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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 chroma-
tography (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 over-
looked.

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
computors, 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
XVIII th 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
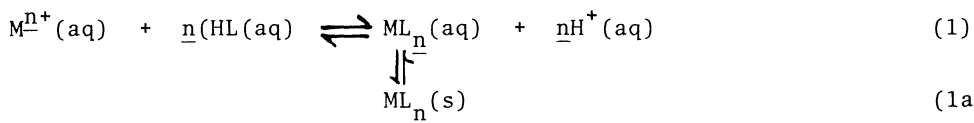or inherent in the pre-concentration stage.

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 stoicheiometric, 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 assoication 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 $(Cuen_2^{2+})(CdI_4^{2-})$ and $(Cuen_2^{2+})(HgI_4^{2-})$ which are insoluble in water, ethanol and ether, or by $(Fe(bipy)_3^{2+})(CdI_4^{2-})$ which provides a very sensitive spot-test for cadmium. Other examples are the well-known thiocyanato complexes containing coordinated pyridine such as $M(SCN)_2 \cdot \underline{n}py$ (M = Cu(II), Cd, Co(II), Fe(II), Mn, Ni, Zn; $\underline{n}$ = 2 or 4). The virtues of large hydrophobic cations conjoined with large anions is illustrated by such insoluble complexes as $(CH_3(C_6H_5)_3N^+)_2CdI_4^{2-}$, $(Fephenan_3^{2+})(ReO_4^-)_2$ 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

$$M^{\underline{n}+}(aq) \; + \; \underline{n}(HL(aq) \; \rightleftharpoons \; ML_n(aq) \; + \; \underline{n}H^+(aq) \tag{1}$$

$$\Big\downarrow\!\Big\uparrow$$

$$ML_{\underline{n}}(s) \tag{1a}$$

$$\text{and} \quad HL(s) \rightleftharpoons HL(aq) \rightleftharpoons H^+(aq) \; + \; L^-(aq) \tag{2}$$
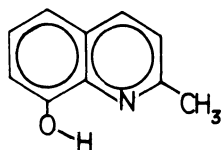
Water of solvation is omitted for the sake of simplicity. The position of equilibrium will be determined by the pH and the relevant proton- and metal-ligand formation constants $\beta_{ML_{\underline{n}}}$ and β_{HL} respectively. By a suitable choice of pH and reagent concentration reaction (1) can 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. Providing only that the lattice energy of the precipitate, $ML_n(s)$, shows no exceptional behaviour, the pH at which precipitation reaches a predetermined value (say 99.9%) will be progressively lower as $\beta_{ML_{\underline{n}}}$ increases, thus permitting

separations which may be adequate for many purposes. The metal chelate is generally of stoicheiometric 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

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. dimethyl-
glyoxime) 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-hydroxy-
quinolinate) is readily prepared as a yellow precipitate from water, the
corresponding complex with 2-methyl-8-hydroxyquinoline (I; R=CH$_3$) 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
β_{ML_3}, the pH must be raised beyond the
level at which the competing reaction

$$Al^{3+}(aq) \;+\; 3OH^- \rightleftharpoons Al(OH)_3(s) \quad (3)$$

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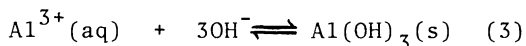
predominates, and aluminium hydroxide,
rather than aluminium tris-(2-methyl-8-hydroxyquinolinate), precipitates
first. This anomalous behaviour is also shown by other derivatives of
8-hydroxyquinoline (I; R=H) substituted in the 2-position(by alkyl or
aryl substituents) and by analogues in which steric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

