stabilität und Kinetik bei Komplexbildungsreaktionen'* associated with the names of *Erlenmeyer* and *Fallab*. While in Basle, *Bernauer* continued this collaboration and, as traditional, the resulting publications appeared in *HCA*. His interests, however, changed after he moved to Neuchâtel, and his contributions from there will be mentioned later.

The other member of what might be described as the 'Basle Group', *Kaden*, published his first paper in *HCA* describing some work done with *Fallab* on the topic *'Reaktivität von Koordinationsverbindungen'* [40]. Collaborative efforts with *Sigel* and *Zuberbühler* (see later), also published in *HCA*, were followed by what became his major research interest, *i.e.*, macrocyclic ligands. The first of these publications appeared in *HCA* in 1970 [41]. The more recent studies on functionalised azamacrocyles have aroused much interest. The structure of two compounds of this type were recently determined by X-ray diffraction.



218. Metal Complexes of Macrocyclic Ligands

Part XXIII[1])

Synthesis, Properties, and Structures of Mononuclear Complexes with 12- and 14-Membered Tetraazamacrocycle-*N*,*N′*,*N″*,*N‴*-tetraacetic Acids

by **Andreas Riesen, Margareta Zehnder,** and **Thomas A. Kaden***

Institut für Anorganische Chemie der Universität Basel, Spitalstrasse 51, CH 4056 Basel

(7.VIII.86)

An ORTEP view of the structure of Ni^{II} and Cu^{II} complexes with one of these ligands is shown below.

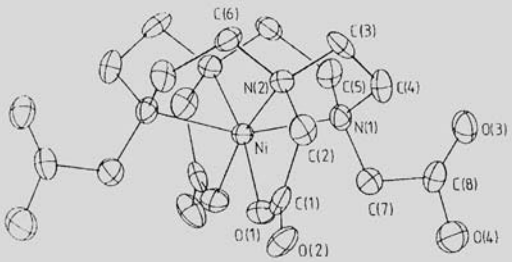


Fig. 1. *ORTEP Plot of Ni(H_2dota)*

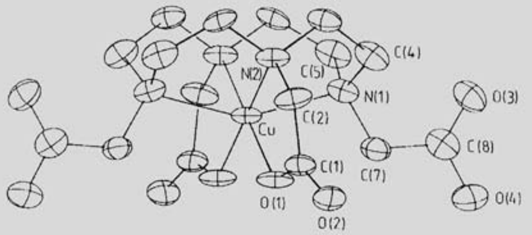
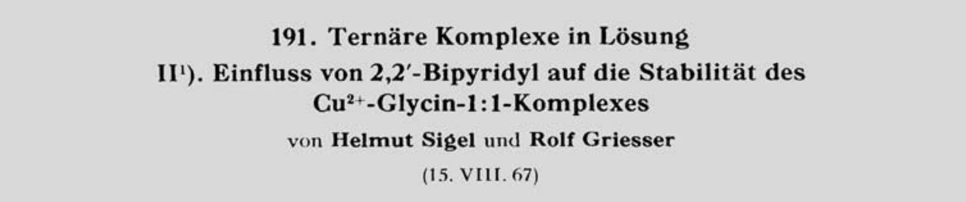


Fig. 2. *ORTEP Plot of Cu(H_2dota)*

Functionalised Cu^{II} macrocycles with pendant carboxylic groups have also been used by *Kaden* and coworkers as intermediates for protein-labelling agents [42].

The start of a new series of papers entitled *'Metallionen-Komplexe von 2-Amino-pyridin-1-oxid'* in 1963 [43] marked the appearance of *Sigel*'s name in *HCA*. This and the subsequent paper, co-authored by *Brintzinger*, were soon followed by *Sigel*'s active participation in the research topic on *'Metallionen und H_2O_2'*, one of the recurrent themes of *Erlenmeyer*'s interests. The results of these studies were regularly published in *HCA*, and the last paper in this series [44] appeared soon after *Erlenmeyer*'s death.

Sigel continued to make extensive use of *HCA* for his publications until 1968, and it is there he published in 1967 the first full paper on what later became his main research topic, *i.e.*, the *'Ternäre Komplexe in Lösung'* [45]. *Sigel* published most of his subsequent



191. Ternäre Komplexe in Lösung
II[1]). Einfluss von 2,2'-Bipyridyl auf die Stabilität des
Cu^{2+}-Glycin-1:1-Komplexes
von **Helmut Sigel** und **Rolf Griesser**
(15. VIII. 67)

work in this area in other journals, but one significant contribution did appear in *HCA* in 1978 [46], and a figure showing *Sigel*'s postulated ternary interaction, reproduced from the above paper, is shown on p. 45.

The recurrent theme in *Zuberbühler*'s academic career, copper and its coordination chemistry, became manifest even in the first of his publications in *HCA*, which appeared

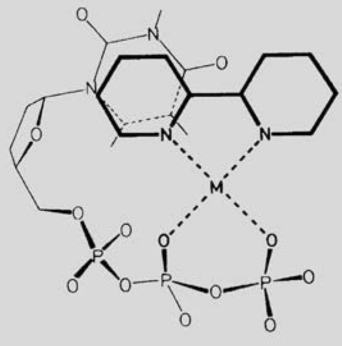
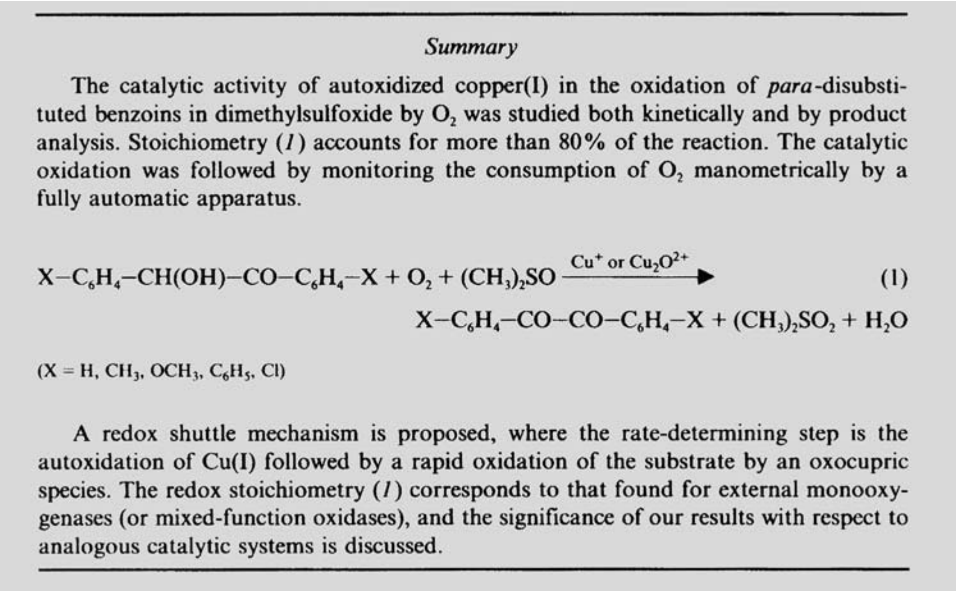


Fig. 4. *A tentative and simplified structure of the ternary stacked complex $M(bipy)(UTP)^{2-}$*

in 1966 [47]. This, and very many of his later papers were co-authored by *Kaden*, particularly those in the series *'Kupferkomplexe von Bisamiden'*. *HCA* was also used for the publication of the series of papers on the 'Autoxidation von Cu^{I}-Komplexen' and 'Cuprous Complexes and Dioxygen' which appeared between 1970 and 1984.

His current research interests, which are centered around complex equilibria involving Cu^{I} and Cu^{II} species, including their reactions with molecular oxygen, are well illustrated by the summary of a fairly recent publication [48] shown below.



