Coordination Chemistry Reviews, 100 (1990) 1–27
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOME SPECIAL ASPECTS OF THE STEREOCHEMISTRY OF COORDINATION COMPOUNDS

JOHN C. BAILAR, JR.

University of Illinois at Urbana-Champaign, Urbana, IL 61801 (U.S.A.)

(Received 7 March 1989)

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A. INTRODUCTION

The study of the stereochemistry of coordination compounds was fundamental to Werner's work and has continued to play a major role in the research on these compounds. An almost countless number of articles on the subject has appeared in the scientific literature, and not a few books (see for example ref. 1). The organometallic compounds, which are now under investigation in many laboratories, are considered by some chemists to be coördination compounds. However, they will not be included in this review, which will cover only the typical "Werner complexes". No attempt has been made to cover the field completely, but cases of interesting or unusual stereochemical features, with a few examples, are included.

Alfred Werner's chief original postulates in regard to the stereochemistry of coordination compounds (either explicit or implied) were the following.

0010-8545/90/$9.45

(1) Coordination numbers of two, four, six and eight are common.

(2) Metals with coordination number four are planar; those with coordination number six are octahedral. This postulate is important for *cis–trans* isomerism.

(3) Chelate rings span *cis* positions (the word "chelate" was coined after Werner's theory but is used throughout to give a uniform nomenclature). Just when Werner first saw the possibility of optical activity in complexes is not known. No mention of this property appears in his early papers, and the possibility was not realized experimentally until 1911 [2].

(4) Chelate rings of five and six members are much more stable than larger or smaller ones.

While these postulates were very useful, later developments have shown some of them to be too restrictive. Thus coordination numbers of three, five and seven are now well known, tetrahedral coordination compounds (coordination number of four) are thoroughly established for beryllium, zinc, nickel and many other metals, and several examples of rings which span *trans* positions are known.

B. COORDINATION NUMBER THREE

Although three is not a common coordination number, it is well established and this subject has been reviewed in ref. 3. It is especially interesting that several of the lanthanide and actinide elements, in spite of their large size, form complexes in which the metal is surrounded by only three ligands. Some of these complexes are planar and some are pyramidal, the difference apparently depending upon the size of the ligands and the nature of the central metal. The lanthanum complex with three 3,5-*t*-butylphenoxy groups is planar, no doubt because of the great bulk of the ligands. The platinum(0) complex $[Pt(P\phi_3)_3]$ [4] is also planar. However, $[Nd\{N(Si{-}Me_3)_2\}_3]$ and the corresponding uranium compound are pyramidal [5]. There are numerous other examples [5,6].

C. COORDINATION NUMBER FOUR

Although Werner recognized the possibility of tetrahedral, four-coordinate complexes, his most significant work, (and that of many of his successors) was concerned with the planar complexes of platinum(II) and the other platinum metals. The existence of two isomeric forms of many such compounds indicated their planar structure, and by utilizing the "*trans* effect" (so named many years later), Werner was able to determine the structures of the *cis* and *trans* isomers. His results have been confirmed by many later investigators and by both chemical and physical methods.

Nickel(II) is of special interest in this regard because it forms both planar *dsp*^{2} and tetrahedral *sp*^{3} four-coordinate complexes. The former are usually yellow or red and diamagnetic, while the latter are commonly blue or green and paramagnetic. The nickel glyoxime complexes, which are important in the analysis of nickel, are illustrative of the *dsp*^{2} compounds. Compounds formed from unsymmetrical glyoximes exist in both *cis* and *trans* forms [7]. The blue tetrammine nickel salts, $[(Ni(NH_3)_4]Cl_2$, are characteristic of the *sp*^{3} compounds.

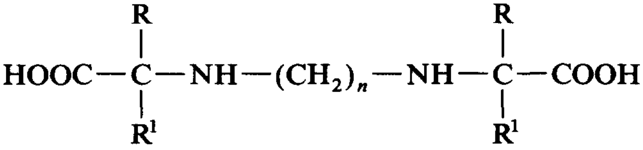
Some nickel(II) compounds can exist in either the tetrahedral or planar forms, depending upon the solvent from which they are recrystallized. These are $[Ni(P\phi_2R)_2X_2]$ (R = an alkyl group; X = halogen). The tetrahedral forms are blue or green and paramagnetic, the planar ones, red or brown and diamagnetic [8].

Chernyaev [9] prepared three isomeric forms of $[Pt(NH_3)(C_5H_5N)(NH_2OH)(NO_2)]^+$ and attempted, without success, to separate them into dextro and levo isomers. He accepted this failure as evidence that the molecule is planar.

The brilliant work of Mills and Quibbel [10] gave additional evidence for the planar structure of platinum(II) complexes. They synthesized the complex [Pt(isobutylenediamene)(*meso*-stilbenediamine)]$^{2+}$ and separated it into dextro and levo isomers. If the bonds of the platinum lie at tetrahedral angles, this would not be possible. Later, Lidstone and Mills [11] obtained a similar result with the palladium(II) compound.

Neither the work or Chernyaev nor of Mills and his students gives absolute proof of the planar nature of the compounds mentioned. A square pyramidal structure, with the metal at the apex, would satisfy the requirements, and Chernyaev's failure to resolve his compound is negative evidence only. However, X-ray studies of platinum(II) and palladium(II) compounds have given conclusive proof of the planar structure [12].

The planar complexes have been the subject of much research, in particular, in attempts to span the *trans* positions. The first compound with which this was achieved was prepared by Schlesinger in 1925 [13]. Schlesinger made the copper(II) derivatives of a series of bis amino acids

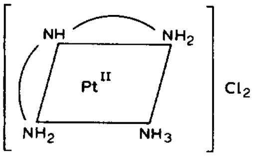


$$HOOC-\overset{\displaystyle R}{\underset{\displaystyle R^1}{\overset{|}{\underset{|}{C}}}}-NH-(CH_2)_n-NH-\overset{\displaystyle R}{\underset{\displaystyle R^1}{\overset{|}{\underset{|}{C}}}}-COOH$$

and found that when $n = 2$ or 3 the compounds are blue, when $n = 10$ they are violet, but when $n = 7$, either form could be obtained. He assumed, and probably correctly, that when the chain is very long, it can coordinate across the diagonal of the square more easily than along one edge. Isslieb and

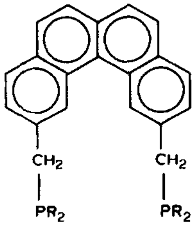
Hohlfeld [14] obtained a similar result with the nickel(II) complexes of $(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$. Here again, quite different compounds are obtained when n is varied. When $NiBr_2$ was treated with the diphosphine ($n = 3$), a red diamagnetic compound with a dipole moment of 11.13 D was obtained; $NiCl_2$ and a diphosphine ($n = 5$) again gave a red diamagnetic compound, but its dipole moment was only 2.37 D. The red color and the diamagnetic character of the two compounds clearly indicates spd^2 bonding and a planar structure. The fact that nickel bromide was used in one case and nickel chloride in the other is probably not important. The difference in dipole moment is about what would be expected if the halogen atoms are *cis* in one case and *trans* in the other. However, it seems strange that Schlesinger had to have an "n" value much greater than Isslieb and Hohlfeld's for the chelate chain to span the *trans* positions.