This combination of circumstances is virtually unique for Al^{3+} since the
larger ions, Ga^{3+}, In^{3+} 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=CH$_3$)
thus providing a route to the determination of Mg^{2+} and Al^{3+} in admixtures.
Beryllium also forms an insoluble bis-chelate in spite of the fact that its
cation (radius Be^{2+} = 0.31 Å) is smaller than that of Al^{3+} (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 coord-
ination 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 Cu^{2+}, Mg^{2+}, Ni^{2+}, UO$_2^{2+}$ and Zn^{2+}, 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 Zn^{2+} or Cu^{2+}) 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 $\sim$ 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 pyrolidinedithiocarbamic acid is added to cobalt(II) buffered
at pH $\sim$ 4, the precipitate of tris-(pyrolidinedithiocarbamate)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 1^{-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). It has been known for over 70 years that a precipitate of
ammonium molybdophosphate (AMP) changes its composition if washed by a
solution of potassium nitrate, and that the replacement of ammonium by
potassium ions is reversible (Ref. 20). This ion-exchange behavious was
rediscovered at intervals and thoroughly studied by van Smit, by Meier and
Treadwall, by Thistlethwaite, and by Healey and his co-workers (Ref. 21).
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)

| Exchanger | $\underline{K}_D$, meq g^{-1} | | | | | |
	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+
Ammonium molybdo-phosphate, AMP	0	3 - 5	192	5430	26	4300
Dowex-50 in the NH_4^+ - ion form	26	46	52	62		
Crystallographic radii, Å	0.95	1.33	1.48	1.69	1.26	1.44

Rb^+ - Cs^+, Na^+ - K^+, $^{90}Sr^{2+}$ and its daughter $^{90}Y^{3+}$ have been reported. It
has been proposed for treating fission wastes (Ref. 22), especially to remove
^{137}Cs, 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 molybdotungstate 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
$H_m XY_{12}O_{40} \cdot \underline{n}H_2O$ ($\underline{m}$ = 3,4, and 5; X = As, Si, P; Y = Mo, W, V), stannic
vanadophosphate has recently been studied for the separations In - Ga,

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 $Pb_7Sr_3(PO_4)_6(OH)_2$ has proved to be an excellent ion-exchanger for 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-μ-dihydroxocobalt(III)]sulphate, $[Co(NH_3)_4(OH)_2]_3Co^{6+}(SO_4^{2-})_3$ as a possible anion-exchanger. Alas, it proved to be too soluble and showed no out-standing 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}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 μg determined with ± 5% precision) in consequence of the reaction (Ref. 30);

$$Zr(SeO_3)_2 \;+\; 6HF \;\rightleftharpoons\; ZrF_6^{2-} \;+\; 6H^+ \;+\; 2SeO_3^{2-} \qquad (4)$$
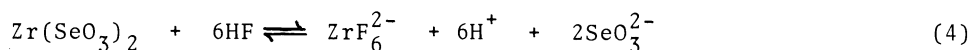
Most separation techniques involve some form of partition between two phases and we will consider in turn those properties of coordination compounds that are relevant to their use in gas-solid, liquid-solid, and gas-liquid chromatography along with the cognate field of liquid-liquid extraction. Up to 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 chromato-graphy of bis-chelates with the exception of that of beryllium bis-tri-fluoro-acetylacetone(II) which formed the basis of a procedure for determining beryllium down to 4×10^{-4} g in 10 - 100 mg samples of lunar dust and rock (Ref. 31). Hexafluorothioacetylacetone forms a number of volatile chelates (III; M = Cd, Cu, Fe(II), Ni, Pb, Pt, Zn)
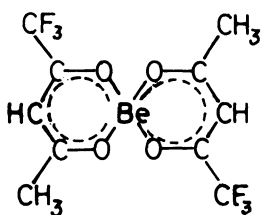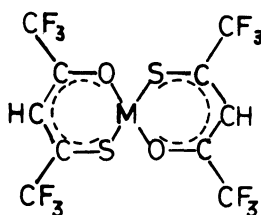

(II)   (III)

