COORDINATION COMPOUNDS IN ANALYTICAL CHEMISTRY

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Abstract - Coordination compounds are used in almost every branch of analytical chemistry. The factors which make them specially suitable for gravimetric and titrimetric analysis, for liquid-liquid extraction and various types of chromatography (e.g., in both mobile or stationary phases in gas chromatography) are illustrated by examples. Stereochemical features, reaction kinetics, conformational changes, and ligand field stabilisation are also shown to be relevant factors in specific cases. The achievement of a measure of controlled selectivity in the reactions of inorganic cations with organic ligands is discussed in relation to recent work on complexones, crown ethers, and cryptates, although the accidental discovery of an unusual coordination compound that owes its usefulness to an unexpected and unpredictable crystal structure is not overlooked.

The most widely read Journals specializing in the field of analytical chemistry carry nowadays a preponderance of articles on purely physical methods of analysis, on automatic analyses of all kinds, on the analysis of multi-component systems and on the relevant computational techniques and statistical treatments.

This trend towards physical and automated methods is appropriate for many routine analyses and often inevitable on purely economic grounds; but it must not be forgotten that despite the progress that has undoubtedly been made in elaborating entirely physical techniques for the determination of multi-component systems, with automatic compensation and correction for inter-element (matrix) effects by the use of individually programmed and dedicated computers, there is still a great deal of analysis conducted appropriately and unavoidably by chemical methods. Indeed, wet chemistry still forms the basis for all the automated procedures using equipment such as the Technicon Autoanalyser. In such procedures coordination compounds play a continuing role and it is doubtless for this reason that the organisers of this the XVIIIth International Conference on Coordination Chemistry have chosen a Plenary Lecture devoted to this general field.

The commonest task of the analyst is to determine quantitatively the amount of some particular species (the analyte) originally present with others in a matrix, and often present in small amount both relatively and absolutely. To achieve this it is usually necessary to carry out a certain amount of pre-concentration so that the amount of analyte available will be sufficient to carry out the appropriate quantitative determination at an acceptable level of precision. Interferences in this determination by all other components of the matrix must be reduced below certain limiting levels by separation procedures which may, to a greater or less extent, be incorporated or inherent in the pre-concentration stage.

Since our theme is to be the application of coordination compounds in analytical chemistry it will be convenient first to consider their classical use for the separation and determination of inorganic cations and anions by precipitation. Here we look for a number of desirable characteristics, viz., low solubility in water; freedom from co-precipitation and occlusion; good filterability; stability towards the stages of washing and drying to constant weight; and a stoichiometric, or at least strictly reproducible composition. To which one should add the ideal of specificity; the hope so temptingly proffered with the introduction of Tschugaeff's dimethylglyoxime
as a reagent for nickel by Brunck in 1907 (Ref. 1); the goal so rarely approached.

Low solubility is a consequence of a high lattice energy associated with a low solvation energy. Although an increase in the thermodynamic stability (formation) constant along a series of metal chelates is often associated with increasing insolubility, this is far from being a determining factor. For example, although the copper complex of dimethylglyoxime is certainly more stable thermodynamically than the nickel complex (Ref. 2), the latter is far more insoluble because of the special features of the packing of discrete molecules in the crystal lattice which provides strong axial Ni-Ni bonds through the lattice (Refs. 3 & 4). To be sure, the effect of introducing heavy halogen atoms into a molecule is often to decrease the solubility by what Feigl (Ref. 5) termed the 'weighting effect'; but it may also increase the solubility by making crystal packing less energetically favourable, or by reducing intermolecular association caused by hydrogen bonding as illustrated by the $R_f$ values of indigo and its 4,7-halogen substituted derivatives (Ref. 6).

Hydrophilicity due to the presence of coordinated water can usually be reduced by replacing it by donor molecules of a less hydrophilic character. This is illustrated by substances derived from aquated cations of copper(II), cadmium and iron(II) in such compounds as (Cuen$^+$)($CdI_4^{2-}$) and (Cuen$^+$)(Hgl$^{2-}$) which are insoluble in water, ethanol and ether, or by (Fe(bipy)$^{2+}$)($CdI_4^{2-}$) which provides a very sensitive spot-test for cadmium. Other examples are the well-known thiocyanato complexes containing coordinated pyridine such as M(SCN)$_2$npym (M = Cu(II), Cd, Co(II), Fe(II), Mn, Ni, Zn; n = 2 or 4). The virtues of large hydrophobic cations conjoined with large anions is illustrated by such insoluble complexes as (CH$_3$(C$_6$H$_5$)$_3$N)$^2$-($CdI_4^{2-}$), (Fepheman$^{2+}$)(ReO$_4$)$_2$ or BH$^+$$BiI_4^-$, where B is cinchonine or a similar heterocyclic base.

The desirable features of coordination compounds in gravimetry are displayed by many of the great variety of metal chelates that have been introduced into analytical practice (Refs. 7, 8 & 9). In the reactions between a cation $M^{n+}$, and a chelating agent, HL (usually a weak acid) we have to consider the equilibria

$$M^{n+}(aq) + nHL(aq) \leftrightharpoons ML_n(aq) + nH^+(aq) \quad (1)$$

and $HL(s) \leftrightharpoons HL(aq) \leftrightharpoons H^+(aq) + L^-(aq) \quad (2)$

Water of solvation is omitted for the sake of simplicity. The position of equilibrium will be determined by the $pH$ and the relevant proton- and metal-ligand formation constants $\beta_{ML}^n$ and $\beta_{HL}$ respectively. By a suitable choice of $pH$ and reagent concentration reaction (1) can be made to go effectively to completion. For a given reagent and a series of cations (of the same charge type), the position of equilibrium in equation (1) will lie further to the right the more stable the complex $ML_n^m$. Providing only that the lattice energy of the precipitate, $ML_n^m(s)$, shows no exceptional behaviour, the $pH$ at which precipitation reaches a predetermined value (say 99.9%) will be progressively lower as $\beta_{ML}^n$ increases, thus permitting separations which may be adequate for many purposes. The metal chelate is generally of stoichiometric composition and can often be used directly as a weighing form. Where this is not the case (e.g. with cupferron and the nitrosonaphthols and some complexes of oxine, the precipitate may have to be ignited to a definite oxide. Generally speaking, the more sparingly soluble the reagent, the less soluble the corresponding metal chelate. Since excess reagent must be used to ensure quantitative precipitation this
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factor can introduce problems when washing the filtered-off precipitate to remove excess reagent, and a good deal of effort has gone into modifying the structure of some important precipitants (e.g. dimethylglyoxime) with a view to increasing the solubility of the reagent without increasing that of the metal complexes (Ref. 10).

