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Cyclopendant ligands

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ABSTRACT. The numerous cyclopendant ligands are described in the review. These contain a cyclic fragment, with donor atoms, with groups added which are capable of coordinating cations. An attempt has been made to systematise the literature data on the methods of synthesis and the properties of cyclopendant ligands. Fundamental results of authors on the application of a quantitative method of assessing the efficiency and selectivity of action of ligands (criteria *A* and *S*) are given.

It has been shown that the use of cyclopendant ligands enables the efficiency and selectivity of complex formation to be increased.

The bibliography contains 182 references.

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I. Introduction

Polydentate reagents capable of binding cations with various coordination polyhedra have acquired considerable importance in coordination chemistry in recent years. By this means not only is the binding energy of the donor centres of the ligand added together but a chelate effect is also displayed (mainly entropic in origin). A polydentate ligand makes it possible to close several chelate rings, increasing in this way the binding equilibrium constant, i.e. the free energy of formation of the complex.

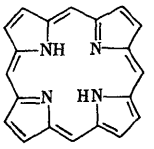
Polydentate reagents are widely used in analytical chemistry, in the technology of separating non-ferrous and rare metals, in processes of flotation and extraction, in the textile industry (mordent dyeing) and in many other areas of science and technology.

Polydentate reagents have acquired great importance mainly because of two properties, viz. the efficiency of binding cations (displayed in the stability if the resulting complexes) and the selectivity of complex-formation. This applies equally both to neutral reagents and to molecules containing both acidic and basic functional groups. The majority of complexones are characterised by a polydentate nature and chain flexibility, which bind donor complex-forming centres. The stability of the resulting complexes is high but the selectivity is comparatively low.

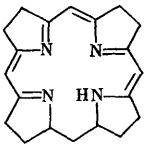
A higher selectivity among cyclic polydentate ligands is possessed by the neutral crown polyethers, basic polynitrogenous macrocycles, cryptands and certain other compounds. The cyclopendant ligands are of interest in this connection and are ligands containing a cyclic (usually macrocyclic) nucleus, frequently including donor centres, to which are added side groups, viz. pendant or lariat groups which also carry donor centres capable of coordination with metal cations.[1,2] Hence the name cyclopendants.†

The simultaneous binding of metal cations with the donor centres of the ring and the pendants frequently achieves high binding stability and selectivity for the cyclopendant ligands. The ligand shape arising in this way may not accommodate every cation.

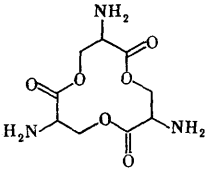
The nature cyclopendant ligands have high binding selectivity. Examples are derivatives of porphin, corrin and polyglycidic ethers, carrying various pendant groups. The variety of cyclopendants, i.e. vitamins, antibiotics, cytochromes, siderophores, etc., is explained by the variety of pendant groups and the central metal ion.



Porphin



Corrin

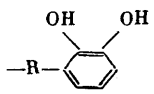


Serine trilactide

The addition of further pendant groups to the plane-coordinated metal complexes porphin and corrin occurs by a form of extra coordination. The pendant substituents occupy an apical position on the *z* axis perpendicular to the plane of the macrocycle.[3] Similar coordination proves to be a most important feature of such compounds as chlorophyll, blood haem, vitamin B-12, etc. With extra coordination the cations of various metals are bound selectively by the donor atoms of the pendant groups. Blood haem coordinates Fe^{3+} ions with the formation of haemin or haematin, chlorophyll acids (*a* and *b*) selectively bind the Mg^{2+} ion with the formation of chlorophyll. In the vitamin B-12 molecule the Co^{2+} ion is coordinated by the four nitrogen atoms of the corrin ring, the CN^- group and the nitrogen atom of a benzimidazole act as extra

† Originates from the Latin pendere (to hang) and the English pendant (a pendant). Occasionally ligands are also known as 'lariatnye' from the English lariat (lasso or rope). It seems to us that the term 'lariat' in relation to the whole ligand precludes the occurrence of donor centres in the ring which are frequently encountered and are reflected in the name cyclopendant. The actual 'pendant' is now widespread in the English language literature.

ligands (see Figures[1,4]). Cytochromes have the same ferroporphin fragment in the molecule. The differences in their properties are caused by the difference in pendant substituents. The phenolic hydroxyls of the pendant groups in the complex enterobactin



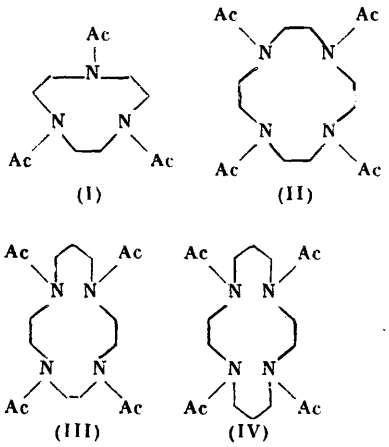
occupy the six coordination positions of the Fe^{3+} cation and form a stable complex.[5] All the natural cyclopendants possess high efficiency of action in addition to high selectivity of complex-formation, forming stable complexes with metal cations. The high stability of such complexes is caused not only by the high binding energy but also by the complete complementarity (spatial fit) of their ligand shape (in the presence of extra coordination) to the coordination polyhedraon of the cation in question.[3]

It is necessary to bear in mind the general principles of complex-formation. The equilibrium of this process is determined by the free energy of complex-formation $A = RT \lg K_{st}$ [sic], where K_{st} is the stability constant.‡ The energy of the coordination bond [sic] ΔH depends on the free energy and on the entropy. Frequently $\lg K_{st}$ is taken as a measure of the strength of the binding of the ligand and the cation in the complex. The strength naturally depends on the nature of the cation and the character of the ligand. This problem has been well studied in the chemistry of coordination compounds and is not examined in the present paper.

However there are other aspects to complex-formation linked mainly with the entropy factor. In the case of a polydentate ligand with several binding centres (donor centres) in one molecule, the problem of the complementarity of a ligand and the coordination polyhedron of the cation becomes important. If the polydentate ligand possesses a flexible chain of atoms than it can take up a conformation, without a large consumption of energy, corresponding to such complementarity. The strength of the resulting complex will be determined by the binding energy of the cation with the donor centres. With inadequate chain flexibility or with a structure such that the population of the complex-forming conformation (for the given cation) is low, the stability of the complex depends not only on the binding energy but also on the complementarity of the complex-forming conformation i.e. its energy of formation. If two polydentate ligands with the same set of donor centres are compared then the energy of complementarity becomes determining. It is clear that reagents with flexible chains of molecules may not be highly selective. Other conditions being equal (parity of the number and character of donor centres), the introduction of more rigid links into the chain of a polydentate ligand increases selectivity.

II. The first synthetic cyclopendants

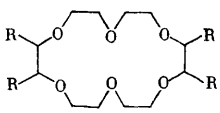
These ligands recall the natural ligands since they contain a cyclic fragment with added pendant groupings possibly acting as extra ligands. In 1975 Hama and Takamoto[6] synthesised and studied the complex-formation of the ligand (I) with transition metals (TM) and also with Cd^{2+} and Pb^{2+}. In 1976 Stetter and Frank obtained and investigated the complex-forming ability of complexones (II)–(IV) in relation to the alkaline earth metals (AEM) and the TM.[7]



Here and subsequently Ac = CH_2COOH.§

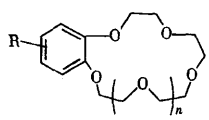
In the same year Behr and collaborators synthesised and investigated ligands (V) with ions of NH_4^+, K^+, $MeNH_3^+$ and $PhCH_2CH_2NH_3^+$ (25 °C, water).[8] The complex-formation of ligands (VI) with Na^+ and K^+ ions at 25 °C in acetone has been studied.[9]

The extraction[10] and complex-forming[11] properties of ligands of formula (VII) in relation to NH_4^+ and the alkali metals have been investigated.



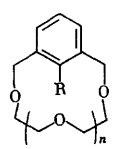
(V)

R = 1. C(O)NMe$_2$
2. COOH etc.



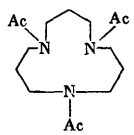
(VI)

n = 1,2, R = NH_2, COOH, COOMe etc.