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 β-aminoketonates have been used with Cu, Ni, Pd and Pt down to the picogram level (Refs. 34 & 35). Chelate complexes of diethyldithiocarbamic acid, $Et_2N\cdot CSSH$, 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; M = 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.
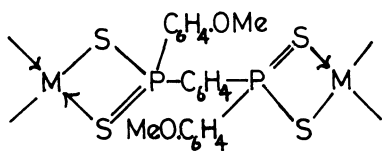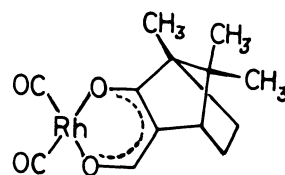
(IV)   (V)

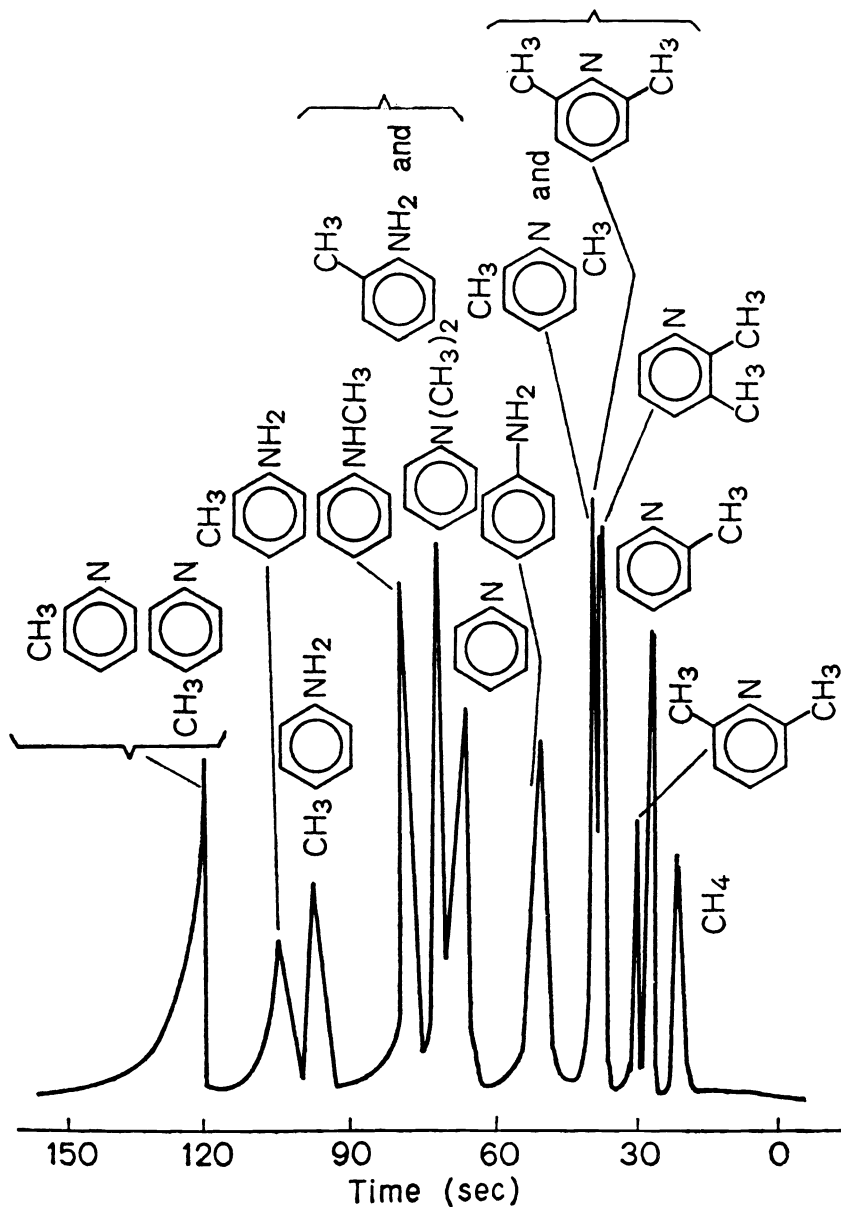Retention volumes remained constant even after many hours use at $100^{o}C$

Fig. 1. Separation of nitrogen bases on a stationary phase of 5%
     cobalt phthalocyanine on Sterling F.T.G., 10 m column
     with NH_3 + H_2 as carrier gas at $178^{o}C$ (Ref. 38).