Summary

The catalytic activity of autoxidized copper(I) in the oxidation of *para*-disubstituted benzoins in dimethylsulfoxide by O_2 was studied both kinetically and by product analysis. Stoichiometry (*1*) accounts for more than 80% of the reaction. The catalytic oxidation was followed by monitoring the consumption of O_2 manometrically by a fully automatic apparatus.

$$X{-}C_6H_4{-}CH(OH){-}CO{-}C_6H_4{-}X + O_2 + (CH_3)_2SO \xrightarrow{Cu^{+}\text{ or }Cu_2O^{2+}} X{-}C_6H_4{-}CO{-}CO{-}C_6H_4{-}X + (CH_3)_2SO_2 + H_2O \quad (1)$$

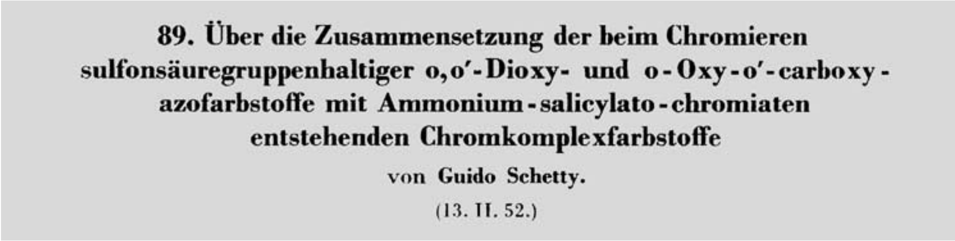
(X = H, CH_3, OCH_3, C_6H_5, Cl)

A redox shuttle mechanism is proposed, where the rate-determining step is the autoxidation of Cu(I) followed by a rapid oxidation of the substrate by an oxocupric species. The redox stoichiometry (*1*) corresponds to that found for external monooxygenases (or mixed-function oxidases), and the significance of our results with respect to analogous catalytic systems is discussed.

Significant contributions to coordination chemistry were also made in industrial research laboratories in Basle. Thus, mention must be made of the almost unique development, in one special area of coordination chemistry which occurred in the Wissenschaftliche Laboratorien der *J. R. Geigy AG*, later incorporated into the Zentrale

Forschungslaboratorien der *Ciba-Geigy AG*. Much fundamental synthetic and structural work on the complexes of dyestuffs was done by *Guido Schetty*. His results, about 30 papers, were published in *HCA* between 1952 and 1976.

There is little doubt that *Schetty*'s 1952 *HCA* publication [49] must be the first account of the application of *Alfred Werner*'s coordination theory to chromium 'salts' of azo-dyes. The initial work on the constitution of these complexes was extended to considerations of structural isomerism [50]. As can be seen from the sketches reproduced below, the structure shown in Fig. 1 shows what we would now call the *mer*-isomer, then referred to as the '*Drew-Pfitzner*' form, while Fig. 2 depicts the *mer*-isomer, then called the *'sandwich type'*. The early correlations between isomeric structure and colour, made using VIS/UV spectroscopy, were later confirmed by X-ray structure determinations [51] (see p. 47) and by NMR spectroscopy [52].



89. Über die Zusammensetzung der beim Chromieren sulfonsäuregruppenhaltiger o,o'-Dioxy- und o-Oxy-o'-carboxy-azofarbstoffe mit Ammonium-salicylato-chromiaten entstehenden Chromkomplexfarbstoffe

von **Guido Schetty**.

(13. II. 52.)

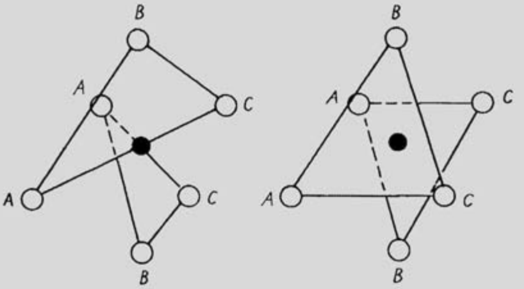


Fig. 1. ∟-Typus Fig. 2. ∠-Typus

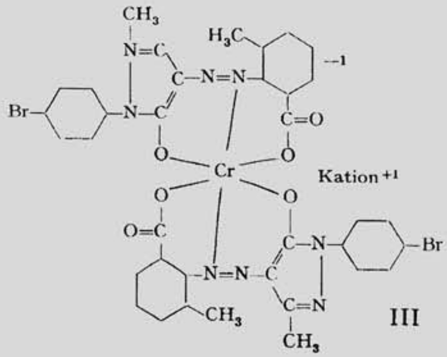
Anordnung der Valenzstellen im Valenzoktaeder (perspektivische Darstellung)

● = Metallatom
○ = Valenzstellen

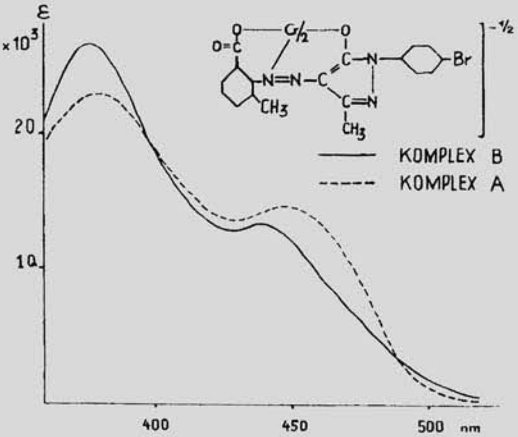
∢ CAB = ∢ ACB = 45°
∢ CBA = 90°

∢ CAB = ∢ CBA = ∢ ACB = 60°

Significant activity in the field of coordination chemistry has been going on at the University of Berne since the mid-sixties and *Andreas Ludi* and *Hans-Ulrich Güdel*



III



Absorptionsspektren der Komplexe III A und B in Methanol
aufgenommen bei einer Konz. von $4 \cdot 10^{-5}$ M auf einem Spektrographen BECKMAN Mod. DK-2A

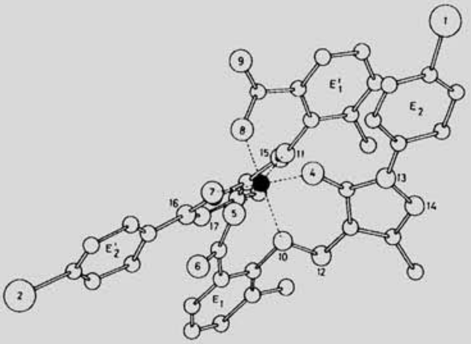
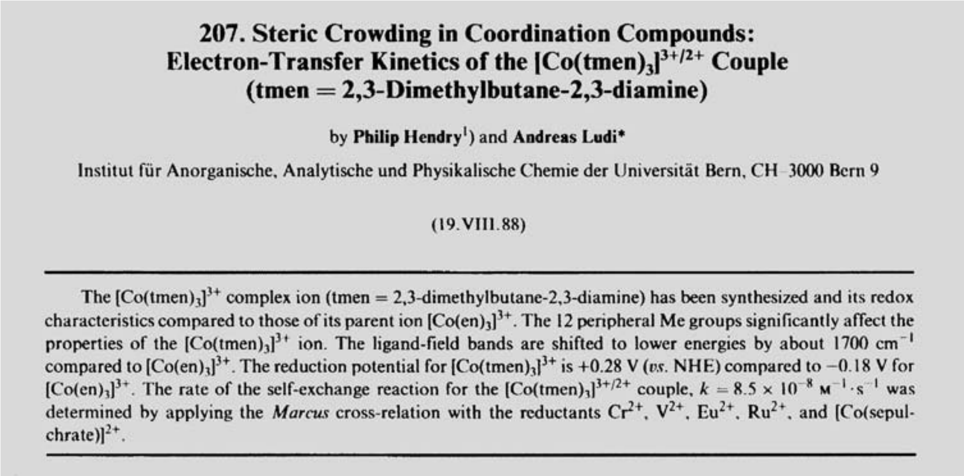


Fig. 5. *Darstellung eines einzelnen Komplexes*
Projektion längs der *a*-Achse

published most of their work in *HCA* until 1969, reporting structural and spectroscopic investigations mainly on cyanide complexes. Since then, only one of *Ludi*'s interesting papers [53] has appeared in *HCA*. Its title and summary are shown below.



207. Steric Crowding in Coordination Compounds: Electron-Transfer Kinetics of the $[Co(tmen)_3]^{3+/2+}$ Couple (tmen = 2,3-Dimethylbutane-2,3-diamine)

by **Philip Hendry**[1]) and **Andreas Ludi***

Institut für Anorganische, Analytische und Physikalische Chemie der Universität Bern, CH-3000 Bern 9

(19.VIII.88)

The $[Co(tmen)_3]^{3+}$ complex ion (tmen = 2,3-dimethylbutane-2,3-diamine) has been synthesized and its redox characteristics compared to those of its parent ion $[Co(en)_3]^{3+}$. The 12 peripheral Me groups significantly affect the properties of the $[Co(tmen)_3]^{3+}$ ion. The ligand-field bands are shifted to lower energies by about 1700 cm^{-1} compared to $[Co(en)_3]^{3+}$. The reduction potential for $[Co(tmen)_3]^{3+}$ is +0.28 V (*vs.* NHE) compared to −0.18 V for $[Co(en)_3]^{3+}$. The rate of the self-exchange reaction for the $[Co(tmen)_3]^{3+/2+}$ couple, $k = 8.5 \times 10^{-8}$ M$^{-1}\cdot$s^{-1} was determined by applying the *Marcus* cross-relation with the reductants Cr^{2+}, V^{2+}, Eu^{2+}, Ru^{2+}, and $[Co(sepulchrate)]^{2+}$.