(VII)

n = 1 to 4, R = COOH, OH, CH_2OH etc.



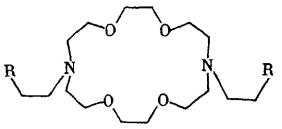
(VIII)

Takahashi and Takamoto in 1977 obtained and investigated (spectroscopically) the complexes $[ML]^0$ of Fe^{3+}, Cr^{3+}, and Co^{3+} cations with ligands (I) and (VIII).[12] In the same year Chang obtained ligands (IX)[13] and in 1978 Takagi and co-workers synthesised and studied the complex-formation of ligand (IX) (R = COOH) with ions of the AEM and TM.[14] Finally, in 1979 ligands (X) and (XI) were synthesised and complexes of (X) with

‡ The values of stability constants of complexes with the various cations used in this study were taken as a rule from reference literature, in which they had been critically assessed.

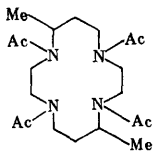
§ Note that the symbol Ac in the literature usually denotes the acetyl residue CH_3CO-. Here Ac = $-CH_2COOH$.

TM were isolated.[15] Ligand (XI), an analogue of enterobactin, binds Fe^{3+} ions effectively.[16]

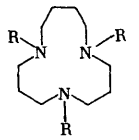


(IX)

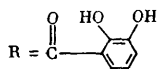
R = CN, CH_2NH_2 [13]
R = COOH [14]



(X)



(XI)

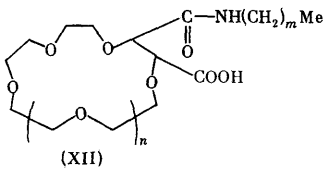


The reagents indicated were the first representatives of the synthetic cyclopendants. A great number of ligands with various groups were obtained later. The polyalkylenepolyamines, crown-ethers and crown-polyaza-polyethers with several modifications and various pendant groups form part of practically all new (synthesised up to 1988) cyclopendant reagents.

III. Cyclopendants: derivatives of oxygen macrocycles (crown-ethers)

Values of $\lg K_{st}$ have been determined for complexes of ligand (V, 2) with NH_4^+, K^+, $MeNH_3^+$ and $PhCH_2CH_2NH_3^+$ cations in water at 25 °C and are 3.51, 5.48, 2.88 and 2.41 respectively.[8] Pendant COOH groups evidently participate in the coordination since the ligand without these groups, 18-crown-6, forms complexes with NH_4^+ and K^+ ions with $\lg K_{st}$ = 1.1 and 2.06.[17]

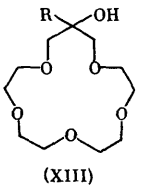
The complex-formation of ligands of formula (XII) with n = 1, m = 7 and 17; n = 1 and 2, m = 3, 7 and 13 with ions of Na^+, K^+ and Rb^+ has been investigated.[18]



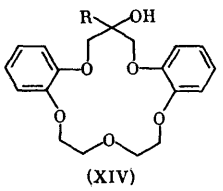
(XII)

The length of the hydrocarbon chain (variation of m) has no effect on the stability of the complexes. An increase in the size of the ring (transition from n = 1 to n = 2) leads to an increase of all the stability constants and a shift in the maximum efficiency of complex-formation towards cations of larger ionic radius.

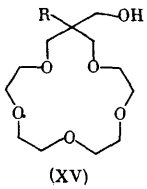
The ligands (XIII)–(XV) have been synthesised[19] and extraction and association constants with Na^+ and K^+ picrates were found. The substituents R showed an electronic and a steric effect on the extraction process.



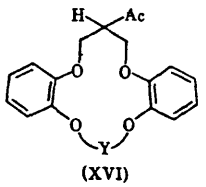
(XIII)



(XIV)



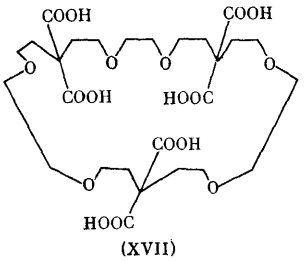
(XV)



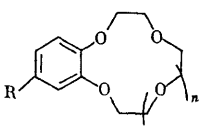
(XVI)

R = H, Me, Ph, n-$C_{10}H_{21}$ etc.
1. Y = CH_2CH_2; 2. Y = $(CH_2)_3$; 3. Y = CH_2OCH_2;
4. Y = $CH_2OCH_2OCH_2$.

The ligands (XVI) are efficient extractants for Na^+, K^+, Rb^+ and Cs^+.[20] The stability constants for (XVI, 3) with Ca^{2+}, Na^+ and K^+ ions have been determined.[21]



(XVII)

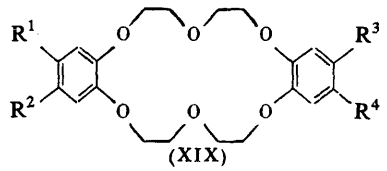


(XVIII)

1. n = 1 to 4, R = PPh_2 [Ref. 23]; 2. n = 2 to 3, R = = $CH(OH)CH_2NHMe$ [Ref. 24]; 3. n = 2, R = COOH, CH_2OH etc. [Ref. 25]; 4. n = 2, R = OH [Ref. 26].

The acid (XVII) was synthesised as a reagent for the UO_2^{2+} ion.[22] Ligands (XVIII) contain various numbers of donor oxygen atoms and various pendant groups R. Equilibrium constants were determined for compounds (XVIII, 1) (with various ring sizes) for the extraction of Li, Na^+, K^+ and Cs^+ picrates. The equilibrium constant for the ion of large ionic radius, K^+ and Cs^+, was increased for these compounds as n was increased. The pendant groups of ligands (XVIII, 1 and 2) seemingly do not participate in coordination with these cations since the corresponding compounds without the pendant groups in the molecule possess practically the same extraction and complex-forming properties.[23,24] Ten ligands (XVIII, 3) with various pendant groups have been synthesised.[25] Their extraction properties in relation to the picrates of Li^+, Na^+ and K^+ have been studied. Complexes of Li^+, Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+} and Ba^{2+} with ligand (XVIII, 4) of composition ML, ML_2, and M_2L have been obtained.[26] X-Ray structural analysis (XSA) of the complex $[KCNS(L)_2]$ showed that the K^+ ion in it was coordinated with ten donor atoms of the ligand. The pendant group and the CNS^- anion did not participate in coordination.

Cyclopendants based on dibenzo-18-crown-6 of formula (XIX) have been synthesised and investigated.



(XIX)

1. $R^1=R^2=R^3=R^4=H$ [Ref. 27]; 2. $R^1=R^4=H$, $R^2=R^3=NH_2$ [Ref. 28]

3. $R^1=R^4=H$, $R^2=R^3=N=CH-$ [Ref. 28];

4. $R^1=R^2=R^3=R^4CH_2PPh_2$ [Ref. 27];

5. $R^1=R^3=H$, $R^2=R^4=\overset{O}{\overset{\|}{C}}NHP(OH)^2$ [Ref. 29]

6. $R^1=R^3=H$, $R^2=R^4=NHP\begin{matrix}A\\ \|\\ O\quad B\end{matrix}$ (A, B = OEt, OBu, OPh) [Ref. 30];

7. $R^1=R^3=H$, $R^2=R^4=NHP(Me)(Ph)$ [Ref. 30].

The complex-formation of ligands (XIX, 2 and 3) with the ions Cu^{2+}, Co^{2+} and K^+ has been studied.[28] It was established that both pendant NH_2 groups of ligand (XIX, 2) participate in coordination with Co^{2+} and Cu^{2+}. The ring oxygen atoms do not participate in the coordination with these cations. The complex [(L)KI], in which K^+ is in the plane of the macrocycle, forms a chelate with the Co^{2+} ion of the same spectral type (infra-red: IR) as does free (XIX, 3). Stability constants for complexes of the alkali metals with ligand (XIX, 4) and dibenzo-18-crown-6 (XIX, 1) have been compared.[27] The pendant groups $CH_2P(O)Ph_2$ hinder the coordination of the cations investigated with the ring oxygen atoms (Table 1).