(Ref. 37). 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).

$$C_6H_5.C.CH_2.C.C_6H_5$$
$$\quad\ \ O \qquad\ \ S$$

$$R.C.CH_2.C.NHC_6H_4.X$$
$$\quad\ O \qquad\ \ S$$
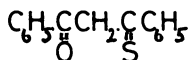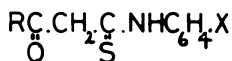
(VI)   (VII; X = H,CH_3, halogens, CN, etc.)

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 2.   Thin layer chromatography of coordination compounds on silica gel (Ref. 45)

Compound	Structure	R_f [a]	R_f [b]
$Cu(acac)_2$	square planar	0.30	0.08 - 0.65
$Cr(acac)_3$	octahedral monomer	0.93	0.77
$Co(acac)_3$	octahedral monomer	0.63	0.70
$Fe(acac)_3$	octahedral monomer	0 - 0.25	0.80
$[Co(acac)_2]_4$	octahedral polymer	0.0	0 - 0.11
$[Ni(acac)_2]_3$	octahedral polymer	0.0	0 - 0.12

[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-
quinolinates of the divalent transition metals (and all the tris-complexes),
magnesium and strontium form water-insoluble complexes, $M(Ox)_2 \cdot 2H_2O$, which
do not extract into chloroform unless the coordinated water is replaced by
excess of un-ionised oxine, as in $Sr(Ox)_2 \cdot 2HOx$ (Ref. 46); butylcellosolve
can serve this function when extracting the magnesium complex (Ref. 47).

With dithizone (H_2Dz), 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 $Mn(HDz)_2py_2$ (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 $UO_2(TTA)_2$ 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-phenan-
throline (IX; R = H) to enhance the extraction of nickel bis-dithizonate
as the adduct, $Ni(HDz)_2 \cdot phenan$ (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 $Ni(H_2O)_6^{2+}$ and H_2Dz (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 perrhenate could be extracted into chloroform whereas
the corresponding molybdate remained in the aqueous phase (Ref. 51).
Other large uni-negative anions such as MnO_4^-, ClO_4^-, IO_4^-, etc. can be
extracted and separated from the more easily aquated polyvalent MoO_4^{2-},
WO_4^{2-} and CrO_4^{2-}. The bulky, hydrophobic cation can also be $CH_3(C_6H_5)_3As^+$,
$(C_6H_5)_3S^+$, $(C_6H_5)_2I^+$, $Fe(phenan)_3^{2+}$, or a large cation derived from a basic
dye such as Rhodamine B which will extract coordinated halo-complexes such
as $SbCl_6^-$, $TlCl_4^-$, $TlBr_4^-$, $GaCl_4^-$, SbI_4^-, $SbBr_6^-$, $FeCl_4^-$ $FeBr_4^-$, $AuCl_4^-$, $AuBr_4^-$ 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 HCl, HNO_3 and H_2SO_4 quantitatively
from aqueous solutions into chloroform or nitrobenzene (Ref. 54). It was