The chemistry of coordination compounds has also been much pursued by *Rolf Scheffold* who made significant contributions in the field Vitamin B_{12} and related compounds. His work will be reviewed at a later date.

The study of coordination compounds has not been absent at the University of Fribourg. The first name that comes to mind in this connection is that of *Alexander von Zelewsky*. His first independent paper in *HCA* reported a pioneering effort in the early days of transition-metal NMR, in this case, of ^{195}Pt [54], done while at UCLA. The data shown in the table below speak for themselves.

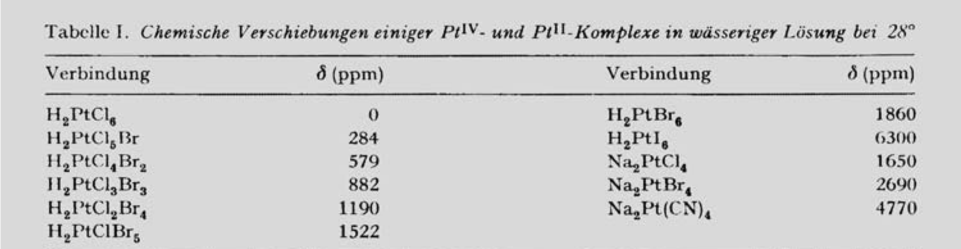


Tabelle I. *Chemische Verschiebungen einiger Pt^{IV}- und Pt^{II}-Komplexe in wässeriger Lösung bei 28°*

Verbindung	δ (ppm)	Verbindung	δ (ppm)
H_2PtCl_6	0	H_2PtBr_6	1860
H_2PtCl_5Br	284	H_2PtI_6	6300
$H_2PtCl_4Br_2$	579	Na_2PtCl_4	1650
$H_2PtCl_3Br_3$	882	Na_2PtBr_4	2690
$H_2PtCl_2Br_4$	1190	$Na_2Pt(CN)_4$	4770
$H_2PtClBr_5$	1522		

Having established himself in Fribourg, *von Zelewsky* published the first of his papers on *'Metal Complexes of Radicals'* [55], making extensive use of his previous experience with ESR [56]. An impressive spectrum of one of his complexes is shown on p. 49 [55].

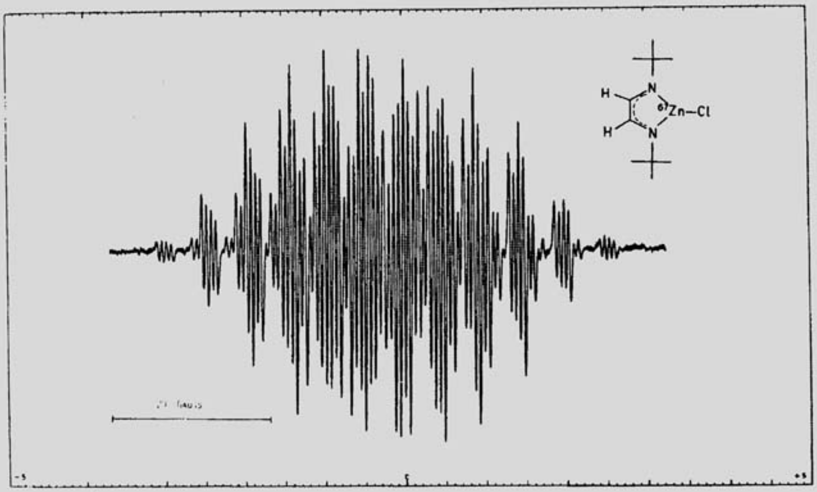
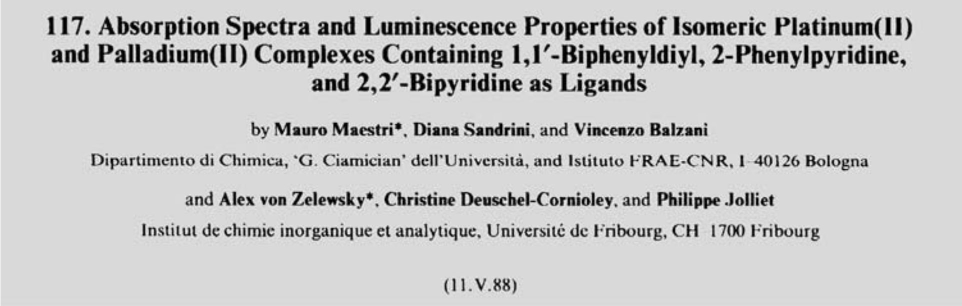


Fig. 7. *ESR. spectrum of* ^{67}*Zn(GLIR)Cl* (89,5% ^{67}Zn)

von Zelewsky's interest in the synthesis, spectroscopy and electrochemistry of Ru^{II} complexes, developed with the assistance of *P. Belser*, led to a fruitful collaboration with *Vincenzo Balzani*. Later, cyclometallated compounds of Pt^{II} and Rh^{II} were prepared, and their properties compared with those of the corresponding complexes containing only nitrogen donors [57].



117. Absorption Spectra and Luminescence Properties of Isomeric Platinum(II) and Palladium(II) Complexes Containing 1,1′-Biphenyldiyl, 2-Phenylpyridine, and 2,2′-Bipyridine as Ligands

by **Mauro Maestri***, **Diana Sandrini**, and **Vincenzo Balzani**

Dipartimento di Chimica, 'G. Ciamician' dell'Università, and Istituto FRAE-CNR, I-40126 Bologna

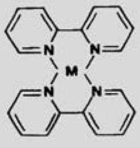
and **Alex von Zelewsky***, **Christine Deuschel-Cornioley**, and **Philippe Jolliet**

Institut de chimie inorganique et analytique, Université de Fribourg, CH-1700 Fribourg

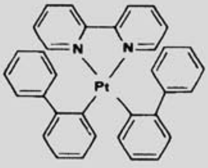
(11.V.88)

[M(bph)(bpy)]

[M(phpy)$_2$]

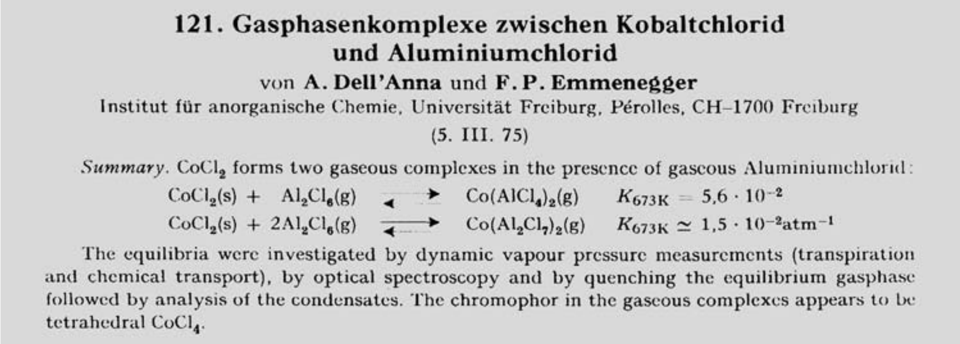


[M(bpy)$_2$]$^{2+}$



[Pt(H$_2$bph)$_2$(bpy)]

The *HCA* reader associates *Franzpeter Emmenegger*'s name mainly with the study of inorganic salts and metal complexes in the gas phase, particularly with the classic study shown below [58].