If the metal-ligand bonds in a metal chelate are weakened by steric factors a new feature is introduced. Thus while aluminium tris-(8-hydroxyquinolinate) is readily prepared as a yellow precipitate from water, the corresponding complex with 2-methyl-8-hydroxyquinoline (I; R=CH₃) cannot be prepared in aqueous solution (although it does form in non-aqueous media). The basic reason is that in order to displace the equilibrium of equation (1) to the right sufficiently to compensate for the lowered value of $\beta_{ML}$, the pH must be raised beyond the level at which the competing reaction

$$\text{Al}^{3+}(aq) + 3\text{OH}^- \leftrightarrow \text{Al(OH)}_3(s)$$

predominates, and aluminium hydroxide, rather than aluminium tris-(2-methyl-8-hydroxyquinolinate), precipitates first. This anomalous behaviour is also shown by other derivatives of 8-hydroxyquinoline (I; R=H) substituted in the 2-position (by alkyl or aryl substituents) and by analogues in which steric hindrance to coordination is caused by annelation which includes the 2-position (as with 2-hydroxyacridine or 9-hydroxy-1,2,3,4-tetrahydroacridine) (Refs. 11, 12 & 13).

This combination of circumstances is virtually unique for Al³⁺ since the larger ions, Ga³⁺, In³⁺ and Tl⁺³⁺ where steric hindrance would be expected to be less pronounced, give normal tris-complexes. It is analytically significant that the alkaline earths and divalent transition metals can all be precipitated as bis-complexes with 2-methyl-8-hydroxyquinoline (I; R=CH₃) thus providing a route to the determination of Mg²⁺ and Al³⁺ in admixtures. Beryllium also forms an insoluble bis-chelate in spite of the fact that its cation (radius Be²⁺ = 0.31 Å) is smaller than that of Al³⁺ (0.5 Å). This is clearly the consequence of beryllium using $2s2p^3$ hybridisation to form a tetrahedral complex in which there can be no steric hindrance to coordination from bulky 2-constituents since the two coordinating ligands now lie in planes at right-angles to each other. Although a 2-methyl substituent lowers the formation constant of complexes of 8-hydroxyquinoline or its analogues with such cations as Cu²⁺, Mg²⁺, Ni²⁺, UO₂²⁺ and Zn²⁺, substitution in positions 5, 6 or 7 usually strengthens the metal-ligand bonds (Ref. 14).

8-Hydroxyquinoline is far from being a selective precipitant, and whereas selectivity is certainly improved by replacing the donor oxygen by sulphur, the resulting 8-mercaptoquinoline now suffers from the ease with which it can be oxidised, a disadvantage shared by a number of analytically valuable thiols (such as toluene-3,4-dithiol), by solutions of dithizone, and by a group of dialkyldithiocarbamates which are best stored as their zinc complexes until needed.

The lack of selectivity of 8-hydroxyquinoline can be turned to good advantage when the problem is one of collecting a wide spectrum of cations from a dilute solution - a problem of increasing importance in the study and control of environmental pollution. Here its use as a 'scavenger' can often be supplemented by other non-selective reagents and it lends itself especially well to pre-concentrations by liquid-liquid extraction of its metal chelates (Refs. 15 & 16). Vanderborght and Van Grieken (Ref. 17) noted that whereas active charcoal will absorb many cations directly (capacity 1 mg g⁻¹ for Zn²⁺ or Cu²⁺) it has a greater capacity for organic substances and argued that a hydrophobic metal chelate in which the metal is 'encapsulated' by an organic reagent should be absorbed more strongly, especially if the ligand had an aromatic structure with π-orbitals to increase the strength of interaction with the active charcoal. They found that the capacity of active charcoal for metal oxinates was some 30 times...
greater than for the metals alone, and by using an excess of oxine (2.5 - 25 ppm of oxine at pH ~ 8) they could collect from natural waters 90 - 100% of transition metals, Cd, Hg, Hf and lanthanides, 80 - 90% of Cu and Pb, 30% Ag, 0 - 20% Sb, less than 10% of alkaline earths with virtually no alkali metals.

In addition to acting as 'scavengers' for a whole range of cations it is possible to devise systems which are particularly efficient for some of them. If pyrrolidinedithiocarbamic acid is added to cobalt(II) buffered at pH ~ 4, the precipitate of tris-(pyrrolidinedithiocarbamate)cobalt(III) proves to be a most efficient collector for Cr(VI), Cd, Ni and Pb (over 90% from initial concentrations of 0.1 mg l⁻¹), less good for Cu, Fe(II) and Fe(III), and poor for Zn, Mn and Cr(III) (Ref. 18). The use of columns of e.g. CuS and PdS to collect Pd(II) has recently been extended to the use of chelating agents or complexes such as silver dithizonate, preferably supported on columns of plastized foam material to improve contact and increase flow rates. In the nature of things these are more specific in their behaviour, limiting their collecting properties to those cations capable of forming insoluble metal chelates and able to displace the original metals (zinc, silver, etc.) under the experimental conditions (Ref. 19).