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 ($\underline{M}_r$ 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 ClO_3^-, ClO_4^-, ReO_4^-, and complex anions such as $ZnCl_4^{2-}$, $Co(SCN)_4^{2-}$, $UO_2(Ox)_3^{2-}$, or anionic species such as $MY^{\underline{n}-4}$ derived from a cation $M^{\underline{n}+}$ and EDTA ($Na_2H_2Y \cdot 2H_2O$) (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, $(NH_4^+)[Co(NH_3)_2(NO_2)_4^-]$ 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; R_3N), uranium, plutonium and neptunium can be separated in the form of $(R_3NH)_2(UO_2Cl_4)$, $(R_3NH)_2PuCl_6$ and $(R_3NH)_2NpO_2Cl_2$, 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 $Au(CN)_2^- \gg Ag(CN)_2^-$ (linear ions); $Hg(CN)_4^{2-} \gg Cd(CN)_4^{2-} > Zn(CN)_4^{2-}$ (tetrahedral ions); $Pt(CN)_4^{2-} > Pd(CN)_4^{2-} \gg Ni(CN)_4^{2-}$ (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(iso-quinolyl) (X; R = H) will form stable complexes with all the $\underline{d}$-block, divalent transition metal cations, M^{2+} (M = Mn^{2+} to Zn^{2+}), 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 = CH_3). Steric hindrance to coordination is also shown by biquinolyl (XI). Although none of these ligands will give extractable tris-complexes
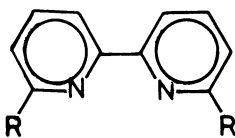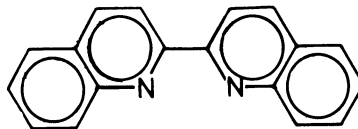
(VIII)
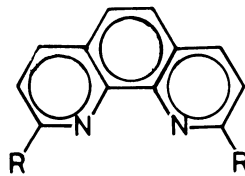
(IX)
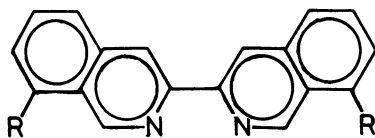
(X)

(XI)

with iron(II), they can all give extractable bis-complexes with copper(I)
which, of course, employs $4\underline{s}4p^3$ 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 $Cu(biquin)_2^+Cl^-$. 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
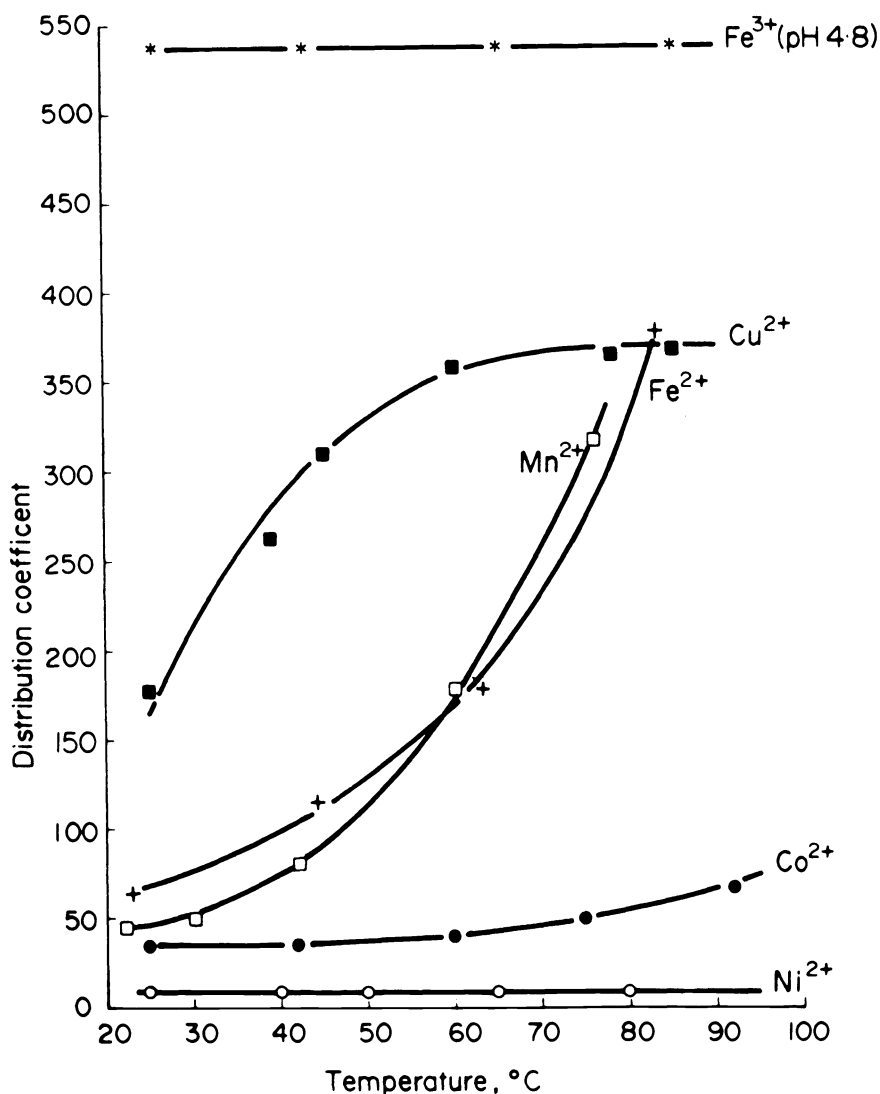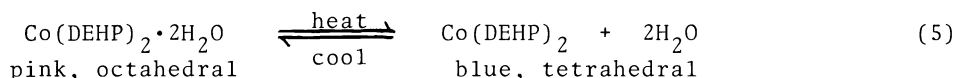