121. Gasphasenkomplexe zwischen Kobaltchlorid und Aluminiumchlorid

von **A. Dell'Anna** und **F. P. Emmenegger**

Institut für anorganische Chemie, Universität Freiburg, Pérolles, CH–1700 Freiburg

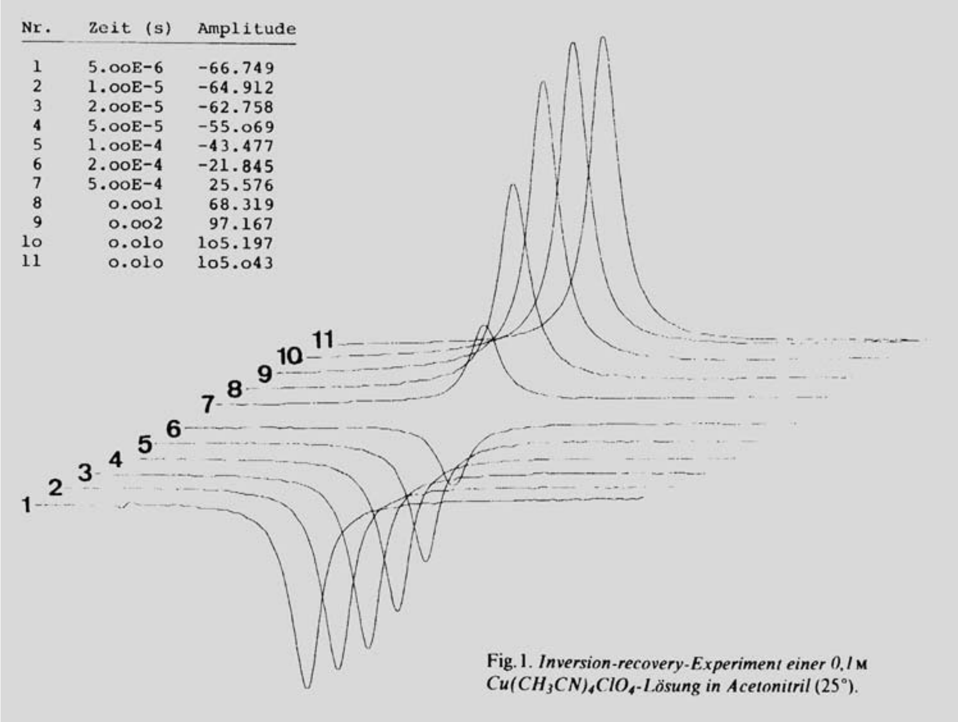
(5. III. 75)

Summary. $CoCl_2$ forms two gaseous complexes in the presence of gaseous Aluminiumchlorid:

$$CoCl_2(s) + Al_2Cl_6(g) \rightleftarrows Co(AlCl_4)_2(g) \qquad K_{673K} = 5{,}6 \cdot 10^{-2}$$
$$CoCl_2(s) + 2Al_2Cl_6(g) \rightleftarrows Co(Al_2Cl_7)_2(g) \qquad K_{673K} \simeq 1{,}5 \cdot 10^{-2} atm^{-1}$$

The equilibria were investigated by dynamic vapour pressure measurements (transpiration and chemical transport), by optical spectroscopy and by quenching the equilibrium gasphase followed by analysis of the condensates. The chromophor in the gaseous complexes appears to be tetrahedral $CoCl_4$.

Another significant contributor to Fribourg Inorganic Chemistry is *Carl W. Schläpfer*, particularly for his classic paper on ^{63}Cu-NMR [59].



Nr.	Zeit (s)	Amplitude
1	5.00E-6	-66.749
2	1.00E-5	-64.912
3	2.00E-5	-62.758
4	5.00E-5	-55.069
5	1.00E-4	-43.477
6	2.00E-4	-21.845
7	5.00E-4	25.576
8	0.001	68.319
9	0.002	97.167
10	0.010	105.197
11	0.010	105.043

Fig. 1. *Inversion-recovery-Experiment einer 0,1* M *$Cu(CH_3CN)_4ClO_4$-Lösung in Acetonitril* (25°).

Mention was made earlier of *Bernauer*'s contribution to the 'Basle School'. After his move to Neuchâtel, his name first appeared in *HCA*, associated with that of *A. Jacot-Guillarmod*, dealing with topics of organometallic chemistry. However, his interest in stereoselective reactions became apparent in 1970 [60], and since then, several key papers have appeared in *HCA*, *e.g.*, one describing the first asymmetric synthesis of amino acids using copper complexes with *Schiff* bases [61], another reporting a newly discovered stereoselective electron-transfer reaction [62], and a most recent contribution [63] reporting the first example of chiral recognition at the surface of a metalloprotein.

38. Stereoselectivity and Chiral Recognition in the Electron-Transfer Reaction between Spinach Ferredoxin and Optically Active Cobalt(III) Complexes[1])

by **Klaus Bernauer**[a])*, **Michel Monzione**[a]), **Peter Schürmann**[b]), and **Véronique Viette**[a])

[a]) Institut de Chimie, Université de Neuchâtel, 51, Av. de Bellevaux, CH-2000 Neuchâtel
[b]) Laboratoire de Biochimie Végétale, Université de Neuchâtel, Chantemerle 18, CH 2000 Neuchâtel

(22.XII.89)

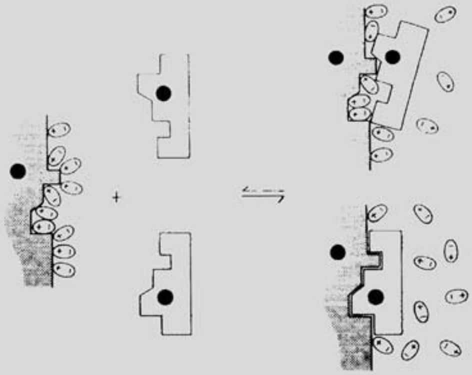


Fig. 5. *Schematic representation of the formation of a precursor complex or a transition state between a metalloprotein and the enantiomers of an optically active complex*

The premature death of *Werner Marty* deprived the University of Neuchâtel of a very able scientist. The title of one particularly interesting publication describing some of the work that was being done at that time is shown below [64].

201. A Unified Interpretation of Kinetic Data on the Acid-Induced Cleavage and of Product-Analysis Data on Spontaneous Cleavage of the Mono-ol Cation μ-Hydroxo-bis[pentaamminecobalt(III)] ($[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$)

by **François P. Rotzinger**[1]) and **Werner Marty***

Institut de chimie, Université de Neuchâtel, Av. de Bellevaux 51, CH 2000 Neuchâtel

(19.VII.85)

His successor, *Georg Süss-Fink*, in a recent *HCA* paper [65], describes an elegant new synthetic route to anhydrous acetonine.

53. Katalytische Carbonylierung von Aceton-oxim an Bisoximato-diruthenium-Komplexen: Ein einfacher Zugang zu wasserfreiem Acetonin. Isolierung und Molekülstruktur von $[Ru_2(CO)_5(Me_2CNO)_2(Me_2CNOH)]$

von **Meinhard Langenbahn, Helen Stoeckli-Evans** und **Georg Süss-Fink***

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel

(7.1.91)

The active pursuit of coordination chemistry at the Institut de Chimie Minérale et Analytique de l'Université de Lausanne started under the guidance of *André E. Merbach*. His initial publication in this area reported the use of NMR for the study of aminocarboxylates of the rare earths [66]. This was followed up by a series of papers [67] applying this technique to the study of complexes of Group-V halides.

The three most important contributions made by *Merbach* and coworkers were all published in *HCA*. The first of them describes the use of high-pressure, high-resolution NMR as a tool in chemical kinetics, *i.e.*, for the determination of the volumes of activation for the assignment of reaction mechanisms [68]. Some of the experimental curves published in this paper are shown below.