Bailar and his students attacked the problem in a very different way [15]. They chlorinated *trans*-dichlorodiammineplatinum(II) to give *trans*-tetrachlorodiammineplatinum(IV). This was then treated with bis(2-aminoethyl)amine, and in the later experiments, with (2-aminoethyl)-*N*-methylamine which replaced three of the chloro groups from the coordination octahedron. The resulting compound was then reduced in HCl solution (electrolytically, to avoid the addition of reagents) in the hope that the remaining chloro group and the secondary (or tertiary) nitrogen atom *trans* to it would be released. This hope was realized and the *trans*-spanned compound was formed. The eight-membered ring which resulted was somewhat unstable and repeated recrystallization from water yielded

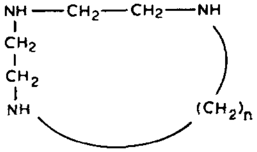


Conclusive evidence for the structure of the compound was obtained when it was heated with hydrochloric acid. This removed the eight-membered ring from the complex, yielding the original starting material, *trans*-dichlorodiammineplatinum(II).

De Stephano et al. [16] took a quite different approach when they constructed a rigid ligand in which the donor atoms are too far apart to attach themselves to the *cis* positions in a platinum complex but are far enough apart to coordinate in the *trans* positions:



These workers prepared compounds of nickel(II), palladium(II) and platinum(II). The *trans* structure of the latter was proven by its NMR spectrum. The problem was attacked in a still different way by Nonayama and Nonayama [17], who constructed a series of cyclic triamines in which two sides of the cycle contained two $-CH_2-$ groups, while the third side was varied, with the number of methylene groups being two, five, six, seven, eight or ten. They allowed these amines to react with palladium(II) chloride.



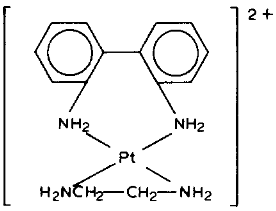
When the number of $-CH_2-$ groups was two or three, only two of the nitrogen atoms attached themselves to the metal, but when the number was increased so that the third side of the triamine could span the *trans* positions, it did so.

The author of the present review and his students are now attempting to synthesize a platinum(II) complex with two *trans*-spanning ligands, one on each side of the plane. The method involves the synthesis of meridional $[Pt\{(NH_2CH_2CH_2)_2NCH_3\}_2\}^{4+}$ and its reduction to the planar platinum(II) complex, in the expectation that the tertiary nitrogen atoms will be released from the platinum atom.

The discovery by Rosenberg et al. [18] that *cis*-$[Pt(NH_3)_2Cl_2]$ can be used effectively in the treatment of certain cancers has elicited great interest and has stimulated much research on platinum as well as on many other elements. Rosenberg et al. have shown that only *cis*-$[Pt(NH_3)_2Cl_2]$ is effective; the *trans* compound is without merit for this purpose. This is probably due to the fact that when the compound is injected, it reacts with the guanine at the 5- and 7-positions to form a chelate ring. The *trans* compound cannot do so. Several thousand other compounds have been synthesized and tested in the hope of finding compounds that will be more effective, less toxic and more soluble.

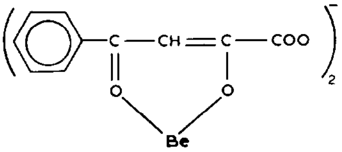
Since the biological system is asymmetric and optically active, the question arises as to whether the two isomers of an asymmetric platinum compound might behave differently toward cancer. Kidani and coworkers have found that indeed they do [19]. These workers replaced the ammonia molecules of cisplatin with 1,2-cyclohexanediamine (dach). When tested on cancerous mice, the *trans*-1-dach (1-R, 2-R dach) compound proved to be more effective than its *trans* D-isomer or the achiral *cis* isomer. They obtained still further improvement by introducing sugar carboxylates (e.g. gluconurates) in place of the chloro groups.

The stereoisomerism of the platinum(II) complex with 2,2′-diaminobiphenyl has been studied by Habu and Bailar [20]:

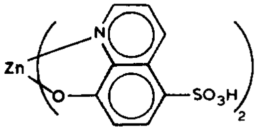


These workers resolved the ethylenediamine-2,2′-diaminobiphenylplatinum(II) ion into its optical isomers and found that they retain their optical activity for a long time. This, of course, is reminiscent of the biphenyl problem studied by Adams and coworkers 60 years ago [20(a)]. It was established by them that if there are large groups on the *ortho* positions of biphenyl, the two phenyl rings cannot be in a plane, so that the molecule is asymmetric. In the case of 2,2′-diaminobiphenyl, however, the rings are constrained to lie at an angle from each other by their attachment to the platinum atoms. If two molecules of the diaminobiphenyl were attached to the platinum, there should be two optically active forms and a *meso* form. However, this possibility was not tested.

Not all four-coordinate complexes are planar, of course. Many are tetrahedral. The latter tend to be labile, and in most cases, stereochemical isomers lose their identity rather quickly. A case in point is that of the beryllium complex with benzoylpyruvate which Mills and Gotts resolved through its strychnine salt [21]:



This compound racemizes rapidly, losing half its activity in about 15 min. The corresponding bis(benzoylacetone) complex was resolved by adsorption on quartz powder; it racemizes in a few hours at room temperature [22]. Liu and Bailar [23] resolved the zinc complex of bis(8-quinolato-5-sulfonic acid) through its strychnine salt. This complex lost its activity only slowly when heated in aqueous solution.