Distribution coefficients are substantially larger than for a typical cation exchange resin, Dowex-50 (see Table 1) and clean separations of

TABLE 1. Distribution coefficients for univalent cations (Ref. 15)

<table>
<thead>
<tr>
<th>Exchanger</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
<th>Ag⁺</th>
<th>Tl⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium molybdophosphate, AMP</td>
<td>0</td>
<td>3 - 5</td>
<td>192</td>
<td>5430</td>
<td>26</td>
<td>4300</td>
</tr>
<tr>
<td>Dowex-50 in the NH₄⁺ - ion form</td>
<td>26</td>
<td>46</td>
<td>52</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystalllographic radii, Å</td>
<td>0.95</td>
<td>1.33</td>
<td>1.48</td>
<td>1.69</td>
<td>1.26</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Rb⁺ - Cs⁺, Na⁺ - K⁺, 90Sr²⁺ and its daughter 90Y³⁺ have been reported. It has been proposed for treating fission wastes (Ref. 22), especially to remove 137Cs, and to concentrate this isotope selectively from urine preliminary to low-level β-counting (Ref. 23). If the AMP is admixed with an inert material such as asbestos, improvements in the hydro-dynamic properties of a column are made though at the expense of increased volume and decreased bed capacity. Various organic polymers have been examined as binding materials to produce columns suitable for the removal of Cs from Purex high-level radioactive waste (Ref. 24), and beads of silica gel incorporating 65 wt. % of AMP have been prepared with good chemical, thermal, and radiochemical stability accompanied by good mechanical and hydrodynamic properties and resistance to abrasion (Ref. 25).

Although ammonium molybdat tungstate and tungstosilicate are too soluble for similar use, Katil has shown (Ref. 26) that ammonium phosphotungstate can be used to separate Cs⁺ and Rb⁺, and of the whole group designated by H₃₈XY₁₂₀₄₀·NH₄O (m = 3, 4, and 5; X = As, S, P; Y = Mo, W, V), stannic vanadophosphate has recently been studied for the separations In - Ga,
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Mg - Ca, and Mn - Ni (Ref. 27). Many ferrocyanides have been examined for applications in radiochemical and other separations (Ref. 28), and a synthetic apatite of composition $\text{Pb}_7\text{Sr}_3(\text{PO}_4)_6(\text{OH})_2$ has proved to be an excellent ion-exchanger for $\text{F}^-$ (Ref. 29), though it may be felt that such coordination compounds should not come within the scope of this talk. Before leaving the topic of anion-exchanging materials I should mention that it must be at least 30 years ago that I examined Werner's classical wholly inorganic tris-chelate of cobalt(III), viz. tris[tetrammine-dihydroxocobalt(III)] sulphate, $[\text{Co(NH}_3)_4(\text{OH})_2]_3\text{Co}^{6+}(\text{SO}_4^{2-})_3$ as a possible anion-exchanger. Alas, it proved to be too soluble and showed no outstanding specific properties.

One last example of an unusual application of a solid coordination compound is the use of the highly insoluble zirconium selenite for the determination of fluoride ion. The selenite is labelled with $^{75}\text{Se}$ by neutron activation and made into a chromatographic column after admixture with powdered PTFE. On treatment with a solution containing fluoride ions, the activity of the eluent (0.25M-HCl) is a measure of the added fluoride (100 - 200 $\mu$g determined with ± 5% precision) in consequence of the reaction (Ref. 30);

$$\text{Zr(SeO}_3)_{2-} + 6\text{HF} \rightleftharpoons \text{ZrF}^{2-} + 6\text{H}^+ + 2\text{SeO}_3^{2-} \quad (4)$$

Most separation techniques involve some form of partition between two phases and we will consider in turn those properties of coordination compounds that are relevant to their use in gas-solid, liquid-solid, and gas-liquid chromatography along with the cognate field of liquid-liquid extraction. Up to 1970 most emphasis on the gas chromatography of metals was directed towards exploiting the volatility of particular metal chelates. The problem here is to achieve a coordination compound that can be vaporised at as low a temperature as possible and which is thermally stable. Much work has been carried out by using 1,3-diketones and their fluorinated derivatives for the gas chromatography of tris-chelates of Al, Cr(III), Sc, Rh and the lanthanides; not too much success has attended the gas chromatography of bis-chelates with the exception of that of beryllium bis-trifluoroacetylacetone(II) which formed the basis of a procedure for determining beryllium down to $4 \times 10^{-4}$ g in 10 - 100 mg samples of lunar dust and rock (Ref. 31). Hexafluorothioacetylacetone forms a number of volatile chelates (III; $\text{M} = \text{Cd, Cu, Fe(II)}, \text{Ni, Pb, Pt, Zn}$)

![Diagram](II)

![Diagram](III)

with low melting points ranging from 54.5°C (Zn) to 108°C (Cd) which lend themselves to gas-chromatographic separations (Refs. 32 & 33). Monothio-trifluoroacetylacetone has been used to determine Ni down to $10^{-11}$ g and bidentate and tetradentate $\beta$-aminoketonates have been used with Cu, Ni, Pd and Pt down to the picogram level (Refs. 34 & 35). Chelate complexes of diethylidithiocarbamic acid, $\text{Et}_2\text{N} \cdot \text{CSSH}$, have also been studied recently. Those of Fe(III), Co(III), Ni and Zn are highly stable thermally: complexes of Ag and Cu(II) are stable up to 240°C, and those of Co, Ni, Pd and Pt up to 300°C, many elegant separations have been achieved.

Quite another aspect of gas chromatography concerns the use of coordination compounds as the stationary phase. A coordination polymer such as (IV; $\text{M} = \text{Ni or Co(II)}$) has been found to have excellent thermal and chemical stability and can be used for separating a variety of aliphatic, aromatic
and heterocyclic bases.

Retention volumes remained constant even after many hours use at 100°C.