Fig. 2. The effect of temperature on the distribution coefficients
         of first row transition elements between equal volumes of
         an aqueous phase pH 5.0 - 5.2 and a 30% solution of sodium
         diethylhexylphosphate (NaDEHP) in a high b.p. hydrocarbon
         oil, Catenaz 11 (Ref. 59).

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

$$\text{Co(DEHP)}_2 \cdot 2H_2O \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{Co(DEHP)}_2 + 2H_2O \quad (5)$$
$$\text{pink, octahedral} \qquad\qquad \text{blue, tetrahedral}$$

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, $\Delta_{oct.} - \Delta_{tetr.} = 5/9\Delta_{oct.}$. This amounts to 0.0 $\Delta_{oct.}$ for Mn(II),
0.133 $\Delta_{oct.}$ for Fe(II), 0.267 $\Delta_{oct.}$ for Co(II) and no less than 0.844 $\Delta_{oct.}$
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 aminopolycarboxylic 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 complex-
ones 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 ($K_{ML} >> 10^7$)

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

(XII); EDTA   (XIII); Uramildiacetic acid
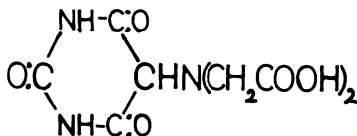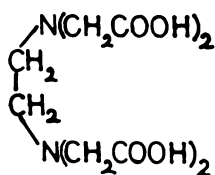
$K_{BaL} < K_{SrL} < K_{CaL} > K_{MgL}$ can be explained on steric grounds if it is assumed that
the ligand is sufficiently flexible when bonding through its two donor
nitrogen and four donor oxygen atoms to adapt its enclosure to ions of size
decreasing down from Ba^{2+} to Ca^{2+} whereas steric repulsion 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).

HOOC.CH$_2$N—(CH$_2$)$_n$N—CH$_2$COOH

CH$_2$ CH$_2$

CH$_2$ CH$_2$

HOOC.CH$_2$N—(CH$_2$)$_m$N—CH$_2$.COOH
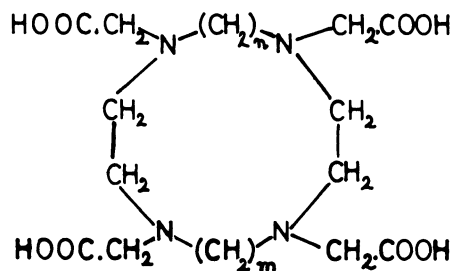
(XIV) $\underline{n} = \underline{m} = 2$

(XV) $\underline{n} = 2,\ \underline{m} = 3$

(XVI) $\underline{n} = \underline{m} = 3$

TABLE 3.   Stability constants, log $\underline{K}_{ML}$, of complexes of amino-polycarboxylic acids with alkaline earth cations. Valid for 20°C and I = 0.1M(KCl)(Ref. 62)

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

$\Delta_{Ca,Mg}$ =log $\underline{K}_{CaL}$ - log $\underline{K}_{MgL}$; $\Delta_{Sr,Ca}$ = log $\underline{K}_{SrL}$ - log $\underline{K}_{CaL}$;

EDTA = ethylenedinitriletetraaxetic acid (XII);
CDTA = cyclohexanediaminetetraacetic acid.