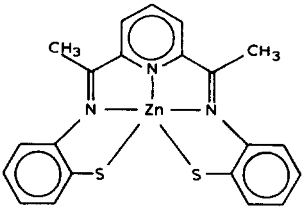
D. COORDINATION NUMBER FIVE

Compounds showing a coordination number of five were rare until recent years, but now a good many have been found. The discovery of $Fe(CO)_5$ by Mond and Langer in 1891 [24] was remarkable both because the metal shows a zero oxidation state and because it shows a coordination number of five. The structure of this compound was shown by electron diffraction to be triangular bipyramidal [25]. Many other five-coordinate compounds have been reported, but, for the most part, only the gross shape of the molecules has been determined. Two geometries have been well established: the triangular bipyramid and the square pyramid. For compounds of the types Ma_3b_2 or $M(AA)ab_2$ etc., geometric isomerism is possible, but examples have not been reported. Similarly, optical isomerism is possible in more complex cases, but again examples are lacking.

Among the square pyramidal complexes, mention should be made of $VO(acac)_2$ and SbF_5^{2-}. In the former, the vanadium atom is slightly above the base of the pyramid [26], but in SbF_5^{2-} the metal atom is below this base, owing to the unshared pair on the antimony atom [27].

The trigonal bipyramidal structure has been established, for example, in $[Cr(NH_3)_6][CuCl_5]$ [28] and in the dimeric $[Cu(en)_3][CuCl_4]$ (en = ethylenediamine) [29] which contains the very badly distorted ion $[Cu_2Cl_8]^{4-}$.

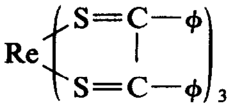
A very interesting five-coordinate zinc complex has been reported by Goedken and Christoph [30] and is shown here:



This molecule is a trigonal bipyramid, but it is badly distorted so that it is "decidedly helical", and hence it is chiral. A remarkable case is that of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$, in which both a regular square pyramid and a distorted triangular bipyramid of nearly C_2 symmetry have been shown to co-exist [31,32]. There is only a very small energy difference between the two forms, and if the hydrate is dehydrated, the trigonal bipyramidal isomer is lost. If the ethylenediamine in the counter-ion is replaced by 1,3-propanediamine, only the square pyramidal structure is formed [32].

E. COORDINATION NUMBER SIX

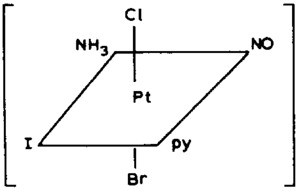
Compounds exhibiting the coordination number six [6] are abundant and have received more attention than any others. Werner considered three possibilities for the shape of these substances: the trigonal prism, the planar hexagon and the octahedron. He concluded that six-coordinate compounds had the last of these configurations because many of the complexes of the formulae Ma_4b_2, $M(AA)_2b_2$ and Ma_3b_3 were known to exist in two isomeric forms. (The other two configurations would each allow three configurations.) This was negative evidence, but the experience of many years has borne out his judgment. A few compounds have been shown to be triangular prisms, and they deserve brief mention. In 1965, it was found [33] that tris(*cis*-1,2-diphenylethylene-1,2-dithiolato)rhenium is a trigonal prism:



Several other compounds of this structure have since been prepared, as well as some which are intermediate in structure between the octahedron and the triangular prism. (After all, the regular octahedron is simply a prism which has been twisted through 30°.)

The vast majority of six-coordinate complexes are octahedral. The octahedra may be badly distorted but they are still octahedra. In this review, only some examples of special stereochemical interest will be discussed.

Chernyaev and Krasovskaya [34] have prepared all five of the possible isomers of $[Pt(NH_3)_2Br_2Cl_2]$ and derivatives of most of them. The *cis,cis,cis* isomer is chiral, but they did not resolve it. Essen and Gel'man [35] have prepared several of the 15 geometrical isomers of $[Pt(NH_3)(C_5H_5N)BrClI(NO_2)]$, e.g.



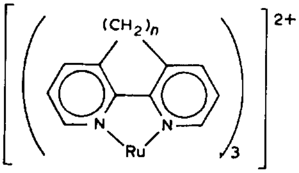
All such compounds are chiral, but apparently no attempt was made to resolve them. In each of these cases, the syntheses depended to a large extent upon the "*trans* effect" which seems to be greater in platinum compounds than in those of other metals. However, that it exists in the complexes of other metals was demonstrated by Bailar and Peppard [36] in their synthesis of the three isomers of $[Co(en)(NH_3)_2Cl_2]Cl$. The *cis,cis* isomer, like the one in which the ammonia molecules occupy the *trans* positions and the chloro groups the *cis* positions, is violet, but it has a much deeper color, and it is considerably more soluble in water. The *cis,cis* isomer is chiral and it was partially resolved. This compound can also be prepared by the stepwise replacement of carbonate ligands from $Na_3[Co(CO_3)_3] \cdot 3H_2O$ [37].

When unsymmetrical or asymmetric ligands attach themselves to a metal ion, some of the possible isomeric products are formed in preference to others. Thus the cobalt(III) complex of propylenediamine (1,2-diaminopropane) could be formed in 16 isomeric forms, beside those that result from asymmetry about the N–H bonds. The major possible isomers are

D*ddd*(*f* and *m*)	L*lll*(*f* and *m*)
D*ddl*(*f* and *m*)	L*lld*(*f* and *m*)
D*dll*(*f* and *m*)	L*ldd*(*f* and *m*)
D*lll*(*f* and *m*)	L*ddd*(*f* and *m*).

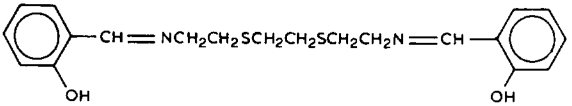
Here, D and L represent the optical activity about the metal atom, *d* and *l* that of the asymmetric carbon atom, and *f* and *m* indicate the facial or meridional orientation of the propylenediamine molecules. In actual practice, the D*ddd* and L*lll* compounds are formed in great preponderance. Jaeger [38], who was interested in crystallography, attempted to explain this phenomenon on the basis of symmetry, but his results were not satisfactory. Dwyer et al. [39], by very careful experimental work, were able to isolate small amounts of the D*lll* and L*ddd* isomers and to measure the equilibrium concentrations of these and the D*ddd* and L*lll* compounds. From these results, these authors calculated the differences in energy between the isomers. The equilibria were explained and the calculations of Dwyer et al. were confirmed by Corey and Bailar [40], who approached the problem by using conformational analysis. The latter authors pointed out that in, let us say, complexes of ethylenediamine, the amine chains are staggered, and that each C–C bond can be either almost parallel ("lel") to the *C* axis of the complex or quite oblique ("ob") to it. In other words, the chelate rings are puckered. If there are substituents on the diamine molecule, as in propylenediamine, these substituents tend to be either axial or equatorial; clearly, they will tend to be axial. It is possible to calculate the energy difference between the various forms, and from this to estimate the relative amounts of the different isomers that will be present at equilibrium.