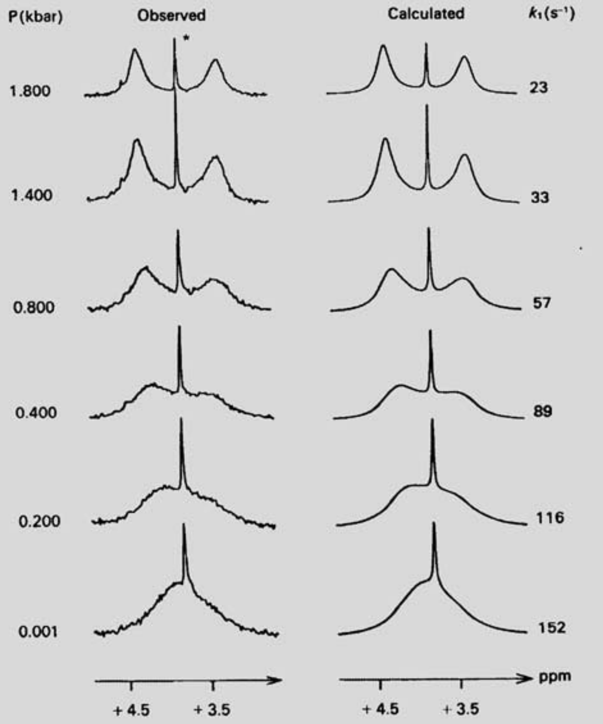
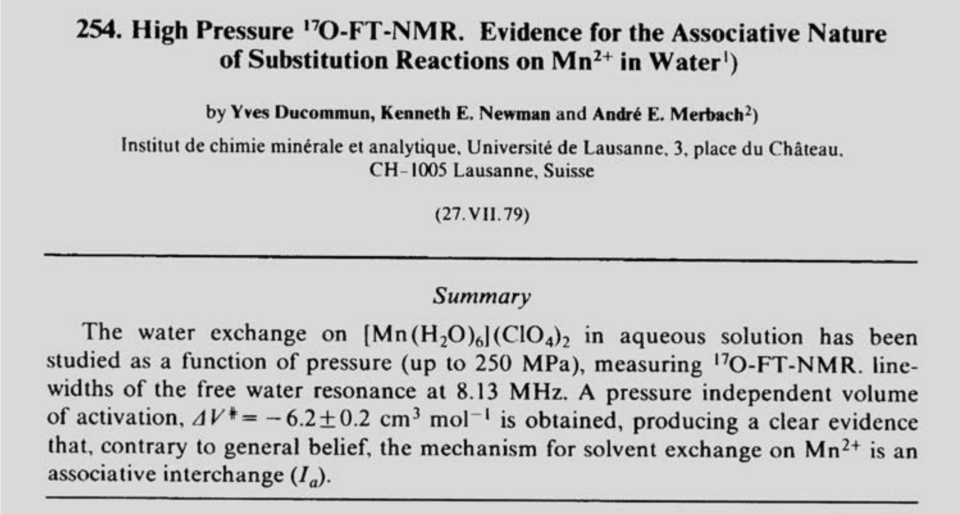


Fig. 1. *Observed and calculated* ^{1}*H-NMR. spectra for the* D *ligand exchange* $TaBr_5 \cdot Me_2O + {}^*Me_2O \rightleftarrows TaBr_5 \cdot {}^*Me_2O + Me_2O$ *as a function of pressure, in* CH_2Cl_2 *at 286.1 K.* (*) = signal of the ^{13}C satellite of the solvent. ($[TaBr_5 \cdot Me_2O] = 0.130$ m, $[Me_2O] = 0.114$ m; $\delta(TaBr_5 \cdot Me_2O) = 4.36$ ppm, $\delta(Me_2O) = 3.33$ ppm).

The second reports the pioneering use of ^{17}O-NMR:



254. High Pressure ^{17}O-FT-NMR. Evidence for the Associative Nature of Substitution Reactions on Mn^{2+} in Water[1])

by **Yves Ducommun, Kenneth E. Newman** and **André E. Merbach[2])**

Institut de chimie minérale et analytique, Université de Lausanne, 3, place du Château,
CH-1005 Lausanne, Suisse

(27.VII.79)

Summary

The water exchange on $[Mn(H_2O)_6](ClO_4)_2$ in aqueous solution has been studied as a function of pressure (up to 250 MPa), measuring ^{17}O-FT-NMR. linewidths of the free water resonance at 8.13 MHz. A pressure independent volume of activation, $\Delta V^{\neq} = -6.2 \pm 0.2$ cm^3 mol^{-1} is obtained, producing a clear evidence that, contrary to general belief, the mechanism for solvent exchange on Mn^{2+} is an associative interchange (I_a).

Finally, high-pressure ^{1}H-NMR was used to determine volumes of activation for solvent-exchange reactions [70]. The elegance of this method can be gauged from the figure shown below.

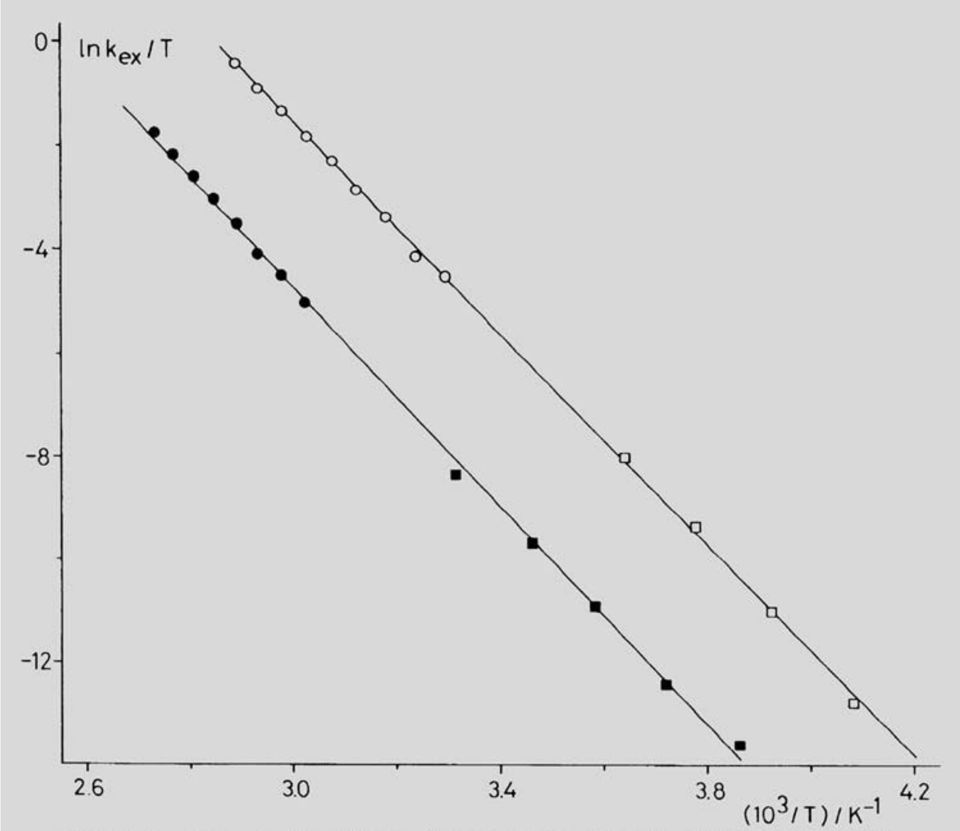


Figure. *Ln*(k$_{ex}$/*T*) *as a function of 1/T for* $[Al(DMF)_6]^{3+}$ (●, ■) *and for* $[Ga(DMF)_6]^{3+}$ (○, □) *from line-broadening* (circles) *and SF-NMR.* (squares).

Raymond Roulet's earlier publications described the preparation of dicationic diolefinic complexes [71] and some cyanoalkyl derivatives of Pt^{II} [72]. More recently, he has reported in *HCA* a number of investigations of the dynamics of Pt-metal clusters. A rather novel type of dynamic behaviour could be established by the use of ^{2}H-NMR techniques:

16. Intramolecular Dynamics of Tetranuclear Iridium Carbonyl Cluster Compounds

Part III[1])

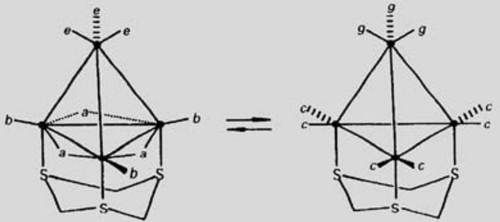
Crystallographic and Dynamic Evidence for the Intermediate of the 'Merry-go-round' Process in Nonacarbonyl-μ_3-(1,3,5-trithiane)-tetrairidium

by **Gianfranco Suardi**[2]), **Andres Strawczynski, Renzo Ros**[3])*, and **Raymond Roulet***
Institut de Chimie Minérale et Analytique de l'Université de Lausanne, 3, place du Château, CH 1005 Lausanne

and **Fabrizia Grepioni** and **Dario Braga***
Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, I 40126 Bologna

(16.X.89)

Scheme



1b 1u

The Ph. D. work of *Jean-Claude Bünzli*, done under the supervision of *André Merbach*, was mentioned earlier [67]. His independent research interest later turned to structural and spectroscopic studies of lanthanide complexes. The characteristic features of these investigation are well-rendered two recent publications [74], describing synthetic, structural, and spectroscopic studies of the europium complexes with a crown ether:

168. The Eu(III) Ion as Luminescent Probe: Investigation of the Metal-Ion Sites in a Dicyclohexyl-18-crown-6 Complex[1])

by **Dominique Plancherel, Linpei Jin**[2]), **Romano Massara**, and **Jean-Claude G. Bünzli***
Institut de chimie minérale et analytique, Université de Lausanne, 3, place du Château, CH-1005 Lausanne