Fig. 1. Separation of nitrogen bases on a stationary phase of 5% cobalt phthalocyanine on Sterling F.T.G., 10 m column with NH₃ + H₂ as carrier gas at 178°C (Ref. 38).
The use of cobalt(II) phthalocyanine (5% on Sterling F.T.G.) has a further advantage in that it can exploit steric hindrance to coordination. Thus, 2-methyl substituted pyridines are eluted before pyridine itself (with its unhindered nitrogen atom) despite their higher relative molecular masses (cf. Fig. 1) (Ref. 38).

The use of a silver salt in the stationary phase for the gas chromatography of alkenes was one of the earliest examples of exploiting stereoselective features in coordination (Ref. 39), and Gil-Av and Schurig have shown more recently that dicarbonylrhodium(I)-3-trifluoroacetylcamphorate (V) provides an excellent stationary phase for the gas chromatography of monoalkenes, for complex formation is stronger and the effects of structural changes in the alkenes are more marked in distinguishing between cis- and trans-, and position isomers (Ref. 40).

There have been innumerable papers describing the applications of metal chelates in column and thin-layer chromatography (cf. Ref. 41 for metal dithizonates alone). The non-polar character, high thermodynamic stability and intense colour of many such chelates lend themselves to t.l.c., and by using uniform, ultra-thin layers (1 - 6 μm) produced by the anodic oxidation of very pure aluminium foil, less than 1 ng of several metals can be separated and identified as their dithizonates (Ref. 42).

In the latest of a long series of papers, Ludwig and his co-workers have studied the t.l.c. of chelates of thiodibenzoylmethane (VI) and noted that although derivatives of the more polar acetonylthioamides (VII) are less strongly coloured, they give significantly different $R_F$ values (Ref. 43).

![VI](Ref. 37)

![VII](Ref. 37)

Yamamoto and Yamamoto have carried out a more detailed study of the chromatography of the acetylacetonates of Al, Cr(III) and Co(III) which are eluted in the order of their decreasing molar volumes; the results are discussed in terms of the relevant solubility parameters (Ref. 44).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$R_F$ a</th>
<th>$R_F$ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(acac)$_2$</td>
<td>square planar</td>
<td>0.30</td>
<td>0.08 - 0.65</td>
</tr>
<tr>
<td>Cr(acac)$_3$</td>
<td>octahedral monomer</td>
<td>0.93</td>
<td>0.77</td>
</tr>
<tr>
<td>Co(acac)$_3$</td>
<td>octahedral monomer</td>
<td>0.63</td>
<td>0.70</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td>octahedral monomer</td>
<td>0 - 0.25</td>
<td>0.80</td>
</tr>
<tr>
<td>[Co(acac)$_2$]$_4$</td>
<td>octahedral polymer</td>
<td>0.0</td>
<td>0 - 0.11</td>
</tr>
<tr>
<td>[Ni(acac)$_2$]$_3$</td>
<td>octahedral polymer</td>
<td>0.0</td>
<td>0 - 0.12</td>
</tr>
</tbody>
</table>

a Elution with diethyl ether.

b Elution with benzene - diethyl ether - acetylacetone, 50:50:1.

Oksala and Krause examined the t.l.c. of coordination compounds such as square planar Cu(acac)$_2$, the octahedral monomers, Cr(acac)$_3$, Co(acac)$_3$ and Fe(acac)$_3$, and the octahedral polymers [Co(acac)$_2$]$_4$ and [Ni(acac)$_2$]$_3$ and conclude that non-labile, coordinatively saturated complexes should move with large $R_F$ values on elution with solvents of moderate polarity, provided there is no permanent dipole in the compound. Labile compounds
show increased $R_f$ values when excess ligand was present in the eluent (Ref. 45). The authors note that "complexes capable of undergoing a ready expansion of coordination number are expected to show greater retention under similar conditions." Since $R_f$ values can usually be correlated quite well with the distribution coefficients obtained in liquid-liquid extraction, this conclusion seems surprising since in all studies of the synergic effect there is an increase in extraction, implying a higher distribution ratio in favour of the organic phase and pointing to higher $R_f$ values: the decreased hydrophilicity more than compensates for the increased molar mass. Clearly there is still room for further investigations in the field of the chromatography of coordination compounds.

In all chromatographic work we are concerned with the partition of a solute between two phases and this phenomenon is exploited in its most direct form in liquid-liquid extraction between two immiscible liquid phases. The properties of a coordination compound that favour its extraction from an aqueous into an organic phase are large size and low hydrophilicity. Any factor which will increase the former and decrease the latter will enhance the distribution coefficient. For example, unlike the bis-8-hydroxy-quinolinites of the divalent transition metals (and all the tris-complexes), magnesium and strontium form water-insoluble complexes, $\text{M(0x)}_2 \cdot \text{H}_2\text{O}$, which do not extract into chloroform unless the coordinated water is replaced by excess of un-ionised oxine, as in $\text{Sr(Ox)}_2 \cdot \text{H0x}$ (Ref. 46); butylcellosolve can serve this function when extracting the magnesium complex (Ref. 47).

With dithizone ($\text{H}_2\text{Dz}$), manganese(II) only forms a weak complex which is extracted into an organic solvent only at a moderately high pH value where it is prone to oxidation. Displacement of the water by pyridine or other nitrogen base gives the extractable complex $\text{Mn(HDz)}_2 \cdot \text{py}$ (Ref. 48). This phenomenon is clearly reminiscent of the synergic effect in the extraction of uranium(VI) from nitric acid where the addition of tributylphosphate (TBP), or even more effectively of tributylphosphine oxide (TBPO), increases the extraction of the bis-chelate $\text{UO}_2(\text{TTA})_2$ by several orders of magnitude (Ref. 49). The same favourable features of increased bulk and reduced hydrophilicity are seen in Freiser's use of 1,10-phenanthroline (IX; R = H) to enhance the extraction of nickel bis-dithizonate as the adduct, $\text{Ni(HDz)}_2 \cdot \text{phenan}$ (Ref. 50). This procedure has an additional advantage in that it speeds up an otherwise extremely slow rate of extraction of nickel dithizonate alone. It seems possible that the slow reaction between $\text{Ni(H}_2\text{O)}_2^{2+}$ and $\text{H}_2\text{Dz}$ (or its conjugate base) to give a square planar complex is replaced by one between the reagent and a nickel-phenanthroline complex from which some water has already been displaced - and where there is no change in octahedral coordination anyway.