A very interesting series of compounds has been described by Thummel et al. [40(a)]. They prepared a series of bridged dipyridyls

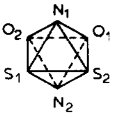


and made ruthenium(II) complexes of them. When $n = 2$ or 3, the two rings are conformationally mobile, but when $n = 4$, the two pyridine rings are forced out of planarity with each other. All three bridged-ligand molecules in a given complex apparently assume the same configuration, thus giving the complex an added factor in its chirality. The complex containing two dipyridyl ligands and one bridged dipyridyl ($n = 4$) appeared in four different isomeric forms, D*d*, D*l*, L*d* and L*l*.

Dwyer and Lions [41] prepared the cobalt(III) complex of the sexidentate



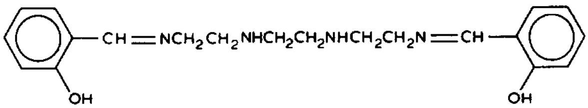
Theoretically, this molecule can wrap itself around a metal ion to form four different geometric isomers, but Dwyer and Lions found only one. They assumed that this had the structure



basing this assumption on the fact that the double bond on the nitrogen is rigid and could adapt itself to the 90° angle more readily than to the 60° angle which is required for the other three isomers. This argument was given credence by the work of Sweet [42] who prepared the analogous compound with –NH– groups where Dwyer and Lions had –S–. X-ray analysis shows this compound to have the structure which the reasoning of Dwyer and Lions would have predicted. Dwyer and Lions resolved their compound into its optical isomers and observed the large value of $[\alpha]_{5461} = 7000°$. By putting substituents into the phenyl rings and by other substitutions Dwyer et al. [43] obtained compounds with still higher rotations, reaching, in one case, $[M]_D = 87\,000°$. Lions wrote to the author of this review, "I am keen to reach 100 000° ". Unfortunately, both Dwyer and Lions died before they attained this goal.

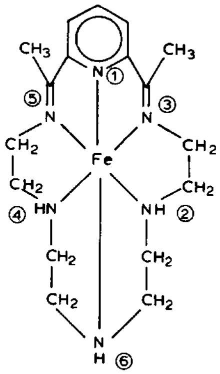
Dwyer, Lions and their coworkers said that when the number of carbon atoms between ligating atoms was increased, other stereoisomers were formed [44].

Das Sarma and Bailar [45] prepared several metallic complexes of

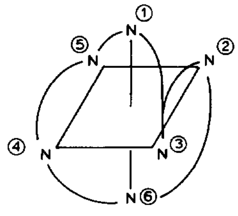


and resolved them into their optical isomers. Even the aluminum complex was obtained in an optically active form.

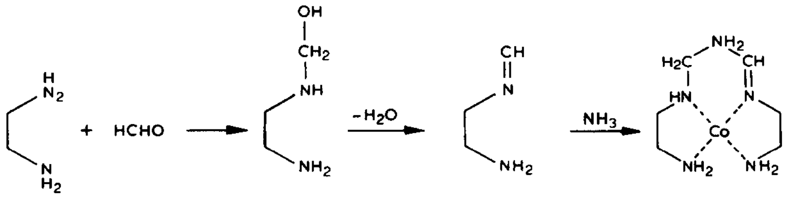
A very interesting sexidentate ligand was prepared by Curry and Busch [46]. Using the ferrous ion as a template, they caused 2,6-diacetylpyridine to react with tetraethylenepentamine to form the complex



The iron was quickly oxidized in air to the ferric state, but one nitrogen atom (presumably that in the 6-position) lost its proton, so that the complex still had a charge of +2. It was assumed, probably correctly, that nitrogen atoms in 3- and 5-positions would be *trans* to each other. This means that the structure of the coordinated ion must be



When amines coordinate to metal ions, the $-NH_2$ groups do not lose all their reactivity. This is shown by the formation of macrocycles, and in the case of the tris(ethylenediamine)cobalt(III) ion, by the formation of "sepulchrates", so called because the metal ion is completely buried within the surrounding ligand [47]. In a very clever piece of work, Sargeson [47] treated $[Co(NH_2CH_2CH_2NH_2)_3]^{3+}$ with formaldehyde and then with ammonia, thus forming caps between the ends of the ethylenediamine ligands. The plan can be shown schematically as follows:



(This scheme is repeated at each end of the ethylenediamine molecule and for the addition of a third N–Co link at each end of each ethylenediamine molecule.)

Still another sexidentate ligand should be mentioned: the ethylenediamenetetraacetate ion. Busch and Bailar [47(a)] prepared the cobalt(III) complex and resolved it into enantiomorphic forms by means of the strychnine salt and by adsorption on quartz powder.

An unusual reaction, shown by some complexes, involves an optical inversion. The first such reaction was reported by Bailar and Auten [48] in 1934. Recalling that Walden had found that L-chlorosuccinate reacts with potassium hydroxide to give D-lactate, but with silver oxide to give the L-isomer, and that Werner and McCutcheon [49] had reported that the reaction of L-*cis*-$[Co(en)_2Cl_2]Cl$ with potassium carbonate gives D-$[Co(en)_2CO_3]^+$, they carried out the corresponding reaction with silver carbonate; the product is L-$[Co(en)_2CO_3]^+$. It was later found [50] that the optical rotations of the products of the reactions of the dichloro salt with carbonate do not depend upon the presence of potassium or silver, but upon the method by which the reactions are performed. For example, it was found that if the stoichiometric amount, or less, of silver carbonate was used, the resulting carbonato complex was dextrorotatory, but if an excess of silver carbonate was used, the product was levorotatory [50]. Dwyer et al. [51] observed that if the solution is basic, inversion takes place, whether the substituting ion is carbonate or nitrite. These workers found that the presence of silver ion is important, but not as important as the concentration of hydroxide ion. These views were enlarged and expanded upon by Boucher et al. [52] who studied the bis(ethylenediamine) compound and the *α*-*cis*-triethylenetetramine compound.