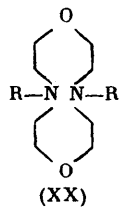
Table 1. Values of $\lg K_{st}$ for complexes $[ML]^+$ of ligands (XIX, 1 and 4) (solvent, ethanol : chloroform 1 : 1, T = 25 °C).[27]

Cation	(XIX.1)	(XIX.4)
Li^+	3,48	3,09
Na^+	3,97	3,86
K^+	4,51	3,95
Cs^+	3,49	3,47

The complex-forming properties of ligands (XIX, 5–7) have not been investigated.[29,30] In the complex $[(CoCl_2)_2KCl(L)]$ the K^+ ion is in the plane of the macrocycle but the Co^{2+} ions are bound only with the oxygen atoms of the pendant groups [L = (XIX, 4)].[27] As an extractant, ligand (XIX, 4) is better in separation factor for the U/Am pair than the best of a large series of reagents.[31]

IV. Cyclopendants based on crown-polyaza-polyethers

These compounds contain a cyclic polyaza-polyether fragment, the pendant groups being added at the nitrogen atoms. Ligands (XX) have been synthesised.[32]

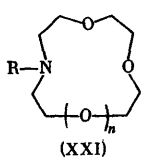


(XX)

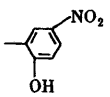
1. $R = CH_2CH_2\overset{O}{\overset{\|}{C}}NMe_2$
2. $R = (CH_2)_3\overset{O}{\overset{\|}{C}}NMe_2$
3. $R = CH_2CH_2OH$
4. $R = CH_2COOH$

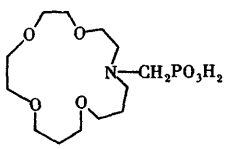
X-Ray structural analysis of the free ligand (XX, 2) showed that its donor atoms (N and O) are disposed at the vertices of an octahedron. The thermodynamic parameters ($\lg K_{st}$, $\Delta H°$ and $\Delta S°$) have been determined for ligands (XX, 1–3) with ions of the alkali and alkaline earth elements and Ag^+.[32] Evidently the pendant groups participate in the coordination with cations since the stability of the resulting complexes depends strongly on the nature of these groups. Thus ligand (XX, 1) forms far more stable complexes with a given cation than (XX, 2 and 3). Compound (XX, 4) has been mentioned[33] without citing its synthesis and properties.

Complex-formation of ligand (XXI, 1) with ions of the alkaline earth metals has been studied.[34]



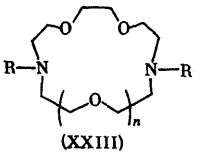
(XXI)

1. R = CH_2CH_2OH, n = 1;
2. R = CH_2, n = 2, 3;
3. R = $CH_2PO_3H_2$, n = 2.



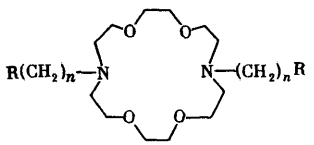
(XXII)

Moving from n = 2 to n = 3 leads to a change in the selectivity of extraction of alkaline earth metals by ligands (XXI, 2).[35] The complex-forming ability of ligands (XXI, 3), (XXII) and (XXIII, 4) with $CH_2PO_3H_2$ as pendant group was investigated in water in relation to the Na^+ ion.[36]



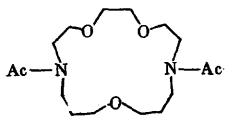
(XXIII)

1. $n=2$, R=$CH_2PO_3H_2$ [36];
2. $n=1$, R=Ac [38];
3. $n=2$, R=Ac [37, 39];
4. $n=2$, R=CH_2Ac [14];
5. $n=2$, R =  [43]; etc. [40—42].

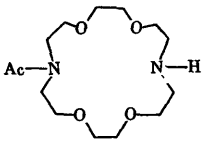


(XXIV)

$n=1-3$, R=PO_3H_2, COOH, NH_2 etc.



(XXV)



(XXVI)

The synthesis of ligands (XXIV) has been described, their ability to dissolve $BaSO_4$ was recorded in the same paper.[37]

The complex-formation of ligands (XXIII, 2—4) has been studied in relation to a large number of cations. The stability constants of complexes of (XXIII, 2—4), (XXV) and (XXVI) are given in Table 2. The stability of complexes of other ligands of formula (XXIII) has not been determined.[40—42]

Table 2. Values of $\lg K_{st}$ for complexes [ML] of ligands (XXIII, 2—4), (XXV) and (XXVI).

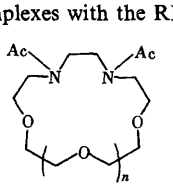
Cation	(XXIII,2)	(XXIII,3)	(XXIII,4)	(XXV)	(XXVI)
K^+	1.7	3.9	–	–	–
Mg^{2+}	7.4	–	<2	<2	–
Ca^{2+}	8.7	8.4	4.0	7.7	–
Sr^{2+}	7.9	8.3	4.4	7.7	–
Ba^{2-}	7.3	7.6	3.8	7.7	–
Co^{2-}	13.7	–	see*	7.0	–
Ni^{2+}	12.2	7.4		7.5	5.4
Cu^{2+}	16.0	14.5	~6—7	>14	10.5
Zn^{2-}	14.1	8.4	see*	8.0	5.4
Cd^{2+}	13.0	11.1	–	–	7.8
Pb^{2+}	12.9	13.6	8.1	–	10.4
La^{3+}	10.1	12.2	–	–	6.6
REE	10.3—11.9	10.8—12.2	–	–	6.0—7.4

Note. The numbers given are rounded up to tenths. Experimental conditions: T = 25 °C, μ = 0.1 (Me_4NCl), solvent was water.
* Complex-formation was so weak that at $a > 1$ the ions of Co^{2+}, Ni^{2+} and Zn^{2+} precipitated as hydroxides (a is the number of equivalents of alkali per mole ligand).

The increase of the cyclic fragment on going from ligand (XXIII, 2) to ligand (XV) is accompanied by a reduction in the stability constant of the complexes of all cations apart from Ba^{2+}, the most bulky of the cations being compared. A reduction in the stability constant of the complexes also occurs on increasing the length of the pendant group on going from (XXIII, 3) to (XXIII, 4). The removal of one pendant group in ligand (XXVI) compared with (XXIII, 3) leads to an appreciable reduction in the stability of the complexes. This means that carboxyl pendant groups participate in the coordination.[44] An increase in the cyclic fragment with the simultaneous inclusion of one more donor oxygen atom in it involves a reduction in the stability of complexes of ligand (XXIII, 3) with cations of small ionic radius and an increase in the stability of complexes with cations of larger ionic radius compared with ligand (XXIII, 2). For cations of ionic radius > 1.1 Å and rare earth elements (REE) the complexes of ligand (XXIII, 3) are more stable, for all the remainder the complexes of (XXIII, 2) with a smaller cyclic fragment are the more stable. The stability constants of complexes of REE with ligand (XXIII, 3) fall continuously from Ce^{3+} and Lu^{3+} with the reduction in ionic radius of these cations.[39] In contrast, the complex-formation of REE ions with ligand (XXIII, 2) is maximal at the Eu^{2+} ion.[45] The rare earth elements of larger and smaller ionic radii form less stable complexes with this ligand.

The cyclopendant ligands based on crown-polyazapolyethers display interesting complex-forming properties. Usually the complexes with the classical complexones of Sr^{2+} are less stable than the complexes of Ca^{2+}. Ligands (XXIII, 3) and (XXV) form complexes of practically identical stability with Ca^{2+} and Sr^{2+}, but ligand (XXIII, 4) chelates Sr^{2+} more efficiently than Ca^{2+}. Ligand (XXV) shows a very high difference in stability constants for the complexes of the small Mg^{2+} ion and the bulky Ca^{2+} ion. It is interesting that Co^{2+} and Ni^{2+} form complexes of lower stability than the ions of the alkaline earth metals with the ligands (XXIII, 3), (XXV) and (XXIII, 4) (see Table 2), which is also unusual for complexones of linear structure. This may be caused by the fact that the ions of the transition metals have a lower ionic radius than the ions of the alkaline earth metals. The stability constants of the complexes of Ca^{2+}, Sr^{2+}, and Ba^{2+} with ligand (XXV) do not depend on the ionic radius of the cation.