(20.VIII.87)

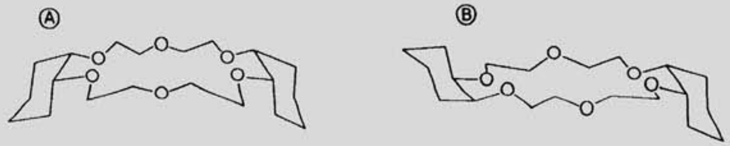


Fig. 1. *Conformations of the* cis-syn-cis (A) *and* cis-anti-cis (B) *isomers of dicyclohexyl-18-crown-6* L_A *and* L_B, *respectively*

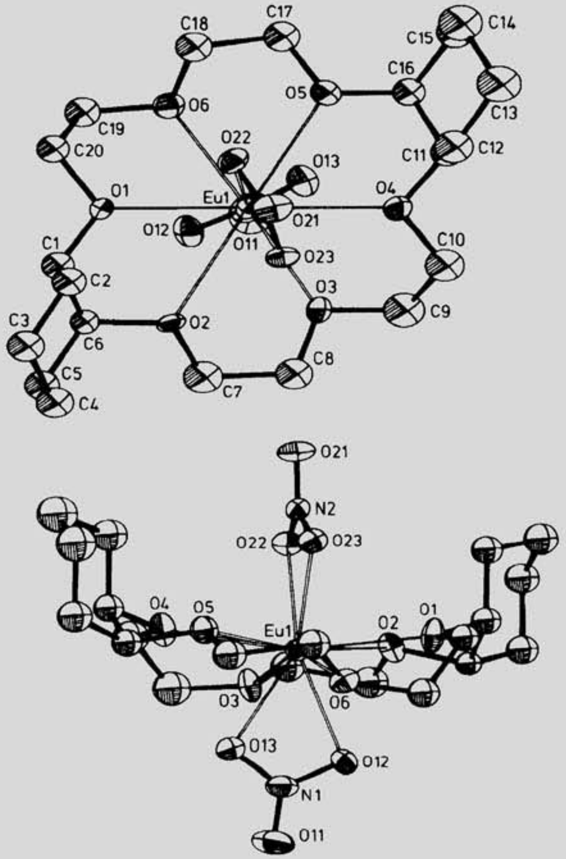


Fig. 5. *Molecular structure of the* $[Eu(1)(NO_3)_2 \cdot L_A]^+$ *complex cation showing the atom-numbering scheme.* Thermal ellipsoids are drawn at 20% probability.

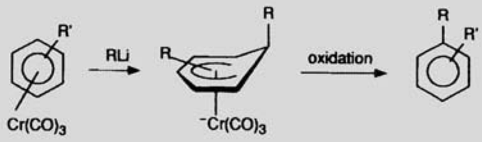
Last but not least, if a reader happens to wonder, why the exciting research work of *Carlo Floriani* is not mentioned here, he should be made aware that, up to now, he has not availed himself of *HCA* to publish his results.

By 1962, coordination chemistry was actively pursued at the *Cyanamid European Research Laboratories* in Cologny outside Geneva. *Christian Klixbull Jørgensen*, one of the leading figures in the world of inorganic spectroscopy was there at that time. The first paper he published in *HCA* [75] was the transcript of a lecture he gave at the '9th International Conference on Coordination Compounds' which was held in St. Moritz in 1967. However, other chemists in Cologny published their organometallic and coordination chemistry in *HCA* from 1962 to 1968. Noteworthy among them are the early IR studies of metal carbonyl compounds carried out by *K. Noack* [76], the characterization of many alkene and π-allyl iron complexes by *H. D. Murdoch*, *E. Weiss*, *M. Green*, and *E. A. C. Lucken* [77], of the titanium cyclopentadienyl derivatives by *J. J. Salzmann* [78], and the investigation of the coordination and organometallic chemistry of osmium by *F. Calderazzo* and *F. L'Eplattenier*. Some of the later developments of this work were published by *L'Eplattenier* [79] after his move to Neuchâtel. (Mention should be made here that *L'Eplattenier* also published in *HCA* some work on tricyclic and tetracyclic metal complexes [80] after he went to *Ciba-Geigy AG*.) After the closure of the *Cyanamide European Research Laboratories*, *Jørgensen* moved to the University of Geneva, but most of the work done there has appeared in journals other than *HCA*.

Coordination compounds of a more traditional type have been investigated at the University of Geneva by *Alan Williams*. His work deals mainly with the reactivity of cobalt-oxygen compounds [81].

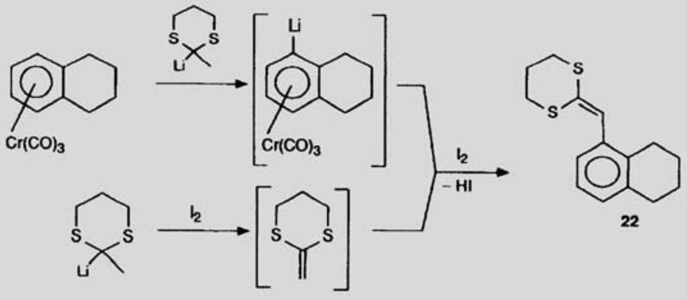
Finally, also at the University of Geneva, *E. Peter Kündig* has been very active in the field of organic synthesis mediated by transition-metal π-complexes. A good illustration of this type of approach [82] is summarized in the general reaction scheme shown below,

Scheme 1



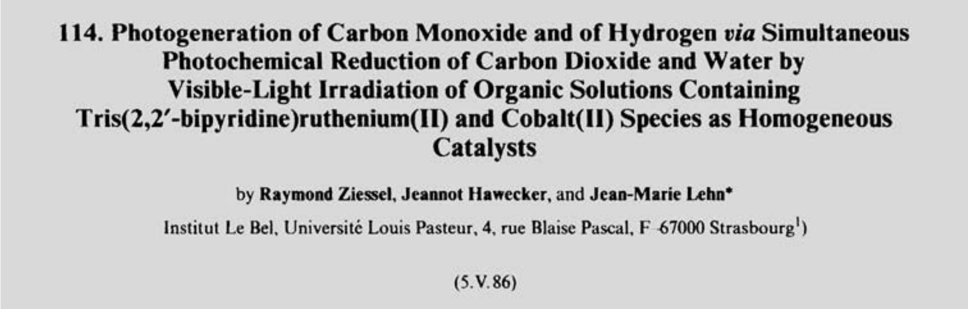
an actual example being:

Scheme 2



This brief survey of the field of coordination chemistry which has been published in *HCA* during the last 75 years would be sadly incomplete, if due place were not given to the relevant work of *Jean-Marie Lehn* at the Institut Le Bel of the Université Louis Pasteur in Strasbourg. This poses a difficult task, as most of the forty odd papers published in *HCA* cover several fundamental aspects of this discipline. The obvious 'practical reasons' limit the choice to three.

There is an obvious fascination in the study of CO_2 reduction, *i.e.*, its ecological imperative. Thus, the contribution shown below [83] must be not only considered as being of major scientific value, but also of highest topical interest. The 'state-of-the-art' in this area is summarized in the figure reproduced below.



114. Photogeneration of Carbon Monoxide and of Hydrogen *via* Simultaneous Photochemical Reduction of Carbon Dioxide and Water by Visible-Light Irradiation of Organic Solutions Containing Tris(2,2′-bipyridine)ruthenium(II) and Cobalt(II) Species as Homogeneous Catalysts

by **Raymond Ziessel**, **Jeannot Hawecker**, and **Jean-Marie Lehn***

Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, F-67000 Strasbourg1)

(5.V.86)

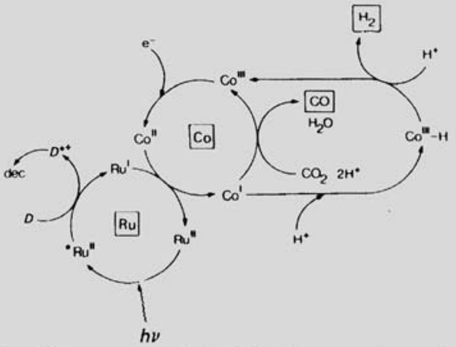
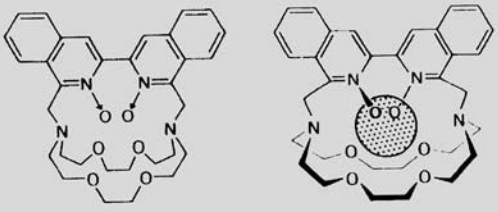


Fig. 7. *Schematic representation of the process occurring in the simultaneous and competing generation of CO and H_2 by photoinduced reduction of CO_2 and H_2O using the system $[Ru(bpy)_3]^{2+}/Co(II)/donor$* (D) *and following a pathway of reductive quenching of the excited state of the ruthenium photosensitizer.* Only heterolytic formation of H_2 by protonation of a cobalt-hydride is shown; see also text; the ligands of the metal ions are not indicated.