In addition to the liquid-liquid extraction of formally uncharged metal chelates, coordination compounds play a dominant role in the extraction of ion-pairs. Only 25 years have elapsed since Tribalat first showed that tetraphenylarsonium permanganate could be extracted into chloroform whereas the corresponding monovalent remained in the aqueous phase (Ref. 51). Other large uni-negative anions such as $\text{MnO}_4^-$, $\text{ClO}_4^-$, $\text{IO}_4^-$, etc. can be extracted and separated from the more easily aquated polyvalent $\text{MoO}_4^{2-}$, $\text{WO}_4^{2-}$ and $\text{CrO}_4^{2-}$. The bulky, hydrophobic cation can also be $\text{CH}_3\text{(C}_6\text{H}_5)_3\text{As}^+$, $(\text{C}_6\text{H}_5)_5\text{S}^+$, $(\text{C}_6\text{H}_5)_2\text{I}^+$, $\text{Fe(phenan)}_3^{2+}$, or a large cation derived from a basic dye such as Rhodamine B which will extract coordinated halo-complexes such as $\text{SbCl}_6^-$, $\text{TlCl}_4^-$, $\text{TlBr}_4^-$, $\text{GaCl}_4^-$, $\text{SbI}_4^-$, $\text{SbBr}_6^-$, $\text{FeCl}_4^-$ $\text{FeBr}_4^-$, $\text{AuCl}_4^-$, $\text{AuBr}_4^-$ etc. The conjugate acids of malachite green, methyl violet and many other dye-stuffs behave similarly.

The most fruitful development in this field stemmed from the discovery by Smith and Page in 1948 that liquid long-chain amines such as dioctylamine were able to extract strong acids such as $\text{HCl}$, $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ quantitatively from aqueous solutions into chloroform or nitrobenzene (Ref. 54). It was
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Soon realised that the ammonium salts so produced could exchange their anions for others and so behave in a manner formally analogous to the familiar anion-exchange resins. Many "liquid anion-exchangers" are commercially available. A typical example is Aliquat-336(Cl), a viscous yellow liquid, basically methyltricaprylammonium chloride with 27-33 carbon atoms on the average (Mr 475), the alkyl groups consisting mainly of octyl and decyl chains. Such compounds can be used to extract an astonishing variety of anions varying from simple species such as the halide ions, to oxyanions such as ClO₃⁻, ClO₄⁻, ReO₄⁻, and complex anions such as ZnCl₂⁻, Co(SCN)₂⁻, UO₂(0x)²⁻, or anionic species such as MY⁻ derived from a cation Mn³⁺ and EDTA (Na₂H₂Y•2H₂O) (Ref. 55), or the strongly coloured complexes of metals with metallochromic indicators such as Xylenol Orange. By treating Aliquat-336(Cl) with a concentrated solution of Erdmann's salt, (NH₄⁺)(Co(NH₃)₂(NO₂)₄⁻) the chloride ion is replaced by the Erdmannate ion, thus affording a coloured liquid anion-exchanger which lends itself to a variety of analytical determinations (Ref. 56). As typical of the elegant separations that can be carried out by the extraction of ion-pairs derived from liquid anion exchangers by a xylene solution of a commercial tertiary amine (Alamine-336; R₃N), uranium, plutonium and neptunium can be separated in the form of (R₃NH)₂(UO₂Cl₄), (R₃NH)₂PuCl₆ and (R₃NH)₂NpO₂Cl₂, by adjusting the composition of the initial aqueous phase (HCl) and that of the various strip solutions (Ref. 57). Very many metal complexes can be extracted in this way into solvents such as methylisobutylketone which can then be nebulized to provide the most advantageous route to their determination by atomic absorption or fluorescence spectroscopy. Some interesting observations have yet to be extended, explained, and interpreted. Thus, among complex cyanides the order of increasing extraction is Au(CN)₃⁻>Ag(CN)₂⁻ (linear ions); Hg(CN)₄²⁻>Cd(CN)₄²⁻>Zn(CN)₂⁻ (tetrahedral ions); Pt(CN)₄²⁻>Pd(CN)₂⁻>Ni(CN)₂⁻ (square planar ions). Tetrahedral ions are more strongly extracted than square planar ions of the same charge (Ref. 56).

In forming bulky, extractable ion-pairs the possibilities of steric hindrance to coordination must always be born in mind. Whereas 2,2-bipyridyl (VIII; R = H), 1,10-phenanthroline (IX; R = H) and 2,2-bis(isoquinolyl) (X; R = H) will form stable complexes with all the d-block, divalent transition metal cations, Mn²⁺ (M = Mn²⁺ to Zn²⁺), steric hindrance prevents the formation of tris-complexes by homologues of these ligands with methyl groups adjacent to the nitrogen atoms (VIII, IX and X; R = CH₃). Steric hindrance to coordination is also shown by biquinolyl (XI). Although none of these ligands will give extractable tris-complexes

\[
\text{VIII: } R = H \quad \text{IX: } R = H \quad \text{X: } R = H \quad \text{XI: } R = H
\]
with iron(II), they can all give extractable bis-complexes with copper(I) which, of course, employs \(4s^4p^3\) hybridised orbitals. The two ligands then lie in planes at right angles to each other and there is now no steric hindrance in the formation of the tetrahedrally coordinated complex in such an ion-pair as Cu(biquin)\(^+\)Cl\(^-\). These circumstances lead to a most satisfying way for determining copper (as Cu(I)) in the presence of iron (as Fe(II)) (Ref. 13). The low results at one time obtained in determining traces of copper in stainless steels with this reagent has been shown to be due to the formation of an interesting coordination compound of chromium with citrate which is so constructed that it can also accommodate copper(II) stably (Ref. 56).