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 perference 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 crown ether (dibenzo-18-crown-6; XIX, $\underline{n} = \underline{m} = 2$) as an unexpected by-product insoluble in methanol but readily soluble on the addition of sodium salts. The naturally occuring macrocyclic antibiotics valinomvcin 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
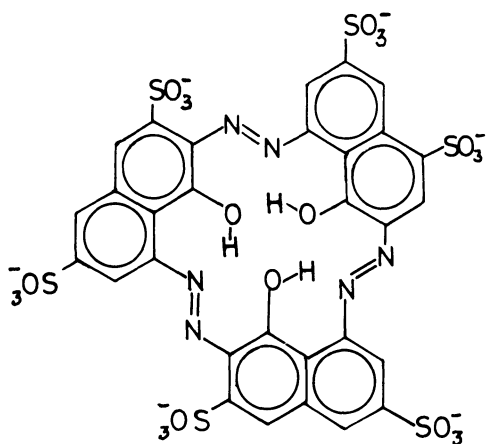
complexing agents has stimulated an enormous amount of work (Refs. 64 - 69) which has, unfortunately, seldom been directed towards purely analytical applications, but see Note a.

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; $\underline{n} = \underline{m} = 2$ will solubilize potassium permanganate in a solvent such as dichloromethane or benzene. The macrocycles (XX; $\underline{n} = 2$ or 3) will solubilize $NaMnO_4$ instantaneously, but not $KMnO_4$, or lithium, rubidium,
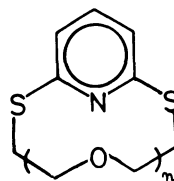
(XVII)

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
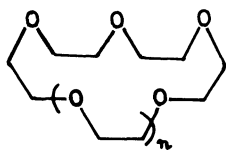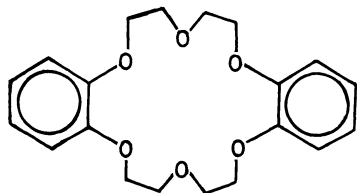
(XVIII)   (XIX)   (XX)

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 de-localized 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 (λ_{max} 390 nm in $CHCl_3$) and gives an extractable blood-red potassium complex (KA·HA; λ_{max} 460 nm). The absorbance at 560 nm is linearly proportional to the concentration of potassium up to 300 ppm. The dis-appointingly low distribution ratio, $[K^+]org/[K^+]aq = 0.017$ can probably be attributed to the presence of very hydrophilic nitro groups.
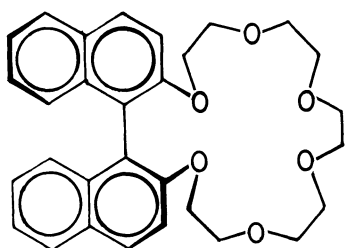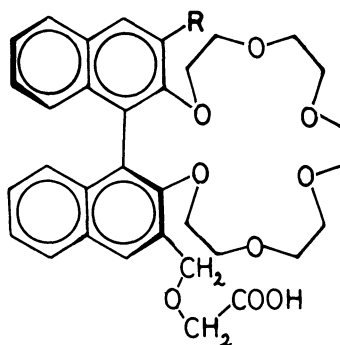
(XXI)   (XXII)