Inversions have been found also in the reactions of dichlorocobalt(III) compounds with ammonia and amines. The first such case to be reported concerned the reaction of *cis*-L-$[Co(en)_2Cl_2]Cl$ with anhydrous ammonia at several temperatures [53]. This reaction can lead either to the *trans* isomer or to either of the *cis* isomers. The results are shown in Table 1. Since the reaction at 80 °C involved only the solid complex, it is assumed that rearrangement did not take place in that case but that inversion took place when the material was in solution at low temperature. It was shown by Greenwood [54] and by Archer and Bailar [54] that in the ammonia reaction the inversion takes place in the first step

TABLE 1

Results for the reaction of cis-L-$[Co(en)_2Cl_2]Cl$ with anhydrous ammonia at several temperatures

Reagent	Temperature (°C)	*Cis/trans* ratio in product	$[\alpha]_D$ (deg)
Liquid NH_3	−77	2.5/1	−32
Liquid NH_3	−33	2.85/1	−22
Liquid NH_3	+25	3.7/1	+18
Gaseous NH_3	+80	∞	+38
NH_3 in CH_3OH	+25	2.1/1	+31
NH_3 in C_2H_5OH	+25	3/1	+39

$$[Co(en)_2Cl_2]Cl \underset{\bigcirc}{\longrightarrow} [Co(en)_2(NH_3)Cl]Cl_2 \longrightarrow [Co(en)_2(NH_3)_2]Cl_3$$

Kyuno and Bailar [55] extended these studies to the reaction of ammonia and optically active propylenediamine and with the *α* and *β* isomers of

[Co(trien)Cl$_2$]Cl (trien = triethylenetetramine). The α isomer reacts at low temperatures with inversion, but the β isomer does not invert.

It might be supposed that complexes of metals other than cobalt would show inversions in comparable reactions. In general, this has not been observed. Such compounds as *cis*-[Cr(en)$_2$Cl$_2$]Cl [56], *cis*-[Rh(en)$_2$X$_2$]Cl [57] and *cis*-[Ir(en)$_2$Cl$_2$]Cl [57] have not been found to react with inversion.

However, Archer et al. [58] found an inversion in the reactions of [Fe(diimine)$_3$]$^{2+}$ with cyanide (diimine is *o*-phenanthroline or dipyridyl]:

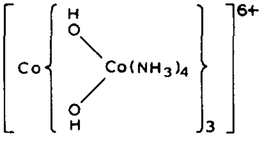
$$[\mathrm{Fe(diimine)_3}]^{2+} + 2\mathrm{CN}^- \rightarrow [\mathrm{Fe(diimine)_2(CN)_2}]^+ + \mathrm{diimine}$$

This compound was first reported by Archer et al. [58], and was later studied in detail [59]. These authors made a thorough investigation of the kinetics of the various reactions involved. The reaction was found to take place in two steps:

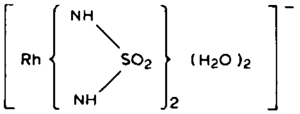
$$[\mathrm{Fe(diimine)_3}]^{2+} \longrightarrow [\mathrm{Fe(diimine)_2(CN)(H_2O)}]^+ \longrightarrow [\mathrm{Fe(diimine)_2(CN)_2}]$$

with inversion and partial racemization taking place in the first step. Jackson [60] has written an excellent review of these inversion reactions.

Werner felt that his resolution of *cis*-[Co(en)$_2$(NH$_3$)Cl]$^{2+}$ into its optical isomers would finally and firmly establish the validity of his theory, but some of the skeptics of his work objected because this compound contained carbon! He then prepared and resolved the "hexol" salt [61] which is purely inorganic:



This was unique for nearly two decades until Mann [62] resolved the rhodium sulfamido complex:



Furthermore, a third purely inorganic compound was recently added to the last [63]. This is [PtS$_{15}$]$^{2-}$, which contains three S_5^{2-} chains, each serving as a chelating ligand. Still more recently, Shimba et al. [64] have added two more such ions: *cis,cis,cis*-$[Co(NH_3)_2(H_2O)_2(CN)_2]^+$ and *cis,cis,cis*-$[Co(NH_3)_2(H_2O)_2(NO_2)_2]^+$. These ions were synthesized by using the method of stepwise replacement of carbonato groups from $[Co(CO_3)_3]^{3-}$ [37].

As is well known, Louis Pasteur developed three methods of separating the isomers of optically active organic compounds. These methods are described below.

(1) The formation of diastereoisomers with a naturally occurring optically active acid or base often gives isomers of unequal solubility. Such substances as tartaric acid and strychnine have been widely used, as have optically active derivatives such as antimonyl tartrate and bromocamphorsulfonic acid. This is still a common method.

(2) Bacterial action. If often happens that a bacterium will attack one of a pair of enantiomers but not the other. This method is somewhat limited because the bacteria adapt themselves to the less desirable form as the more desirable form is used.

(3) Mechanical separation of asymmetric crystals. This is a tedious method and is seldom used.

(4) A fourth method, which is widely used, depends upon the preferential adsorption on an optically active surface, usually in a column. The adsorbent can be either organic or inorganic (e.g. quartz).

All these methods are equally applicable to inorganic coordination compounds. The first resolution of an optically active complex [2] was accomplished by the use of *d*-α-bromocamphor-π-sulfonate; many other organic substances have been used. In recent years, inorganic complexes have also found use: e.g. $(-)_{589}[Co(en)_2Ox_2]C_2H_3O_2$ and $(-)_{589}[Co(en)_2(NO_2)_2]C_2H_3O_2$ in the resolution of $Na[Co(en)Ox(mal)]$ (mal = malonate) *cis,cis*-$[Co(NH_3)_2(CN)_2mal]^-$ and $[Co(en)(CN)_2CO_3]^-$ [65], and the resolution of $[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ and $[Co(Nb_6O_{19})(gly)(H_2O)]^{6-}$ (gly = glycine) by $(+)_{589}[Co(en)_3]Br_3$ [66].

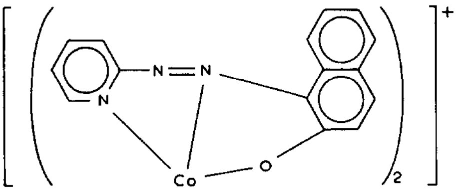
To use this method, one must, of course, choose an optically active ion of the proper charge which does not racemize in the solvent of choice. Sometimes one diastereoisomer has such small solubility that only one-half of the calculated amount of resolving agent is added and the precipitate is removed by filtration, leaving the other isomer in solution. Organic chemists do not seem to have adopted the use of inorganic ions as resolving agents, although they should also be applicable to their work.