Chang and collaborators investigated the kinetics of the dissociation of complexes of lanthanides with ligands (XXIII, 2 and 3).[46,47] The complex-formation of REE ions with ligands (XXVII) with different sizes of cyclic fragment has been investigated.[48] The value of $\lg K_{st}$ for complexes of (XXVII, 1) increased continuously with the reduction in ionic radius from La^{3+} to Lu^{3+}. An increase in the ring size led to an increase in the stability of the complexes of REE with ligands (XXVII, 1—3) but transfering from ligand (XXVII, 3) to (XXVII, 4) did not cause a further increase in K_{st} for the complexes with the REE.



(XXVII)

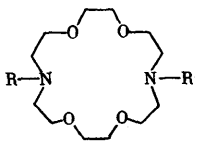
1. n = 0
2. n = 1
3. n = 2
4. n = 3

The complex of the Cu^{2+} ion with ligand (XXIII, 3) has been investigated by XSA.[49] It was found that Cu^{2+} is in a square plane formed from two nitrogen atoms of the ring and two oxygen atoms of the carboxyl groups.

The selectivity factor of a ligand in relation to Zn^{2+} and Ca^{2+} ions is important in medicine when checking the elimination of Pb^{2+} ions from animals.[50]

$$\lg K_{st\ Pb^{2+}} / \lg K_{st\ Zn^{2+}} = \varphi_1 \text{ and } \lg K_{st\ Pb^{2+}} / \lg K_{st\ Ca^{2+}} = \varphi_2.$$

For example, the size of φ_1 is 1.6 for ethylenediaminetetraacetate (EDTA). With the aim of obtaining a reagent with a high selectivity factor the ligand (XXIII, 5) mentioned above, containing a crown-diaza-polyether ring and pendant α-pyridylmethyl groups, was synthesised.[43] Values of the stability constants are given in Table 3 for ligands (XXVIII) with five different pendant groups.



(XXVIII)

1. R = H; 2. R = CH_2CHMe (OH); 3. R = CH_2COOH;
4. R = CH_2–(N-heterocycle); 5. R = CH_2CH_2SH

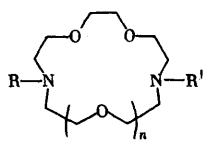
A characteristic feature of these ligands is their ability to chelate efficiently cations of large ionic radius. This leads to very high values for φ_1 and φ_2 [particularly with pendant (4)]. The stability constants for complexes of the small Zn^{2+} ion and the bulky Cd^{2+} and Pb^{2+} differed sharply.

Table 3. Values of $\lg K_{st}$ for complexes [ML] of ligands (XXVIII) with various pendant groups (T = 25 °C).

Cation	1	2	3	4	5*
Ca^{2+}	1.74	3.59	8.39	3.63	7.0
Sr^{2+}	2.60	4.05	8.29	4.87	–
Ba^{2+}	2.97	4.65	7.63	4.99	–
Ni^{2+}	–	–	7.39	8.80	–
Cu^{2+}	6.10	5.97	14.49	13.55	–
Zn^{2+}	3.10	3.00	8.42	6.96	16.3
Cd^{2+}	5.25	7.64	11.07	10.96	22.9
Pb^{2+}	6.80	8.57	13.55	11.67	26.1
La^{3+}	3.00	3.24	12.21	3.58	–

* Predicted values for ligand (XXVIII, 5).[43]

The preferential complex-formation of ligands (XXVIII, 1–5) with cations of large ionic radius leads to the result that ions of Sr^{2+} and Ba^{2+} are chelated more efficiently than Ca^{2+} ions by groups 1, 2 and 4 which is unusual for the classic complexones and is important in medical investigations.



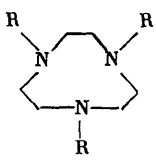
(XXIX)

1. R=R′=CH_2COOH, n=2
2. R=R′=CH(Me)COOH, n=2
3. R=R′=CH_2COOH, n=1
4. R=H, R′=CH_2COOH, n=2

The kinetics of the reaction of Cu^{2+} ion with ligands (XXIX, 1–4) have been studied.[52]

V. Cyclopendants: derivatives of nitrogenous macrocycles

1. Cyclopendants based on 1,4,7-triazacyclononane



(XXX)

1. R = H [73]
2. R = $CH_2PO_3H_2$ [55,·56]
3. R = $(CH_2)_2PO_3H_2$ [57]
4. R = CH_2COOH [6, 12]
5. R = $(CH_2)_2OH$ [58]
6. R = $(CH_2)_2NH_2$ [59, 60]
7. R = $(CH_2)_3NH_2$ [61]
8. R = CH_2CHOH (Me) [62]
9. R = $(CH_2)_2SO_3H$ [63]
10. R = $CH_2P(O)Ph_2$ [64–66]
11. R = CH_2–(N-heterocycle) [90, 91]

The stability constants of the complexes of a large number of cations with (XXX, 2) and (XXX, 3) have been determined, consequently it is possible to compare quantitatively the efficiency and selectivity of their complex-formation.

2. Means of assessing the efficiency and selectivity of ligands

A quantitative assessment of the complex-forming ability of ligands has been given.[67–69] The efficiency is the mean value of the sizes of $\lg K_{st}$ for complexes of composition ML.

$$A = \left(\sum_{i}^{n} \lg K_i\right) \Big/ n.$$

As a measure of the selectivity of action of a ligand the mean difference of $\lg K_{st}$ of complexes ML for all the cations taken in pairs.

$$S = \left[\sum_{i=1}^{n}\sum_{i=j}^{n} (|\lg K_j - \lg K_i|)\right] \Big/ n(n-1),$$

where n is the number of cations compared. The simplest algorithm for the calculation is the following.[68]

$$\Delta = \begin{vmatrix} \lg K_1 - \lg K_2 & & & \\ \lg K_1 - \lg K_3 & \lg K_2 - \lg K_3 & & \\ \lg K_1 - \lg K_4 & \lg K_2 - \lg K_4 & \lg K_3 - \lg K_4 & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \lg K_1 - \lg K_n & \lg K_2 - \lg K_n & \lg K_3 - \lg K_n & \ldots \lg K_{n-1} - \ln K_n \end{vmatrix}$$

The sum of the absolute values of all the differences in brackets is

$$\Delta = \frac{1}{2}\sum_{i=1}^{n}\sum_{i=j}^{n} |\lg K_i - \lg K_j|, \quad S = 2\Delta/n(n-1).$$

Other means of assessing selectivity are given in the literature. Occasionally a selectivity factor is used in studies on cryptates and crown-ethers which is the ratio of the stability constants for complexes of two cations, i.e. K_1/K_2.[70–72] In this of course only two cations are compared, the choice of them is arbitrary. The selectivity of action of ligands is assessed as the ratio of the stability constants of the complexes with ions of NH_4^+ and K^+.[72] On examining only two cations with stability constants K_1 and K_2 the previous formula is transformed into

$$S=\lg (K_1/K_2).$$

Certainly the values of A and S depend appreciably on the set of cations being compared, consequently to use them as a characteristic of the complex-forming ability of a ligand is only possible for the same set of cations. It is necessary to consider this when assessing the data calculated in the manual for efficiency and selectivity.[73]

3. Efficiency and selectivity of complexones of triazacyclononane derivatives

Values of $\lg K_{st}$ for complexes and A and S for complex-formation are given in Table 4 for ligands (XXX, 2), (XXX, 3) and (I). The values of the stability constants for the complexes of the remaining ligands (XXX) with the given cations in water were not determined.