Several classes of lanthanide complexes are being actively investigated as they exhibit luminescence which can be valuable in new materials or as labels for time-resolved



1 $[Li^+ \subset \mathbf{1}]$
$[Eu^{3+} \subset \mathbf{1}]$

photo-immunoassays. A recent publication from *Lehn*'s group describes the synthesis of cryptate europium complexes shown below. These luminescent species are of particular interest, because they have long lifetimes as well as high UV-to-VIS conversion efficiencies [84] as can be seen from the figures reproduced from the original publication.

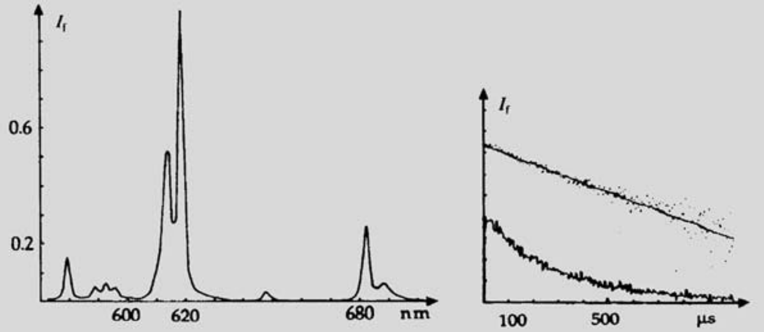
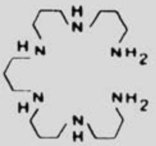
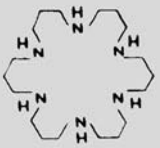


Fig. 3. *Luminescence spectrum* (left) *and luminescence decay* (right) *of the europium cryptate* $[Eu^{3+} \subset \mathbf{1}]3ClO_4^-$ *in MeCN*

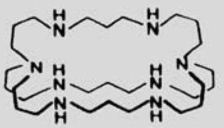
The third aspect is one that the 'traditional' coordination chemist has been loath to consider for a long time, that in which the role of 'central atom' in a complex is taken over by an anion and that of the ligand by a cation. The implication of this is that the binding forces in the complex are not strictly covalent, and that the classical stereochemical rules postulated by *Alfred Werner* have lost their general validity. We have clearly landed in the broader area of molecular recognition. Nevertheless, as will become apparent by looking at the figures and data reproduced below, every coordination chemist would feel quite at home with this subject, and the way it has been handled [85]. Thus, this author would like to end on an 'expansionistic' note.



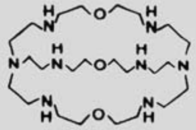
1



2



3



4

$$L + nH^+ + A^{m-} \rightleftharpoons (H_nLA)^{(n-m)+} \qquad (3)$$

$$K_s^n = \frac{[(H_nLA)^{(n-m)+}]}{[H^+]^n[L]\,[A^{m-}]} \qquad (4)$$

Table 2. *Stability Constants log* K_s (± 0.2) *for Halide Binding by the Macrobicyclic Polyammonium Receptor Molecule* **3** *in Aqueous Solution* [a])

Halide	n [b])			
	8	7	6	5
Cl^-	2.40	2.10	1.70	1.50
Br^-	2.95	2.65	2.20	1.70
I^-	3.40	3.00	2.40	1.95

[a]) The log K_s values were determined in the presence of 0.1M TsONa at 25° (*Eqns. 3* and *4*).

[b]) Number of protons involved in the complexes of the type (**3**, nH$^+$, A$^-$).

Perhaps, it is not unnecessary to mention, once again, that solid-state inorganic chemistry has not been included in this account although, in a broad sense, most of it can and should be considered as coordination chemistry. Furthermore, *HCA* contains many other coordination-chemistry contributions by a number of very eminent chemists, past and present. These omissions should obviously be remedied, before *Vol. 75* of *HCA* will have been completed.

Although incomplete, I hope this review will serve a double purpose. The first, and foremost, is to show that the contributions in the field of coordination chemistry which have appeared in *HCA*, despite their having come from a 'minority', have 'international quality'. Thus, it will be worthwhile for coordination chemists all over the world to continue to look at *HCA* as regularly as they peruse '*Inorganic Chemistry*' or '*Organometallics*'.

The second purpose is equally important: it is to encourage coordination chemists to use more regularly *HCA* for their publications. They would be in good company: after all, as mentioned earlier, the first paper in the first issue was by a Nobel Laureate, and it is fitting that one of the articles contained in *Fasciculus octavus* of *Vol. 74*, albeit not quite the last in that issue, is by another Nobel Laureate!

REFERENCES

[1] Ph.-A. Guye, *Helv. Chim. Acta* **1918,** *1,* 3.

[2] A. Werner, *Helv. Chim. Acta* **1918,** *1,* 5.

[3] P. Karrer, *Helv. Chim. Acta* **1920,** *3,* 196.

[4] W. D. Treadwell, E. Wettstein, *Helv. Chim. Acta* **1935**, *18*, 200.

[5] a) W. D. Treadwell, O. Gübeli, D. Huber, *Helv. Chim. Acta* **1941,** *24,* 152; b) W. D. Treadwell, D. Huber, *ibid.* **1943,** *26,* 10.

[6] G. Schwarzenbach, E. Karnpitsch, R. Steiner, *Helv. Chim. Acta* **1945,** *28,* 828.

[7] G. Schwarzenbach, *Helv. Chim. Acta* **1946,** *29,* 1338.

[8] G. Schwarzenbach, *Helv. Chim. Acta* **1952,** *35,* 2344.

[9] W. Schneider, *Helv. Chim. Acta* **1978,** *61,* 1949.

[10] G. Anderegg, *Helv. Chim. Acta* **1963,** *46,* 1833.

[11] G. Anderegg, *Helv. Chim. Acta* **1975,** *58,* 1218.

[12] G. Geier, *Helv. Chim. Acta* **1968,** *51,* 94.

[13] W. Schneider, *Helv. Chim. Acta* **1963,** *46,* 1863.

[14] W. Schneider, P. Baccini, *Helv. Chim. Acta* **1969,** *52,* 1955.

[15] a) N.J. DeStefano, D.K. Johnson, R.M. Lane, L.M. Venanzi, *Helv. Chim. Acta* **1976,** *59,* 2674; b) H.B. Bürgi, J. Murray-Rust, M. Camalli, F. Caruso, L.M. Venanzi, *ibid.* **1989,** *72,* 1293, and ref. cit. therein.

[16] T. R. Ward, L. M. Venanzi, A. Albinati, F. Lianza, T. Gerfin, V. Gramlich, G. M. Ramos Tombo, *Helv. Chim. Acta* **1991,** *74,* 983.

[17] K. H. A. Ostoja Starzewsky, P. S. Pregosin, H. Rüegger, *Helv. Chim. Acta* **1982,** *65,* 785.

[18] J. D. Dunitz, H. C. Mez, O .S. Mills, H. M. M. Shearer, *Helv. Chim. Acta* **1962,** *45,* 647.

[19] G. Consiglio, P. Pino, *Helv. Chim. Acta* **1976,** *59,* 642.

[20] G. Consiglio, C. Botteghi, *Helv. Chim. Acta* **1973,** *56,* 460.

[21] M. Hugentobler, A. J.Klaus, P. Ruppen, P. Rys, *Helv. Chim. Acta* **1984,** *67,* 113.

[22] E. Schumacher, R. Taubenest, *Helv. Chim. Acta* **1964,** *47,* 1525.

[23] a) H. Werner, H. Rasher, *Helv. Chim. Acta* **1968,** *51,* 1765; b) E. Deckelmann, H. Werner, *ibid.* **1969,** *52,* 892; c) H. Werner, V. Harder, E. Deckelmann, *ibid.* **1969,** *52,* 1081.

[24] a) V. Harder, H. Werner, *Helv. Chim. Acta* **1973,** *56,* 1620; b) J. Clemens, H. Neukomm, H. Werner, *ibid.* **1974,** *57,* 2000.