Pasteur's second method, bacterial resolution, has been little studied by inorganic chemists. Bailar et al. [67] found that the bacterium *Pseudomonas aerigenosa* (with traces of elements and enzymes essential for bacterial growth) grows in a dilute solution of D-$[Co(en)_3]Cl_3$, but not in a solution of the levo isomer. Growth is poor, and it was found that the bacteria use only the nitrogen, or part of it, from the coordinated ethylenediamine. The bacteria will continue to grow only if a suitable source of carbon (such as succinate) is provided. The ethylenediamine molecule is not completely destroyed, but seems to be converted to some other ligand such as $NH_2CH_2COO^-$ or $C_2O_4^{2-}$. The bacterium will not grow in a solution of the racemic complex because the levo isomer blocks their growth. Thus these bacteria cannot be used to resolve this complex.

However, Gillard and Thorpe [68] showed that an unspecified soil bacterium, in a mixture of α-[Co(gly)$_3$], sucrose and ammonium chloride caused an enrichment of the dextro isomer; they obtained a material of 60% optical purity.

(i) Adsorption methods

Many coordination compounds are adsorbed on surfaces; this property has been used in two different ways to separate optical isomers. First, if the adsorbing surface is optically active, one of the isomers may be adsorbed more strongly than the other. References have already been made to two such cases. The example given by Sievers and coworkers [69] is most remarkable. These authors separated the isomers of tris(hexafluoroacetylacetonato)chromium(III) by passing the vapors through a column of quartz powder at 55 °C. The work of Hutchinson and Bailar [70] also deserves mention for it may have practical importance. Hutchinson and Bailar passed an aqueous solution of the cobalt(III) complex of the "metallized" azo dye, α-pyridyl-azo-β-naphthol



through columns containing wool, silk or cotton. In each case, the complex was at least partially separated into its optically active isomers.

Another technique involves adsorption on an optically inactive column, followed by extraction with an optically active solvent. For example, the *μ-cis* isomer of cobalt bis(diethylenetriamine) ion was resolved by adsorption on Sephadex and elution with 0.15 M of sodium D-tartrate [71].

Another technique which has been suggested but which has not yet achieved complete resolution is based on experiments done by Jonassen [72] and Hryhorczuk and Bailar [73]. The former treated [Co(L-pn)$_2$CO$_3$]Cl (L-pn = L-propylenediamine) with racemic tartaric acid to give a mixture of

$[Co(L\text{-}pn)_2d\text{-}tart]^+$ and $[Co(L\text{-}pn)_2l\text{-}tart]^+$. This mixture was treated with L-pn which gave $[Co(L\text{-}pn_3)]Cl(L\text{-}tart)$ within 1 h when heated to 70 °C. The unchanged D-tartrato complex liberated the tartrate only when the solution was evaporated to dryness. However, the separation was not complete because the values of $[\alpha]$ for the recovered tartaric acids were only $-5.5°$ and $+6.2°$. In an attempt to obtain greater selectivity, Hryhorczuk and Bailar [73] used D- and L-phenylethylenediamine in place of propylenediamine. The two tartrato complexes were found to be quite different in stability; when D-phenylethylenediamene was used, the D-tartrate complex reacted with lead acetate more rapidly than did its isomer. Here again, however, the separation was not complete.

(ii) Separation of enantiomorphic crystals

Pasteur's method of resolution by mechanically sorting the enantiomorphic crystals has been little used because it is time consuming and tedious. It has recently been discovered, however, that the method is applicable to some coordination compounds. Bernal and coworkers [74] have reported, in an excellent series of papers, that some cobalt and rhodium compounds form enantiomorphic crystals, which can be separated mechanically into the dextro and levo isomers. Two such isomers are *cis*-$[Co(en)_2(NO_2)_2]X$ and *cis*-α-$[Co(tetraen)(NO_2)_2]X$ (X = halide ion). It has been shown that there is strong hydrogen bonding between the nitro groups and the *trans* NH_2 groups, and that this favors the formation of dissymmetric crystals. Crystals of the nitrates of those cations are not dissymmetric, however, because the anion forms hydrogen bonds with the –NH groups. Interestingly, *trans*-$K[Co(NH_3)_2(NO_2)_4]$ also forms enantiomorphic crystals, but these, of course, lose this property when dissolved in water.

(iii) The Pfeiffer effect

The Pfeiffer effect was first observed in 1931 by Pfeiffer and Quehl [75]. The effect is the change in optical rotation of a solution of an optically active compound when a racemic dissymmetric labile substance is added to it. Several investigators have studied this effect and some reviews have been published [76]. The most active research groups have been those headed by Kirschner and Yoneda. Pfeiffer and Quehl reported that zinc α-bromo-π-camphorsulfonate had an optical rotation of $[\alpha] = 4.55°$, but the addition of 3 mol of *o*-phenanthroline (phen), which converted it into $[Zn(phen)_3](OSO_2C_{10}H_{15}O)_2 \cdot 7H_2O$ increased this value to 8.44°. In nearly all the cases studied, a labile hexacoordinate ion is put in the presence of an optically active, optically stable ion, usually, but not necessarily, of opposite sign. It is generally agreed that in most cases the dextro ⇄ levo equilibrium of the labile ion is disturbed by the presence of an optically active counter-ion, and Kirschner has produced good evidence that hydrogen bonding is responsible. When D-tartaric acid was used as the environmental substance with $[Ni(phen)_3]^{2+}$, the effect was plainly seen, but when the hydroxy groups of the acid were replaced by methoxy groups, the Pfeiffer effect did not appear [1(f)]. This fact was borne out by the work of Kuroda et al. [77].

The Pfeiffer effect does not always appear to its full extent immediately, nor does it disappear at once when the environmental substance is removed. Its appearance doubtless depends upon the lability of the complexed inorganic ion. Thus Kirschner added L-malic acid to a solution of $[Ni(phen)_3]Cl_2$. The optical rotation began to decrease at once, at first rapidly and then more slowly, until it reached a constant value after about 120 h. When an amount of D-malic acid, equal to that of the L-malic acid, was then added, the reverse change took place at the same rate, the rotation finally reaching zero [1(f)].