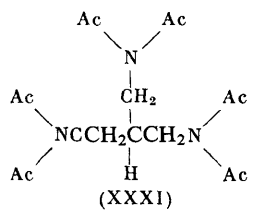
The selectivity of action of complexones (I), (XXX, 2) and (XXX, 3) is explained with the aid of a model of the spatial fit of the ligand shape (in an energetically favourable conformation) with the stereochemical requirements of the cation.[1,57] On coordination the metal cation falls into the cavity formed by the ligand as into a basket, the bottom of which is the nitrogen heterocycle and the walls are the pendant groups. Only a cation of suitable ionic radius may be placed in the basket cavity. This also determines the selectivity of complex-formation of the given ligands. The existence of a basket structure was confirmed by X-ray data on the complex of (XXX, 2) with the Fe^{3+} ion which has a very high stability ($\lg K_{st}$ = 29.6 [56]). The Fe^{3+} (ionic radius r = 0.64 Å) in a complex of composition $[FeH_3L]^0$ is in fact in the cavity of this ligand as in a basket.[74]

The complexone (XXX, 2) is selective, other conditions being equal, for cations of small ionic radius¶ such as Mg^{2+}, Zn^{2+} and Fe^{3+} with which it forms stable complexes. On turning to a cation with larger ionic radius, such as Ca^{2+}, Cd^{2+} or La^{3+}, the stability of the complexes is reduced by many orders of magnitude.[56] A large difference is shown in the values of K_{st} for complexes of Mg^{2+} and Ca^{2+}. Usually complexes of Ca^{2+} are more stable than complexes of Mg^{2+} with a small difference in the values of their stability constants. It is rare to encounter cases when the complexonate with Mg^{2+} is more stable than the complexonate with Ca^{2+} and their stability constants differ by one to two orders of magnitude. Only the *N*-oxide of nitrilotris(methylphosphonic acid) chelates the Mg^{2+} ion more effectively, the difference in K_{st} values being 2.6 log. units.[76] The difference of about 5 orders of magnitude observed for (XXX, 2) is unprecedented. It also shows the highest difference of all the complexones in the stability constants for the complexes of Zn^{2+} and Cd^{2+}.[73]

Cations of large ionic radius form fairly stable complexonates with the acid (XXX, 2). Calculations by molecular mechanics showed that just one low energy conformation is possible for this ligand, a 'ladle' in which two pendant groups continue as though forming the internal cavity of the ligand but one is tilted away like the handle of a ladle. The cavity of the ladle is larger and may take up huge cations occupying five of their coordination positions. When octahedral coordination is characteristic of the cation, the sixth place is occupied by the remaining monodentate ligand.

The Cu^{2+} ion also has a small radius but it is inclined to be pentacoordinate and forms a complex in the form of a ladle with (XXX, 2) (XSA data).

The size of the cavity of a complexone basket, into which the metal cation is placed, may vary either with a change in the size of the cyclic fragment or with a change in the length of the pendant groups. The complexone (XXX, 3) with phosphonoethyl pendant groups was synthesised to study this effect. The nitrogen atoms and the phosphorus are separated by ethylene bridges. The efficiency of complex-formation of this complexone is lower than that of (XXX, 2). Evidently this is linked with the lower stability of the six-membered chelate rings formed by it with the pendant groups compared with the five-membered formed by the phosphonomethyl pendant groups of complexone (XXX, 2). However the stability constants of both complexes are equal for the copper cation which requires a ligand shape of a tetragonal pyramid (see Table 4). The selectivity of action of the new cyclopendant in relation to the second group of cations is greater than for acid (XXX, 2). Complexones (XXX, 2) and (XXX, 3) have the same set of donor centres consequently the difference in complex-formation with various TM is impossible to explain by the non-uniformity of the covalent binding energy. This means that the spatial factor has a leading role. There is a very large difference in stability for the complexes of Co^{2+} and Ni^{2+} with (XXX, 3). Usually the complexes of Ni^{2+} are somewhat more stable than the complexes of Co^{2+} and have a small difference in stability constant.[73] Complexone (XXXI) shows the maximum difference in size of K_{st} for these cations, $\lg K_{st}$ [CoL] = 13.8 and $\lg K_{st}$ [NiL] = 18.0.[77] Complexone (XXX, 3) gives the same difference in stability constants but in this case the Co^{2+} complex is more stable than the Ni^{2+} complex.



(XXXI)

Table 4. Values of $\lg K_{st}$ for complexes [ML] and values of A and S.

Cation	(XXX.2)	(XXX.3)	(I)	Cation A, S	(XXX.2)	(XXX.3)	(I)
Be^{2+}	11.5	13.4	–	Zn^{2+}	24.9	17.00	18.3
Mg^{2+}	11.01	6.10	9.69	Cd^{2+}	19.7	15.83	16.0
Ca^{2+}	6.38	<2	8.92	Hg^{2+}	23.0	–	–
Sr^{2+}	5.34	<1	6.83	Pb^{2+}	22.1	sce *	16.6
Ba^{2+}	4.37	<1	5.10	Fe^{3+}	29.6	–	–
Mn^{2+}	16.6	12.77	14.3	La^{3+}	14.3	–	–
Co^{2+}	19.7	13.38	17.5	A **	6.8	–	7.6
Ni^{2+}	19.4	9.20	–	S **	3.5	–	2.6
Cu^{2+}	21.3	21.3	19.8	A ***	20.4	16.1	17.2
				S ***	3.6	4.1	2.7

* Complex insoluble in water.

** For the set of cations Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}.

*** For the set of cations Mg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}.

¶ Values of the ionic radii have been reported.[75]

Lengthening the small chain linking the nitrogen atom and phosphorus in (XXX, 3) increases the size of the basket, corresponding to the selectivity of complex-formation, when compared with complexone (XXX, 2). The larger octahedron characteristic of Co^{2+} requires a larger volume for the cavity than the tetrahedron characteristic of Ni^{2+} (at almost the same ionic radius). As a result, complexone (XXX, 3) fits better with the Co^{2+} ion than with the Ni^{2+} ion and this difference leads to the observed selectivity of action. Complexone (XXX, 3) forms a much less stable chelate than (XXX, 2) with the Mg^{2+} ion, which is too small for the cavity of ligand (XXX, 3). On the other hand, evidently the Ca^{2+} ion is too large for the basket of this ligand without even considering the more voluminous ions of Sr^{2+} and Ba^{2+} (the binding here is undoubtedly ionic). The stability constants of the complexes of (XXX, 2) with Co^{2+} and Cd^{2+} were no different, but for the new complexone the complex with the more bulky Cd^{2+} ion was significantly more stable than the complex with Co^{2+} (see Table 4). The difference in stability constants for (XXX, 2) with the small Zn^{2+} ion and the larger Cd^{2+} ion was very great but for (XXX, 5) it was far less. The bulky Mn^{2+} ion forms a more stable complex than Ni^{2+}. This leads to a breaking of the Irving–Williams series[78] which is characteristic of the traditional complexones. It is therefore seen that the size of the basket for complexone (XXX, 3) is somewhat larger than that for (XXX, 2).

When investigating the complex-formation of ligands (XXX, 1) and (XXX, 3) with Cu^{2+} and Zn^{2+} ions in water it was shown[58] that hydroxyethyl substituents, although playing no part in coordination, reduced the complex-forming ability of the amines as a result of electronic and steric effects. Since complexes are formed in the case of ligand (XXX, 5) which are more stable than the complexes of the free amine (XXX, 1), it must be deduced that the problem of the participation of the hydroxyethyl pendant groups in coordination with cations remains open.

The thermodynamics of complex-forming of complexone (I) with Mg^{2+}, the AEM and Cu^{2+} ions, have been investigated (Table 5).[81]

Table 5. Thermodynamic parameters for complex-formation of complexone (I) with certain cations (T = 25 °C).

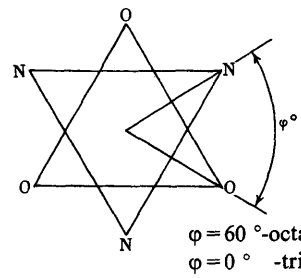
Cation	lg K_{st}	$\Delta H°$, kcal mole^{-1}	$\Delta S°$, kcal mole^{-1} K^{-1}
Mg^{2+}	9.69	+0.4	45
Ca^{2+}	8.92	−5.9	21
Sr^{2+}	6.83	−2.1	24
Ba^{2+}	5.10	−1.38	18.6
Cu^{2+}	21.63	−13.4	54

The greater stability of the complex of (I) with Mg^{2+} compared with Ca^{2+} is caused purely by the entropy factor. It might be supposed that for complexone (XXX, 2) also, the greater stability of the Mg^{2+} complex compared with that of Ca^{2+} is caused by the entropy factor, when the conformation of the free ligand is ideal for the approach of the small Mg^{2+} ion.