[25] J. H. Ammeter, L. Zoller, J. Bachmann, P. Balzer, E. Gamp, R. Bucher, E. Deiss, *Helv. Chim. Acta* **1981,** *64,* 1063.

[26] P. Kölbener, H.-U. Hund, H. W. Bosch, C. Sontag, H. Berke, *Helv. Chim. Acta* **1990,** *73,* 2251.

[27] A. Salzer, T. Egolf, W. von Philipsborn, *Helv. Chim. Acta* **1982,** *65,* 1145.

[28] C. Tavagnacco, G. Balducci, G. Costa, K. Täschler, W. von Philipsborn, *Helv. Chim. Acta* **1990,** *73,* 1469.

[29] W. Roth, F. Zuber, E. Sorkin, H. Erlenmeyer, *Helv. Chim. Acta* **1951,** *34,* 430.

[30] W. Roth, B. Prijs, H. Erlenmeyer, *Helv. Chim. Acta* **1954,** *37,* 2010.

[31] H. Brintzinger, R. Zell, H. Erlenmeyer, *Helv. Chim. Acta* **1964,** *47,* 1642.

[32] *Chimia* **1967,** *21,* 405.

[33] a) S. Fallab, *Helv. Chim. Acta* **1953,** *36,* 3; b) S. Fallab, H. Erlenmeyer, *ibid.* **1953,** *36,* 6.

[34] S. Fallab, H. Erlenmeyer, *Helv. Chim. Acta* **1959,** *42,* 1152.

[35] O. Bekâroğlu, S. Fallab, *Helv. Chim. Acta* **1963,** *46,* 2120.

[36] M. Zehnder, U. Thewalt, S. Fallab, *Helv. Chim. Acta* **1979,** *62,* 2009.

[37] H. Brintzinger, S. Fallab, H. Erlenmeyer, *Helv. Chim. Acta* **1955,** *38,* 558.

[38] H. Brintzinger, *Helv. Chim. Acta* **1961,** *44,* 1199.

[39] K. W. Bernauer, S. Fallab, H. Erlenmeyer, *Helv. Chim. Acta* **1956,** *39,* 1993.

[40] T. Kaden, S. Walz, S. Fallab, *Helv. Chim. Acta* **1960,** *43,* 1639.

[41] T. Kaden, *Helv. Chim. Acta* **1970,** *53,* 617.

[42] M. Studer, T. A. Kaden, H. R. Mäcke, *Helv. Chim. Acta* **1990,** *73,* 149.

[43] H. Sigel, H. Brintzinger, *Helv. Chim. Acta* **1963,** *46,* 701.

[44] H. Erlenmeyer, P. Waldmeier, H. Sigel, *Helv. Chim. Acta* **1968,** *51,* 1795.

[45] H. Sigel, R. Griesser, *Helv. Chim. Acta* **1967,** *50,* 1842.

[46] Y. Fukuda, P. R. Mitchell, H. Sigel, *Helv. Chim. Acta* **1978,** *61,* 638.

[47] T. Kaden, A. Zuberbühler, *Helv. Chim. Acta* **1966,** *49,* 2189.

[48] H.Gampp, D. Haspra, W. Spieler, A. D. Zuberbühler, *Helv. Chim. Acta* **1984,** *67,* 1019.

[49] G. Schetty, *Helv. Chim. Acta* **1952,** *35,* 716.

[50] G. Schetty, *Helv. Chim. Acta* **1963,** *46,* 1131.

[51] a) G. Schetty, *Helv. Chim. Acta* **1968,** *51,* 577; b) H. Jaggi, *ibid.* **1968,** *51,* 580.

[52] G. Schetty, E. Steiner, *Helv. Chim. Acta* **1974,** *57,* 2149.

[53] P. Hendry, A. Ludi, *Helv. Chim. Acta* **1988,** *71,* 1966.

[54] A. von Zelewsky, *Helv. Chim. Acta* **1968,** *51,* 803.

[55] P. Clopath, A. von Zelewsky, *Helv. Chim. Acta* **1972,** *55,* 52.

[56] W. Schneider, A. von Zelewsky, *Helv. Chim. Acta* **1963,** *46,* 1948; *ibid.* **1965,** *48,* 1529.

[57] M. Maestri, D. Sandrini, V. Balzani, A. von Zelewsky, C. Deuschel-Cornioley, P. Jolliet, *Helv. Chim. Acta* **1988,** *71,* 1053.

[58] A. Dell'Anna, F. P. Emmenegger, *Helv. Chim. Acta* **1975,** *58,* 1145.

[59] U. Ochsenbein, C. W. Schläpfer, *Helv. Chim. Acta* **1980,** *63,* 1926.

[60] F. Humbel, D. Vonderschmitt, K. Bernauer, *Helv. Chim. Acta* **1970,** *53,* 1893.

[61] R. Descheneaux, K. Bernauer, *Helv. Chim. Acta* **1984,** *67,* 373.

[62] K. Bernauer, P. Pousaz, J. Porret, A. Jeangougenat, *Helv. Chim. Acta* **1988,** *71,* 1339.

[63] K. Bernauer, M. Monzione, P. Schürmann, V. Viette, *Helv. Chim. Acta* **1990,** *73,* 346.

[64] F. P. Rotzinger, W. Marty, *Helv. Chim. Acta* **1985,** *68,* 1914.

[65] M. Langenbahn, H. Stoeckli-Evans, G. Süss-Fink, *Helv. Chim. Acta* **1991,** *74,* 549.

[66] A. Merbach, F. Gnaegi, *Helv. Chim. Acta* **1971,** *54,* 961.

[67] A. Merbach, J.C. Bünzli, *Helv. Chim. Acta* **1971,** *54,* 2536, 2543; *ibid.* **1972,** *55,* 580, 1903, 2867.

[68] A.E. Merbach, H. Vanni, *Helv. Chim. Acta* **1977,** *60,* 1124.

[69] Y. Ducommon, K.E. Newman, A.E. Merbach, *Helv. Chim. Acta* **1979,** *62,* 2511.

[70] C. Ammann, P. Moore, A.E. Merbach, C.H. McAteer, *Helv. Chim. Acta* **1980,** *63,* 268.

[71] R. Roulet, R. Vouillamoz, *Helv. Chim. Acta* **1974,** *57,* 2139.

[72] R. Ros, J. Renaud, R. Roulet, *Helv. Chim. Acta* **1975,** *58,* 133.

[73] G. Suardi, A. Strawcynski, R. Ros, R. Roulet, F. Grepioni, D. Brage, *Helv. Chim. Acta* **1990,** *73,* 154.

[74] a) F. Nicolò, D. Plancharel, J.C. Bünzli, G. Chapuis, *Helv. Chim. Acta* **1987,** *70,* 1798; b) B. Plancharel, L. Jin, R. Massard, J.C. Bünzli, *ibid.* **1987,** *70,* 1807.

[75] C.K. Jørgensen, *Helv. Chim. Acta Fasciculus extraordinarius Alfred Werner* **1976,** 131.

[76] K. Noak, *Helv. Chim. Acta* **1962,** *45,* 1847; *ibid.* **1964,** *47,* 1064, 1555.

[77] a) H.D. Murdoch and E. Weiss, *Helv. Chim. Acta* **1962,** *45,* 1927; *ibid.* **1963,** *46,* 1588; b) D.H. Murdoch, E.A.C. Lucken, *ibid.* **1964,** *47,* 1517.

[78] J.J. Salzmann, *Helv. Chim. Acta* **1968,** *51,* 903, and ref. cit. therein.

[79] F. L'Eplattenier, C. Pelichet, *Helv. Chim. Acta* **1970,** *53,* 1091.

[80] F. L'Eplattenier, A. Pugin, *Helv. Chim. Acta* **1975,** *58,* 917.

[81] M.H. Gubelmann, S. Rüttimann, B. Boquet, A.F. Williams, *Helv. Chim. Acta* **1990,** *73,* 1219.

[82] E.P. Kündig, C. Grivet, E. Wenger, G. Bernadinelli, A.F. Williams, *Helv. Chim. Acta* **1991,** *74,* 2009.

[83] R. Ziessel, J. Hawecker, J.M. Lehn, *Helv. Chim. Acta* **1986,** *69,* 1605.

[84] J.M. Lehn, M. Petraszkiewicz, J. Karpink, *Helv. Chim. Acta* **1990,** *73,* 106.

[85] M.W. Hosseini, J.M. Lehn, *Helv. Chim. Acta* **1988,** *71,* 749.