Yet another aspect of current coordination chemistry is well illustrated

![Graph](image_url)

**Fig. 2.** The effect of temperature on the distribution coefficients of first row transition elements between equal volumes of an aqueous phase pH 5.0 - 5.2 and a 30% solution of sodium diethylhexylphosphate (NaDEHP) in a high b.p. hydrocarbon oil, Catenaz 11 (Ref. 59).
Coordination compounds in analytical chemistry

by the commercially important separation of Ni and Co(II) by extraction with diethylhexylphosphoric acid (H.DEHP). Data for a variety of metals are shown in Fig. 2. The most striking feature is the increase in the extraction of cobalt (but not that of nickel) with rise of temperature. At the same time there is a change in colour as the pink octahedral complex extracted at lower temperatures is replaced by the blue, and less hydrophilic tetrahedral complex (Ref. 59).

The increase in entropy in the reaction

\[ \text{Co(DEHP)}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{Co(DEHP)}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{cool}} \text{blue, tetrahedral} \]

displaces the equilibrium to the right with rising temperature and so promotes the extraction of Co(II) into the organic phase. The major factor working against the formation of tetrahedral complexes for all the dipositive cations is the difference between the ligand-field stabilization energy, \( \Delta_{\text{oct}} - \Delta_{\text{tetr.}} = \frac{5}{9} \Delta_{\text{oct}} \). This amounts to 0.0 \( \Delta_{\text{oct.}} \) for Mn(II), 0.133 \( \Delta_{\text{oct.}} \) for Fe(II), 0.267 \( \Delta_{\text{oct.}} \) for Co(II) and no less than 0.844 \( \Delta_{\text{oct.}} \) for Ni(II).

Everyone will be aware of the dramatic developments in titrimetric analysis consequent upon the introduction by G. Schwarzenbach of procedures based on the formation of stable coordination compounds between metals and a variety of amino polycarboxylic acids of which ethylenedinitrile-tetraacetic acid (XII; EDTA) is the best known (Ref. 60). Once it had become clear that substances such as murexide and o-dihydroxyazodyestuffs could serve as metallochromic indicators, and Schwarzenbach had demonstrated how the requisite metal-bonding features could be incorporated into many conventional acid-base indicators (to give e.g. a metalphthalein), a never ending stream of new compounds have been prepared, some of which have proved especially suitable for detecting the end-points in the titrations of particular metals. The basic requirements are, of course, that coordination to a metal should give a thermodynamically stable coordination compound with a colour that contrasts with that of the uncoordinated indicator and which has a lower formation constant than that of the complex formed by the metal and the complexone used as the titrant (Ref. 60). A great deal of work has been carried out to modify the structure of complexones so as to give more stable complexes with particular metals, especially with the alkali metals. Replacement of O by S, N by P, and attempts to exploit steric hindrance in various ways have not met with much success.

The goal of achieving sufficiently high formation constants (\( K_{\text{ML}} >> 10^7 \)) for the titration of e.g. lithium has not been reached although EDTA (XII) and uramildiacetic acid (XIII) and its homologues have shown the most promise (Ref. 61).

The anomalous stability order for the formation constants of EDTA where

\[ K_{\text{Ba}} < K_{\text{Sr}} < K_{\text{Ca}} < K_{\text{Mg}} \]

can be explained on steric grounds if it is assumed that the ligand is sufficiently flexible when bonding through its two donor nitrogen and four donor oxygen atoms to adapt its enclosure to ions of size decreasing down from \( \text{Ba}^{2+} \) to \( \text{Ca}^{2+} \) whereas steric repulsion prevents a closer approach sufficient to give strong binding to the much smaller magnesium ion (cf. Table 5 for ionic radii). This situation has recently been thrown open for further work by the preparation of a new series of complexones based on nitrogen macrocycles, for Stetter and Frank (Ref. 62).
have now reported some quite dramatic results for the complexones XIV-XVI (Table 3).

\[
\text{HOOC.CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{COOH})_n\text{N}\text{CH}_2\text{COOH}
\]

(XIV) \( n = m = 2 \)

(XV) \( n = 2, m = 3 \)

(XVI) \( n = m = 3 \)

<table>
<thead>
<tr>
<th>Ion</th>
<th>(XIV)</th>
<th>(XV)</th>
<th>(XVI)</th>
<th>EDTA</th>
<th>CDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>11.03</td>
<td>6.36</td>
<td>3.02</td>
<td>9.12</td>
<td>10.32</td>
</tr>
<tr>
<td>(\Delta_{\text{Ca},\text{Mg}})</td>
<td>+4.82</td>
<td>+1.70</td>
<td>+6.46</td>
<td>+1.88</td>
<td>+2.18</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>15.85</td>
<td>8.06</td>
<td>9.48</td>
<td>11.00</td>
<td>12.50</td>
</tr>
<tr>
<td>(\Delta_{\text{Sr},\text{Ca}})</td>
<td>-3.05</td>
<td>+3.64</td>
<td>-3.33</td>
<td>-2.20</td>
<td>-2.50</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>12.80</td>
<td>11.70</td>
<td>6.15</td>
<td>8.80</td>
<td>10.00</td>
</tr>
</tbody>
</table>

With complexones XIV and XVI the stability of the calcium complex relative to the magnesium complex is far greater than for EDTA, and with (XV) there is a remarkable preference for strontium relative to calcium, reversing the trend found in all earlier work. Clearly, the aspect of compromise between the size of the enclosure permitted by steric repulsion between the component atoms of the complexone and the size of the encapsulated cation must depend strongly and even critically on the structure and flexibility of the ligand.