According to XSA data the complexes of ligand (I) have the conformation of a basket for which 1,4,7-triazacyclononane serves as the base and the pendant carboxyl groups the walls.

In 1982 Wieghardt and collaborators obtained a large series of complexes of composition $[M^{III}L]$ and $Na[M^{II}L]$, where L = (I), M^{III} = Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+} and M^{II} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}.[84] The authors examined the complexes $[Cr^{3+}L]$, $[Fe^{3+}L]$, $Na[Cu^{2+}L]2NaBr.8H_2O$ by XSA in this study. It was shown that only in the complex with VO^{2+} was ligand (I) pentadentate (one carboxyl group did not participate in coordination). In all the remaining complexes all the donor atoms of the ligand participated in coordination (Scheme 1).

Scheme 1



φ = 60 °-octahedron
φ = 0 ° -trigonal prism

Later, XSA was carried out on complexes of (I) with Ni^{2+} and Ni^{3+} ions.[86] The reaction of (I) with Ni^{2+} occurs even in dilute HNO_3. The complex $[NiL].H_3O$ (crystalline) was isolated from this solution the XSA of which showed that all the nitrogen atoms and the oxygen atoms of the carboxyl groups coordinated with the Ni^{2+} ion and the hydroxonium ion is separate from the complex anion. In dilute HNO_3 the blue $[Ni^{2+}L]H_3O$ complex is converted into the rose $[Ni^{3+}L]$ complex of trivalent nickel (Table 6).

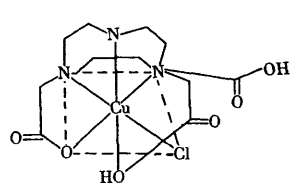
Table 6. Crystal lattice parameters for complexes of ligand (I) with certain cations from XSA data.[84,86]

Cation	φ (Scheme 1), deg	Mean bond length, Å	
		M–N	M–O
Ni^{3+}	53.1	1.93	1.91
Ni^{2+}	48.0	2.04	2.08
Cr^{3+}	49.0	2.06	1.96
Cu^{2+}	26.6	2.12	2.07
Fe^{3+}	25.0	2.18	1.96

The geometries of the complexes of Ni^{3+} and Cr^{3+} with (I) are close to tetrahedral and the geometries of the complexes of ligand (I) with Cu^{2+} and Fe^{3+} ions are close to a trigonal prism. The protonated complex $[CuClLH_2]$ has a ladle conformation.[87]

One of the protonated groups of ligand (I) turns away to the side. Two nitrogen atoms, one chlorine atom and one oxygen atom of the deprotonated carboxyl group are coordinated to the Cu^{2+} ion in the equatorial plane (Scheme 2).

Scheme 2



One nitrogen atom of the ring and an oxygen atom of one of the protonated carboxyl groups are in the axial positions with longer bonds. Such a structure for the complex of Cu^{2+} with complexone (I) may be caused by steric hindrance arising in the coordination of the 1,4,7-triazanonane fragment with the Cu^{2+} ion. It was established by XSA [88,89] that in the complexes of (XXX) with $CuCl_2$ and $CuBr_2$ two nitrogen atoms and two halogen atoms are located in the equatorial plane and the third nitrogen atom occupies the fifth apical position with a longer coordinate bond length. According to XSA of the complex $[CoL](ClO_4)_3$ with ligand (XXX, 6) the Co^{3+} ion is in the plane of the ligand as in a basket with the three-nitrogen ring serving as the base and the pendant ethylamino groups as the walls.[59] The complexes of Co^{3+} and Ni^{2+} of composition $[CoL]Br_3$ and $[NiL]Br_2.H_2O$ with ligand (XXX, 7) containing pendant propylamino groups in the molecule have the structure of a regular octahedron (according to XSA data).[61]

Wieghardt and collaborators have synthesised a large number of complexes of ligand (XXX, 11) with the TM, Cr^{3+}, Fe^{3+}, Pd^{2+}, Ru^{2+} and Ru^{3+}.[90] X-Ray structural analysis was carried out on complexes of $[NiL](ClO_4)_2$, $[MnL](ClO_4)_2$, $[PdL](PF_6)_2$ and $[FeL](ClO_4)_2$ with this ligand.[90,91] The complexes of Mn^{2+}, and Fe^{2+} and Ni^{2+} ions with (XXX, 11) were coordinated with three ring nitrogen atoms and three nitrogen atoms of the α-pyridylmethyl pendant groups. The Pd^{2+} ion was pentacoordinated, one pendant group did not participate in chelation.

Table 7. Values of $\lg K_{st}$ for complexes [ML] of cyclopendant complexones and EDTA, *A* and *S*.

Cation *A*, *S*	(XXXII.2)	(XXXII.3)	(II)	EDTA
Be^{2+}	–	15.9	13.6	9.2
Mg^{2+}	7.3	<2	11.0	8.8
Ca^{2+}	10.3	<2	15.9	10.6
Sr^{2+}	9.8	<1	12.8	8.7
Ba^{2+}	8.8	<1	11.3	7.8
Mn^{2+}	16.9	12.4	17.8	13.8
Co^{2+}	20.8	14.8	18.4	16.3
Ni^{2+}	19.0	12.0	17.3	18.5
Cu^{2+}	25.4	27.1	19.0	18.7
Zn^{2+}	24.8	24.6	18.9	16.4
Cd^{2+}	22.9	20.8	19.0	16.4
Hg^{2+}	25.1	29.6	–	21.5
Pb^{2+}	23.3	16.3	19.9	17.9
A *	9.0	–	12.8	9.0
S *	1.7	–	2.7	1.6
A **	21.9	18.3	18.6	17.0
S **	3.8	7.0	1.0	2.0

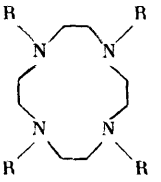
* For the set of cations Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}.
** For the set of cations Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

The Ni^{2+} ion in the complex of composition $Na[NiL.H_2O].5H_2O$ (L = XXX, 9) has a distorted octahedral structure. Three ring nitrogen atoms and an oxygen atom of the $CH_2CH_2SO_3^-$ group were in a square plane. The apical positions were occupied by a second $CH_2CH_2SO_3^-$ group and a water molecule. One pendant group was not coordinated to Ni^{2+}. The complex of copper ion of composition $Na[CuL].3H_2O$ is a distorted pyramid, two ring nitrogen atoms and two oxygen atoms of $CH_2CH_2SO_3^-$ groups form the base and at the vertex of the pyramid is a third nitrogen atom bound to a pendant group uncoordinated to Cu^{2+}.[63] The protonated complex of (XXX, 2) of composition $[CuH_4L].H_2O$ has the same structure according to XSA data[92] as does the complex of Cu^{2+} with ligand (XXX, 9). Two nitrogen atoms and two oxygen atoms of $CH_2PO_3H^-$ groups are at the base of the square pyramid and the third ring nitrogen atom, bound to a protonated pendant group, occupies the apical position. As is seen, a ladle conformation is characteristic for the protonated complexes of ligands (I) and (XXX, 2) and the complex of (XXX, 9) with the Cu^{2+} ion. In this conformation one pendant group of these complexones is turned away to the side and does not participate in chelation.

The coordination of 1,4,7-triazacyclononane with the Cu^{2+} ion occurs, as a rule, in the same manner. Two nitrogen atoms of the cyclic fragment are located in the equatorial plane and the third nitrogen atom occupies the apical position. The coordination of all three ring nitrogen atoms in one plane seemingly encounters difficulties and does not take place.

4. Cyclopendants based on cyclene

The following cyclopendant complexones are known which contain a 1,4,7,10-tetra-azacyclododecane (cyclene) fragment.



(XXXII)

1. R = H [73];
2. R = $CH_2PO_3H_2$ [67];
3. R = $CH_2CH_2PO_3H_2$ [93];
4. R = CH_2COOH [94, 95];
5. R = CH_2CH_2OH [96, 97];
6. R = $CH_2CH_2P(O)Ph_2$ [149].