With Ba^{2+} two molecules of (XXII; R = 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 XXII; R = $-CH_2.O.CH_2.COOH$) 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 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
(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.
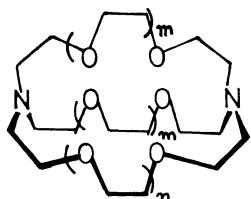
	$\underline{m}$	$\underline{n}$
(a)	0	1
(b)	1	0
(c)	1	1
(d)	1	2
(e)	2	1
(f)	2	2
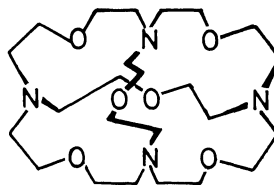
(XXIII)   (XXIV)

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 ΔG(solvation) increases monotonically as the radius
of the cation decreases along a series (Table 5). Much the same order
would be expected for ΔG(complexation) by a polydentate ligand provided
it were able to adjust to all cation sizes. If, however, the cavity is
of a fixed dimension, ΔG(complexation) will increase as the size of the
cation decreases until it reaches this limiting size of the cavity. For
smaller ions, ΔG(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 Tl^+ 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).

Cryptate (XXIII)			Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
	m	n									
(a)	0	1	5.5	3.2	<2.0	<2.0	<2.0	2.5	2.5	<2.0	2.0
(b)	1	0	2.50	5.40	3.95	2.55	<2.0	<2.0	6.95	7.35	6.30
(c)	1	1	<2.0	3.9	5.4	4.35	<2.0	<2.0	4.4	8.0	9.5
(d)	1	2	<2.0	1.65	2.2	2.05	2.0	<2.0	∿2.0	3.4	6.0
(e)	2	1	<2.0	<2.0	<2.0	<0.7	<2.0	<2.0	∿2.0	∿2.0	3.65
(f)	2	2	<2.0	<2.0	<2.0	<0.5	<2.0	<2.0	<2.0	<2.0	-
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).

Cation	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radius in Å	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43
Hydration number	6	6	6	6	6	6	8	8	8
$-\Delta G°$(hydration), kcal mol^{-1}	-1,122	98.5	80.5	75.5	68.0	454	379	340	314
ligand	a	b	c	d	e	f	g		
cavity radius, Å	0.8	1.1	1.4	1.8	2.1	2.4			
number of binding sites	6	7	8	9	10	11			

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 Sr^{2+} (or Ba^{2+}) over Ca^{2+} 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 $\underline{K}$ = 3.4 in water). As
might be expected, the reaction is slow (Ref. 70). Kinetics of the
reactions between Ca^{2+} and cryptates have been studied and shed light on
the conformational changes (exo-exo → exo-endo → endo-endo) in these
ligands that must preceed 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

$$R.CCOK \quad + \quad HCl \longrightarrow \quad KCl \quad + \quad R.COOH \tag{6}$$

exactly the opposite reaction takes place with catecholdiacetic acid
($\underline{o}$-$C_6H_4(OCH_2.COOH)_2$; H_2CDA) 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 :

$$2 \; H_2CDA \quad + \quad KCl \longrightarrow KHCDA.H_2CDA \quad + \quad HCl \tag{7}$$
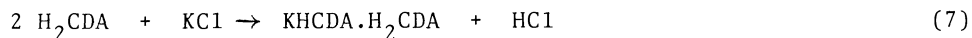
A sandwich of two molecules of H_2CDA provides 8 of the 10 oxygen atoms
which encapsulate the potassium ion, the remaining coordination sphere
being made up by an oxygen atom from each of two other molecules. It
is stated that Li^+, Na^+, NH_4^+ and Cs^+ do not react in a similar fashion
(Ref. 72).

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 (ε = 7,930),
1,10-phenanthroline (ε = 11,100), 4,7-diphenyl-1,10-phenanthroline (ε =
22,140), 2.4.6-(2-pyridyl)-1,3,5-triazine (ε = 22,600) and the water-
soluble 'ferrozine', 3-(2-pyridyl)-5,5-bis(4-sulphophenyl)-1,2,4-triazine
(ε = 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 itslef 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, conform-
ational 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 un-
predictable crystal structure.

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