An early example of a coordination compound capable of enclosing a cation of preferred, favourable ionic radius is provided by the macrocyclic azodyestuff (XVII) prepared by Close and West in 1960. This was described as a specific indicator for calcium (Ref. 63). Up to 1967 the literature on macrocyclic ethers (as XVIII) was limited and the possibility of their being complexing agents was not realised until Petersen obtained the first brown ether (dibenzo-18-crown-6; XIX, \( n = m = 2 \)) as an unexpected by-product insoluble in methanol but readily soluble on the addition of sodium salts. The naturally occuring macrocyclic antibiotics valinomycin and nonactin were known to exert interesting biological effects related to their ability to transport Na\(^+\) and K\(^+\) across cell membranes and were subsequently shown to exhibit a marked preference for the coordination of potassium (or rubidium) ions as against sodium ions. The potentialities of such compounds as models of biological systems, for selective ion electrodes, for conducting analyses and reactions in organic solvents, and as specific
Coordination compounds in analytical chemistry

complexing agents has stimulated an enormous amount of work (Refs. 64 - 69) which has, unfortunately, seldom been directed towards purely analytical applications, but see Note a.

The size of the cavity and the nature of the donor atoms influence the nature of the cations that are trapped preferentially within such macrocycles and also the overall complex stability, although, of course, the nature of the counter ion and the influence of the solvent used must also be considered.

Dibenzo-18-crown-6 (XIX; n = m = 2) will solubilize potassium permanganate in a solvent such as dichloromethane or benzene. The macrocycles (XX; n = 2 or 3) will solubilize NaMnO₄ instantaneously, but not KMnO₄, or lithium, rubidium, caesium, ammonium or silver salts (Ref. 66). An enormous number of compounds analogous to (XVIII), (XIX) and (XX) have been synthesized and examined for their metal-complexing properties but a different approach has been to synthesize 'host' molecules containing rigid binaphthyl units where the two naphthalene rings occupy different planes, each perpendicular to the best plane of the cyclic ether (Ref. 67). A solution of the compound (XXI) in dry THF at -80°C will dissolve potassium metal to give a green reducing solution in which the potassium ion, K⁺, is encapsulated by the ring of oxygen atoms and its electron is delocalized in the aromatic system. With compound (XXII; R = morpholino), the cavity is about 2.4 - 3.1 Å in diameter and can give a formally neutral complex when a potassium ion becomes the 'guest'. This formally neutral species is soluble in water as well as in organic solvents and is stable to acids.

Note a: In a paper presented in Section IV of the present Conference, K. Ueno et al. have synthesized [4'-picrylamino]-benzo]-15-crown-5 (HA) as a new coloured reagent for potassium [74]. The orange compound is almost insoluble in water but easily soluble in organic solvents ($\lambda_{max}$ 390 nm in CHCl₃) and gives an extractable blood-red potassium complex (KA-HA; $\lambda_{max}$ 460 nm). The absorbance at 560 nm is linearly proportional to the concentration of potassium up to 300 ppm. The disappointingly low distribution ratio, [K⁺]org/[K⁺]aq = 0.017 can probably be attributed to the presence of very hydrophilic nitro groups.
With Ba\(^{2+}\) two molecules of \((\text{XXII}; R = \text{morpholino})\) react to give a molecular sandwich in which the barium ion is, in a manner of speaking, completely enveloped in a lipophilic skin, its double positive charge being neutralised by the two carboxylate ions. The complex is soluble in organic solvents, stable to chromatography, and does not give a precipitate of barium sulphate when sulphuric acid is added to its solution. If two carboxylate arms are provided (as \(\text{XXII}; R = -\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}\)) a stable complex with Sr\(^{2+}\) results and the complex was, in fact, prepared by scavenging strontium ions from a bulk sample of barium hydroxide. A Ba\(^{2+}\) ion (radius 1.49 \(\text{Å}\)) does not fit in so well as Sr\(^{2+}\) (Ref. 67). Many thermodynamic studies have been carried out on the kinetics of complex formation and the stabilities of the various metal complexes (Ref. 68).

A second type of complexing agent is provided by the bicyclic macrocycles (\(\text{XXIII}, a - f\)) usually referred to as cryptates (Refs. 64 - 69). Analogous compounds with sulphur replacing some of the oxygen atoms have also been prepared.

The stability of a complex is a compromise between the free energy of solvation and the free energy of complex formation. The selectivity of a ligand for a particular cation will depend on the way in which the free energy of complexation varies with respect to the free energy of the solvated ion. Now \(\Delta G(\text{solvation})\) increases monotonically as the radius of the cation decreases along a series (Table 5). Much the same order would be expected for \(\Delta G(\text{complexation})\) by a polydentate ligand provided it were able to adjust to all cation sizes. If, however, the cavity is of a fixed dimension, \(\Delta G(\text{complexation})\) will increase as the size of the cation decreases until it reaches this limiting size of the cavity. For smaller ions, \(\Delta G(\text{complexation})\) cannot increase further since the cavity cannot get smaller and maintain contact between the guest cation and the bonding sites of the host ligand. These points are illustrated in Tables 4 and 5 in which the favoured ion for a particular cryptate is underlined. All stabilities are found to be much higher in methanol than in water; for stabilities increase as the dielectric constant decreases. This also increases the selectivity by favouring (i) the most stable complexes, and (ii) larger ions relative to smaller ions. Since oxygen sites have a higher polarity but a lower polarizability than nitrogen sites, alkali
cations are more strongly solvated by O than by N, whereas Ti⁺ and Ag⁺ interact more strongly with nitrogen sites. No ligand has yet been

TABLE 4. Stability constants of cryptates. Data for water at 25°C (Ref. 69).