Very little work has been done on labile four-coordinate complexes. The study was initiated by Landis [78] who studied zinc bis(8-aminoquinolate). Pollack et al. [79] extended the study to the bis(8-hydroxyquinoline) and the bis(8-hydroxyquinoline-5-sulfonate) zinc ions.

Nordquist [80] initiated the use of dissymmetric inorganic ions to produce the Pfeiffer effect when he employed D-$[Co(en)_3]^{3+}$. Since that time the use of optically active inorganic ions as environmental substances has become common; they produce the Pfeiffer effect as well as organic substances. Among the inorganic ions which have been used are $[Co(en)_3]^{3+}$, $[Co(phen)_3]^{3+}$ [81], *cis*-$[Co(en)_2XY]^{n+}$ (X,Y = unidentate ligands) [82], and $[Co(sepulchrate)_3]^{3+}$ [81,82].

It has been pointed out that the Pfeiffer effect can be used to determine the configuration of labile, optically active ions, and is useful in this way [79,83]. Clearly, in all these studies, the nature of the environmental substance is most important [84], some producing the effect more markedly than others. The nature of the labile material is also important. With nickel bis(5,5′-dimethyl-2,2′-dipyridyl), L-tartaric acid gave a well-developed Pfeiffer effect, but when the methyl groups were in the 3,3′ positions, the effect was not produced [85].

Even with optically inert complexes, a large excess of the environmental substance can produce the Pfeiffer effect. Kirschner and Bakkar [85(a)] found that the effect appears when a 400-fold excess of D- or L-tartrate is added to a solution of racemic $[Co(en)_3]^{3+}$.

Finally, it should be mentioned that when several complexes in the presence of alkaloidal environmental substances were irradiated with linearly polarized light, the Pfeiffer effect appeared, but opposite in sign to that produced in the dark [86].

(iv) Solid state reactions

Since reactions in the solid state are described elsewhere in this issue, it is only necessary to give here some illustrations of such reactions that involve stereochemical changes:

$$(+)\text{-}[\mathrm{Co(en)_3}]\mathrm{X_3}\cdot n\mathrm{H_2O} \longrightarrow rac\text{-}[\mathrm{Co(en)_3}]\mathrm{X_3} \qquad [87]$$

$$(+)\text{-}cis\text{-}[\mathrm{Co(en)_2(NH_3)_2}]\mathrm{Cl_3} \longrightarrow rac,cis\text{-}[\mathrm{Co(en)_2(NH_3)_2}]\mathrm{Cl_3} \qquad [88]$$

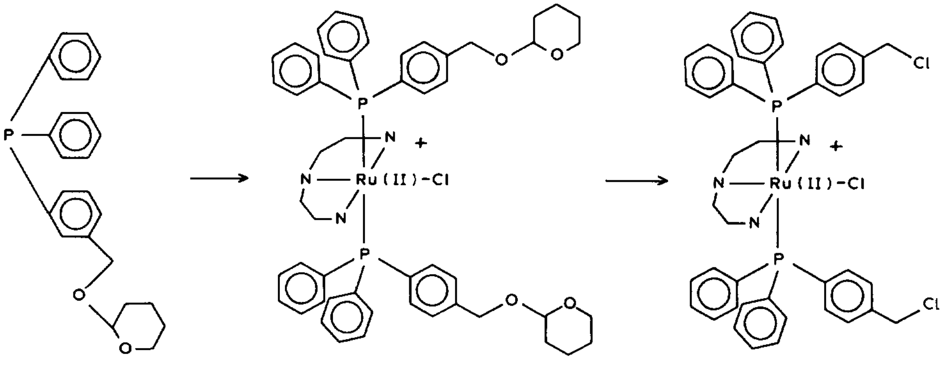
$$trans\text{-}[\mathrm{Co(trien)Cl_2}]^+ \longrightarrow \beta\text{-}cis\text{-}[\mathrm{Co(trien)Cl_2}]^+ \longrightarrow \alpha\text{-}cis\text{-}[\mathrm{Co(trien)Cl_2}]^+ \qquad [89]$$

$$(+)_{\mathrm{D}}\text{-}cis\text{-}\alpha\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{Cl} \longrightarrow rac,cis\text{-}\alpha\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{Cl} \qquad [90]$$

$$\mathrm{D}\text{-}\mathrm{K}[\mathrm{Co(edta)}]\cdot 2\mathrm{H_2O} \longrightarrow rac\text{-}\mathrm{K}[\mathrm{Co(edta)}] \qquad [91]$$

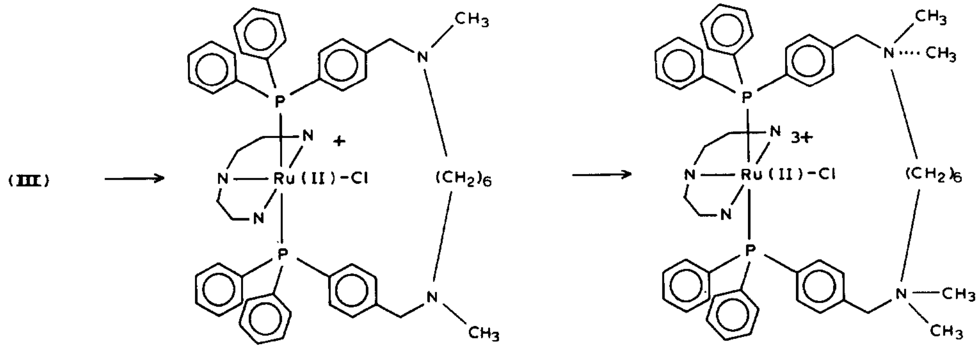
(v) Trans *spanning of the octahedron*

Very recently, a method of forming a ring that spans the *trans* positions in an octahedral complex has been developed [92]. The complex *mer*-[Ru(III)(terpy)Cl_3] (terpy = terpyridine) was treated with **I** to give **II**, which through a series of steps was converted to **III**:



(I) (II) (III)

Compound **III** was treated with *N,N′*-dimethyl-1,5-hexanediamine to close the ring as shown in **IV**:



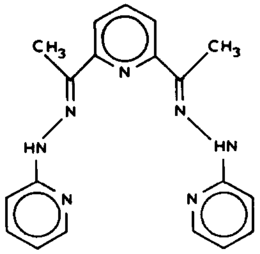
(IV) (V)

The formation of **IV** gave a 46% yield. This product was quaternized by treatment with ammonium iodide to yield the final product **V**.