The formation of more stable complexes with cations of small ionic radius was observed for complexone (XXX, 2) with a nine-membered ring. In (XXXII, 2) the size of the cyclic fragment is larger, consequently a shift of the maximum efficiency of complex-formation in the direction of cations with a large ionic radius might be expected. In reality the overall tendency towards complex-forming ability for this complexone is the formation of stable chelates with cations of relatively large size. In contrast to (XXX, 2) compound (XXXII, 2) gives a more stable complex with Ca^{2+} than with Mg^{2+}. For cations with an ionic radius less than 0.7 Å the complexes of ligand (XXX, 2) are the more stable. Ions with an ionic radius 0.7–0.8 Å form complexes of approximately the same stability but cations of larger size form more stable complexes with (XXXII, 2) (Table 7). The exception is the Cu^{2+} ion (small size) which gives an extremely stable complex with this complexone.

All the cyclopendant organophosphorus complexones, containing a tetra-aza-amine fragment, such as cyclene and 1,5,8,12-tetra-azacyclotetradecane (cyclam), form especially stable complexes with the Cu^{2+} ion, possibly with four ring nitrogen atoms in square coordination. The simultaneous presence in these complexones of a cyclic tetra-amine fragment and pendant alkylphosphonyl groups evidently leads to the high value for the stability constant of the complexes with Cu^{2+}. The carboxyl-containing analogues, ligands (II) and (IV), give complexes with $\lg K_{st}$ 19.0 and 18.6 respectively with the Cu^{2+} ions.[94] The unsubstituted cyclene and cyclam form

complexes with $\lg K_{st}$ equal to 23.3 and 26.5 respectively with the Cu^{2+} ion,[96], i.e. the pendant Ac^- behave as if interfering with coordination. The complex of (XXXII, 2) with the bulky La^{3+} ion is far more stable than the complex of this ion with complexone (XXX, 2). It is possible that this enables a coordination number of eight, natural for La^{3+}, to be put into effect. Seemingly, ligand (XXXII, 2) has a large plane size which leads to an increase in the metal–nitrogen distance on arranging the cation above the plane of the nitrogen atoms (the cations are not located within the plane). Hence its ability to form highly stable complexes with such cations as Cd^{2+}, Hg^{2+}, Pb^{2+} and La^{3+}.

The stability constants for the complexes of Zn^{2+}, Cd^{2+} and Hg^{2+} with complexone (XXXII, 3) with ethylphosphonic acid pendant groups differ significantly from the stability constants of Mn^{2+}, Co^{2+} and Ni^{2+} with the same complexone. None of the known complexones give such a large difference.[73] This ligand forms the most stable complex with the Cu^{2+} ion among all the cyclopendant organophosphorus complexones. It does not form complexes with Mg^{2+} and the alkaline earth elements although organophosphorus complexones of linear structure with four or more phosphonic acid groups in the molecule form fairly stable complexes with Mg^{2+} and Ca^{2+}.[98] Complexone (XXXII, 3) gives the most stable of the known complexes with the Hg^{2+} ion. It exceeds significantly all previously known complexones in selectivity of complex-formation (see Table 7).

Comparison of the complex-forming ability of the ligands (XXX, 2), (XXX, 3) (XXXII, 2 and 3) etc. shows that steric factors operate in a fairly complicated manner in the chelation of various cations. They cannot be reduced solely to the effect of the ionic radius of the cation and are developed on a background of electronic factors. Thus ligand (XXX, 3) shows a very high difference in the stability constants of complexes of Cu^{2+} and Ni^{2+} ions, which are close to one another in size[75] but differ in the stability of the polyhedra formed by them (octahedron, tetrahedron, square plane). Complexone (XXXII, 3) forms a highly stable complex with Zn^{2+}, which is more stable than the complexes with Co^{2+} and Ni^{2+}, but all three possess ionic radii which are close to one another. With the large cations Hg^{2+} and Pb^{2+}, clearly larger than Zn^{2+}, ligand (XXXII, 3) [like (XXXII, 2)] gives highly stable complexes, particularly with the Hg^{2+} ion ($\lg K_{st}$ = 29.6).

When coordinating with complexones (XXX, 3) and (XXXII, 3) the energy of the covalent bonding of a metal cation with the donor centres of the ligand has a fundamental importance and in the end is strongly dependent on the nature of the cation. Furthermore the structure of the coordination polyhedron of the cation also exerts a strong effect. Ligands with phosphonoethyl pendant groups may seemingly be reshaped under the stereochemical requirements of particular cations and this also makes a contribution to the observed high selectivity of these complexones. Evidently the bonding energy also provides the very high difference in stability constants of the complexes of ligands (XXX, 3) and (XXXII, 3) with the Cu^{2+} ion compared with other transition metals having similar ionic radii.

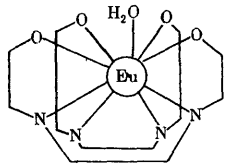
The carboxyl-containing cyclopendant complexone (II) surpasses the organophosphorus complexones in efficiency and selectivity of reaction with the ions of Mg^{2+} and the alkaline earth elements, but is itself significantly surpassed in selectivity of complex-formation with the TM, Cd^{2+} and Pb^{2+} not only by the organophosphorus complexones but also by EDTA, a complexone of linear structure (see Table 7). In contrast to the organophosphorus cyclopendant complexones which are cyclene derivatives, acid (II) forms highly stable water-soluble complexes with the REE. Stability constants are given in Table 8 for complexes of (II), EDTA and diethylenetriaminepenta-acetic acid (DTPA) with REE ions.[99,100]

The complex of (II) with the Eu^{3+} ion of composition $Na[Eu^{3+}L.H_2O].4H_2O$ has been investigated by XSA and ^1H NMR.[101] In this, Eu^{3+} is nine-coordinate with four coordinate bonds from nitrogen atoms lying at the base of prism of mean length 2.71 Å, four from oxygen atoms of the carboxyl groups of mean length 2.34 Å and one bond with a water molecule of length 2.48 Å.

Table 8. Values of $\lg K_{st}$ for complexes [ML] (T = 20 °C, μ = 1.0, NaCl).

Cation	(II)	EDTA	DTPA
Eu^{3+}	28.2	17.3	22.4
Tb^{3+}	28.6	17.9	22.7
Lu^{3+}	29.2	19.8	22.4

The Eu^{3+} ion is in a basket of eight donor atoms of ligand (II). The bond lengths are greater than in complexes of other ligands with the TM.



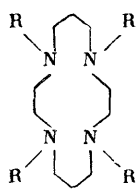
The authors called such a coordination polyhedron a distorted square antiprism.[101] Complexes of the following composition have been investigated by IR and visible spectroscopy: $[Cu(H_2L)]$, $[Ni(H_2L)]$, $[Zn(H_2L)]$, M[Cu(L)] and M[Ni(L)] (M = Ca^{2+}, Sr^{2+}, Ba^{2+}).[102] X-Ray structural analysis was carried out on the first two complexes in the same study. It was shown that they have an octahedral structure. Two nitrogen atoms and two oxygen atoms of carboxyl groups are at the corners of a square plane. On the axis perpendicular to the square plane are two ring nitrogen atoms. Two protonated CH_2COOH groups do not participate in the coordination. X-Ray structural analysis was carried out on the complex $[Cu_2(L)].5H_2O$.[103] The two Cu^{2+} ions in this complex have different coordination spheres. One of them is coordinated in the same way as in the mononuclear complex $[Cu(H_2L)]$. There are two nitrogen atoms and two oxygen atoms at the corners of a square plane. Two nitrogen atoms of ligand (II) are on the axis perpendicular to the square plane. The second Cu^{2+} ion has a square-pyramidal environment. Four oxygen atoms from CH_2COO^- groups lie at the base of the pyramid and a water molecule is found at its apex.

Complexone (II) is the best shift reagent among the ligands (I), (IV), etc. used for the quantitative determination of Eu^{3+} by NMR in water.[104,105] The kinetics of the reaction of (II) with Mg^{2+}, AEM, Ni^{2+}, Cu^{2+} and Zn^{2+} have been studied in water over a wide pH range.[106]

X-Ray structural analysis has been carried out on the complexes $[2Li(L)].Cl_2.2H_2O$, $[Na(L)].CNS$, $[K(L)].SCN$ and $[(L)H_2O]$ with ligand (XXXII, 5).[107] Four cyclene nitrogen atoms and the pendant hydroxyethyl groups participate in the coordination with these cations. For Li^+ one hydroxyethyl participates, for Na^+ three and for K^+ all four. In the monohydrate of this ligand a water molecule is bound to two ring nitrogen atoms and two oxygen atoms of the pendant groups.