<table>
<thead>
<tr>
<th>Cryptate (XXIII)</th>
<th>m</th>
<th>n</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Sr²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 0 1</td>
<td>5.5</td>
<td>3.2</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>2.5</td>
<td>2.5</td>
<td>&lt;2.0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) 1 0</td>
<td>2.50</td>
<td>5.40</td>
<td>3.95</td>
<td>2.55</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>6.95</td>
<td>7.35</td>
<td>6.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) 1 1</td>
<td>&lt;2.0</td>
<td>3.9</td>
<td>5.4</td>
<td>4.35</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>4.4</td>
<td>8.0</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) 1 2</td>
<td>&lt;2.0</td>
<td>1.65</td>
<td>2.2</td>
<td>2.05</td>
<td>2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>3.4</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) 2 1</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.7</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>3.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(f) 2 2</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EDTA (XII) 2.85 1.78 0.96 0.58 0.15 9.12 11.0 8.80 7.78
(XIII) 5.61 3.33 1.94 - - 8.19 8.31 6.93 6.13
Enniatin* 1.28 2.38 2.92 2.74 2.34 1.20 2.95 2.65 2.93
Valinomycin* <0.7 0.67 4.90 5.26 4.41 0.7 2.70 2.23 3.34

*These data refer to measurements in methanol. In this solvent all stability constants are much higher than in water.

TABLE 5. Data for cryptates (XXIII a - e) and dibenzocrown-6 (Ref. 69).

<table>
<thead>
<tr>
<th>Cation</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Sr²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radius in Å</td>
<td>0.78</td>
<td>0.98</td>
<td>1.33</td>
<td>1.49</td>
<td>1.65</td>
<td>0.78</td>
<td>1.06</td>
<td>1.27</td>
<td>1.43</td>
</tr>
<tr>
<td>Hydration number</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>-ΔG⁰(hydration), kcal mol⁻¹</td>
<td>-1,122</td>
<td>98.5</td>
<td>80.5</td>
<td>75.5</td>
<td>68.0</td>
<td>454</td>
<td>379</td>
<td>340</td>
<td>314</td>
</tr>
<tr>
<td>ligand cavity radius, Å</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
<td>e</td>
<td>f</td>
<td>g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of binding sites</td>
<td>0.8</td>
<td>1.1</td>
<td>1.4</td>
<td>1.8</td>
<td>2.1</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

g is dibenzocrown-6

found which shows a special selectivity for Rb⁺. The cryptate (XXIII (c)) is quite exceptional in showing a high selectivity for Sr²⁺ (or Ba²⁺) over Ca²⁺ and has been tested in decorporation experiments (Ref. 69).

By producing a cross-bridge as in the macrotricyclic cryptate (XXIV), a molecule with an almost spherical cavity of radius 1.8 Å is obtained as
cubic crystals, m.p. 196 - 200°C, resulting from a 12-stage synthesis (overall yield ~2%). It dissolves caesium bromide and probably yields the strongest caesium complex yet made (log K = 3.4 in water). As might be expected, the reaction is slow (Ref. 70). Kinetics of the reactions between Ca²⁺ and cryptates have been studied and shed light on the conformational changes (exo-exo + exo-endo + endo-endo) in these ligands that must precede complexation, and on the extent to which water of solvation persists in the transition state (Ref. 71). Such studies are, of course, highly relevant to the analytical uses of this type of complexing agent.

While a clear understanding of basic principles and requirements is leading to the controlled design and synthesis of tailor-made 'host' molecules for particular 'guest' ions, the analyst has reason to be grateful and cannot afford to overlook any opportunities provided by the unpredictable vagaries of crystal structures. For example, while hydrochloric acid is normally able to liberate a carboxylic acid from its potassium salt

\[ R.CCOK + HCl \rightarrow KC1 + R.COOH \]  (6)

exactly the opposite reaction takes place with catecholdiacetic acid \((\text{C}_{6}\text{H}_4(\text{OCH}_2\text{.COOH})_2; \text{H}_2\text{CDA})\) which reacts with an aqueous solution of potassium chloride to yield an insoluble coordination compound of potassium with the concomitant liberation of hydrochloric acid, thus:

\[ 2 \text{H}_2\text{CDA} + \text{KCl} \rightarrow \text{KHCDA.H}_2\text{CDA} + \text{HCl} \]  (7)

A sandwich of two molecules of \(\text{H}_2\text{CDA}\) provides 8 of the 10 oxygen atoms which encapsulate the potassium ion, the remaining coordination sphere being made up by an oxygen atom from each of two other molecules. It is stated that Li⁺, Na⁺, NH₄⁺ and Cs⁺ do not react in a similar fashion (Ref. 72).

Time does not permit of any detailed analysis of the factors which affect the colour (or fluorescence) of the great range of coordination compounds employed in absorptiometry (or fluorimetry) (Ref. 52). To take one specific example, the absorptiometric determination of iron(II) has led to the introduction of a series of reagents yielding tris-complexes of increasing linear absorption coefficients, e.g. 2,2-bipyridyl \((\epsilon = 7,930)\), 1,10-phenanthroline \((\epsilon = 11,100)\), 4,7-diphenyl-1,10-phenanthroline \((\epsilon = 22,140)\), 2,4,6-(2-pyridyl)-1,3,5-triazine \((\epsilon = 22,600)\) and the water-soluble 'ferrozine', 3-(2-pyridyl)-5,5-bis(4-sulphophenyl)-1,2,4-triazine \((\epsilon = 27,900)\). Although the cost of ferrozine is only about half that of 1,10-phenanthroline, the large quantities used in a continuous automatic analyser can raise an economic problem. This has recently been solved by realising that after measuring the absorption due to the tris-complex of iron(II), the sample can be subjected to mild oxidation which will generate the thermodynamically weaker tris-complex of iron(III) from which the iron can be removed by complexation with oxalate at 95°C, thus regenerating the ligand which is not attached itself under these experimental conditions. This solution to a difficult problem in coordination chemistry demanded a careful appraisal of the thermodynamic stabilities of all possible components and a study of the kinetics of all the relevant reactions (Ref. 74).

We must conclude that stereochemical factors, reaction kinetics, conformational changes and ligand field stabilisation energies are all relevant to the uses of coordination compounds in analytical chemistry. Selectivity may be achieved by design or by a lucky chance; for there seems, at present, no way of predicting when some new coordination compound will turn up which owes its potential usefulness to an unexpected and unpredictable crystal structure.
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