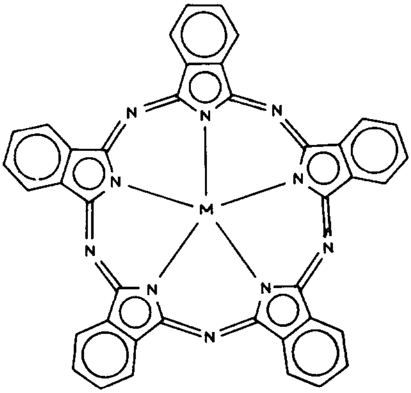
F. COORDINATION NUMBER SEVEN

Coordination number seven is sometimes called upon to account for transient intermediates in chemical reactions, but in most cases there is little support for these hypotheses. There are, however, a good many reasonably stable compounds that show this coordination number (for excellent summaries, see ref. 93). Three geometries are well established: the pentagonal bipyramid, the trigonal prism with an extra ligand outside one of the rectangular faces and the octahedron with the seventh ligand outside one face. The geometry of the complex seems to be determined largely by the nature of the ligands, the geometry of the metal being modified to accomodate the ligand.

Most of the triangular bipyramidal structures contain seven fairly small groups, as in the $[V(CN)_7]^{2-}$ ion [94], in $UI_3(THF)_4$ [95], and in $[U(NCS)_4(dmiba)_3]$ (dmiba = $Me_2CHCONMe_2$) [96], or with a pentadentate molecule and two small unidentate ligands, as in the complex $[ML(H_2O)_2]Cl_2$ where M = Co(II) or Zn, and L is the ligand shown below:



Also of interest is the uranyl "superphthalocyanine" [95(a)] in which the central plane has the structure shown below, with the oxygen atoms of the



uranyl group occupying the axial positions in the molecule. The presence of five units in this phthalocyanine, instead of the usual four, is doubtless due to the large size of the uranium atom.

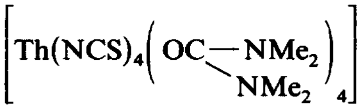
Most of the capped triangular prisms contain six like groups and a unique group, as in $[U(OPMe_3)_6Cl]Cl_3$ [98] and the capped octahedrons are commonly of the type $[MA_4B_3]$ and in $[MoBr_4(P\phi Me_2)_3]$ [99].

G. COORDINATION NUMBER EIGHT

For the coordination number eight, four distinct geometries are known: the cube, the Archimedes antiprism, the dodecahedron with triangular faces, and the hexagonal bipyramid. Cubic coordination is known only for large metallic ions, as in $[U(bipy)_4]$ [100] and $Na_3[PaF_8]$ [101].

The square antiprism and the dodecahedron differ only slightly in energy [102] and some molecules assume the different forms under different conditions [102(a)]. The U^{4+} diporphyrin complex, $UC_{64}H_{32}N_{16}$, is a distorted antiprism [103], as is the uranium tetraphenylporphyrin [104]. With a substituent on one side of each porphyrin molecule, this structure would be chiral, but thus far, no such complex has been prepared. Thorium acetylacetonate, $[Th(acac)_4]$, is likewise a slightly distorted antiprism [105].

Dodecahedral structures are more common than either cubic or antiprismatic ones. Examples are $[Mo(CN)_4(CNCN_3)_4]$ [105(a)], as are

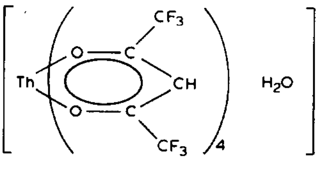


$\left[\mathrm{Th(NCS)_4}\left(\mathrm{OC}\begin{matrix}-\mathrm{NMe_2}\\ \diagdown\mathrm{NMe_2}\end{matrix}\right)_4\right]$ [106] and $[Zr(acac)_4]$ [107].

The hexagonal bipyramid is illustrated by several uranyl compounds such as $[UO_2(Ac)_3]^-$ [108], $[UO_2(NO_3)_3]^-$ [109] and $[UO_2(CO_3)_3]^{4-}$ [110]. In all these compounds the UO_2 group is linear and the bidentate groups form a belt around the bases of the two hexagonal pyramids. A somewhat different eight-coordinate structure, $[Au_9L_8]^{3+}$ ($L = C_6U_5$ or $C_6H_4CH_3$), has been described by Mutterties [111] and by Bellon et al. [112]. In this ion, eight gold atoms are attached to a central gold atom and to adjoining peripheral gold atoms. The authors describe this as "an icosahedron from which one equatorial rectangle has been removed", but this reviewer finds it easier to picture it as an octahedron in which two *trans* positions have been expanded from points into edges, these edges being parallel to each other.

H. COORDINATION NUMBER NINE

The classic case of coordination number nine is the $[ReH_9]^{2-}$ [112], which is in the form of a triangular prism with a hydrogen atom outside of each rectangular face. Another example of this geometry is $[Ln(H_2O)_9](BrO_3)_3$ [113]. When bidentate groups are introduced, the structure is often altered to that of an antiprism with an extra group outside of one square face. An example is [114]



It is interesting that the introduction of the fluorine atoms causes this substance to crystallize with one molecule of coordinated water.

I. COORDINATION NUMBERS TEN AND TWELVE

Only a few compounds are known in which ten or twelve donor atoms are attached to a metal atom or ion. Most, if not all, of these are held by "ionic" bonding, and they retain their structures only in the solid state. Hence, they are of little interest in the present context. The vast majority of these compounds contain five (or six) bidentate ligands attached to a large metallic ion. The ten-coordinate complexes are exemplified by $K_2[Er(NO_3)_5]$ [115], $Na_6[Th(CO_3)_5] \cdot 12H_2O$ [116] and $Na_6[Ce(CO_3)_5] \cdot 12H_2O$ [117]. Of somewhat different type is the interesting clathrate ion $[La\{N(CH_2CH_2\text{-}OCH_2CH_2OCH_2CH_2)_3N\}(NO_3)_2]^+$ [118], in which both nitrogen atoms and all six oxygen atoms of the clathrate molecule are attached to the metal. Also of interest is the La–edta complex, $[La(edta)(H_2O)_4]^-$ [119].

A single example will suffice to illustrate the 12-coordinate complexes. This is $[Th(NO_3)_5(OPMe_3)_2]^-$, which crystallizes as an icosahedron [120].

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