5. Cyclopendants based on cyclam

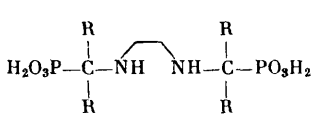
The following ligands containing a 1,5,8,12-tetraazacyclotetradecane (cyclam) fragment are known



(XXXIII)

1. R = H [73]; 2. R = $CH_2PO_3H_2$ [69]; 3. R = CH_2COOH [94]; 4. R = = CH_2CH_2OH [108]; 5. R = $CH_2CH_2NH_2$ [109—114]; 6. R = $(CH_2)_3NH_2$ [112]; 7. R = CH_2CH_2CN [113], 8. R=CH_2— [114, 115]; 9. R = = $CH_2P(O)Ph_2$ [116]; 10. R = $CH_2CH_2P(O)Ph_2$ [116].

Complexone (XXXIII, 2) based on cyclam is significantly lower in complex-forming efficiency than with analogous complexone (XXXII, 2) based on cyclene. With all cations (except Cu^{2+}) a sharp reduction is observed in the stability constants of complexes. A similar reduction in the stability of complexes is also observed for carboxyl-containing complexones on changing from complexone (II) to (IV).[94] Seemingly the reason for the reduction in the stability constants of the complexones in both cases is linked with the size and conformation of the tetra-azacyclic compounds. It might be thought that the cyclic fragment of complexones (XXXIII, 2) and (IV) (cyclam) are conformationally more flexible than the cyclene fragment. If the stability constants of ML complexes of complexone (XXXIII, 2) and ethylenediamine-*N,N'*-bis(methylphosphonic acid) (EDMP),[117] which is an acyclic fragment of complexone (XXXIII, 2), are compared (Table 9) then it is not difficult to understand the parallel change of these values (with the exception of K_{st} for the complexes of Cu^{2+}). EDMP is a complexone of high flexibility.



R = H (EDMP), R = Me (EDIP)

where EDIP is ethylenediamine-*N,N'*-bis(isopropylphosphonic acid).

The observed reduction in the size of the stability constants of the complexes is evidently entropic in origin.

The complexone (XXXIII, 2) forms complexes, which are close to one another in stability (Table 10), with all the cations investigated. Seemingly the size of the cyclic fragment of this ligand is sufficiently large and the ring sufficiently flexible to satisfy the steric requirements of any cations and this also determines its lack of selectivity of action.

Table 9. Values of $\lg K_{st}$ for complexes [ML] of certain cations.

Cation	(XXXIII.2)	EDMP
Mn^{2+}	10.8	7.55
Co^{2+}	15.3	10.8
Ni^{2+}	15.6	12.0
Zn^{2+}	17.6	12.0
Cd^{2+}	16.7	10.9
Cu^{2+}	26.6	18.6
Cations of the alkaline earth metals	<2	<2

Table 10. Values of $\lg K_{st}$ for complexes [ML] of compounds (XXX, 2), (IV) and (XXXIII, 4).

Cation *A, S*	(XXXIII.2)	(IV)	(XXXII.4)
Mg^{2+}	<2	3.0	1.86
Ca^{2+}	<2	9.5	–
Sr^{2+}	<2	6.2	–
Ba^{2+}	<2	4.3	–
Mn^{2+}	10.8	11.2	–
Co^{2+}	15.3	15.0	6.10
Ni^{2+}	15.6	15.3	7.31
Cu^{2+}	26.6	18.6	15.69
Zn^{2+}	17.6	15.8	6.43
Cd^{2+}	16.7	15.5	9.38
Hg^{2+}	–	–	17.94
Pb^{2+}	15.5	14.7	6.28
A *	16.9	14.7	–
S *	5.1	2.4	–
A **	17.9	15.8	8.53
S **	4.3	1.5	3.88

* For the set of cations Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

** For the set of cations Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}.

Table 11. Values of $\lg K_{st}$ and $\Delta \lg K_{st}$ for complexes [ML] of Cu^{2+} and Ni^{2+}.

Cation, $\Delta \log K_{st}$	(XXX.2)	(XXXII.2)	(XXXIII.2)	(XXXII.3)	(XXX.3)	(XXXIII.4)	EDIP
Cu^{2+}	21.3	25.4	26.6	27.1	21.3	15.69	20.35
Ni^{2+}	19.4	19.0	15.6	12.0	9.2	7.31	11.13
$\Delta \log K_{st}$	1.9	6.4	11.0	15.1	12.1	8.38	9.22

The selectivity of complex-formation in relation to the copper ion (Cu^{2+}) may be assessed by the difference:

$$\Delta \lg K_{st} = \lg K_{st}(Cu^{2+}) - \lg K_{st}(Ni^{2+}).$$

These values are given in Table 11 for the cyclopendant organophosphorus complexones and for the best of the other cyclopendants in this respect (XXXIII, 4),[108] and also for the linear complexone EDIP.[117]

It follows from the data shown that the ligands (XXXIII, 2) and especially (XXX, 3) and (XXXII, 3) surpass significantly the others in efficiency (A) and selectivity (S) of binding the Cu^{2+} ion.

The complexes of ligand (IV) of composition $[MH_2L]$ ($M = Ni^{2+}$, Cu^{2+} and Zn^{2+}) have been investigated.[102] X-Ray structural analysis of the binuclear complex $[Cu_2(L)].6H_2O$ shows that both Cu^{2+} ions have a square-pyramidal conformation. Two nitrogen atoms and two oxygen atoms of a COO^- group form the base of the pyramid. A water molecule is located at the vertex of the pyramid for one Cu^{2+} ion and a COO^- group for the other. The carboxyl-containing cyclopendants (II) and (IV), in contrast to their phosphorus analogues, form water-soluble complexes with the REE. The values of K_{st} for these complexes increase from 14.5 (Nd^{3+}) to 16.6 (Yb^{3+}).[99] It was established that complexes $[ML]^-$, where $M = Tb^{3+}$, Yb^{3+}, Pr^{3+} and Lu^{3+}, and L = (IV) are conformationally very rigid.[119]

Hay and coworkers[108] investigated the complex-formation of ligand (XXXIII, 4) (Table 10) with Cu^{2+}, Ni^{2+} and Pb^{2+} ions. The values of $\lg K_{st}$ for the complexes were in good agreement with those found previously.[118] X-Ray structural analysis of the complex of this ligand with the Ni^{2+} ion shows that the environment of the Ni^{2+} ion is almost a regular octahedron. Four ring nitrogen atoms are set at the corners of the square and oxygen atoms from CH_2CH_2OH groups are in the perpendicular positions. One pendant group in the complex with Ni^{2+} is deprotonated.

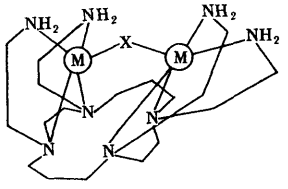
The ligand (XXXIII, 5) has eight donor positions in the molecule and as a rule forms binuclear complexes $[M_2L]$. Protonation constants for this ligand and stability constants were found for complexes with the Cu^{2+} ion of composition $[CuH_2L]^{4+}$ and $[Cu_2L]^{4+}$ ($T = 25$ °C, $\mu = 0.5$, 0.5 M $NaNO_3$).[120]

X-Ray structural analysis of the complex of composition $[Cu_2L(ClO_4)_2].(ClO_4)_2$ has been carried out.[110] The environment of both Cu^{2+} ions is square-pyramidal. Four nitrogen atoms lie at the base of the pyramid and an oxygen atom of a ClO_4^- group is in the apical position with a much longer bond. A complex of the same structure is also formed with ligand (XXXIII, 5) by the Ni^{2+} ion, viz. $[Ni_2L(ClO_4)_2].(ClO_4)_2$.[111] The complex $[Cu_2L].Br(ClO_4)_3$ has a chain like structure and the bromine atom serves as a bridge between the Cu^{2+} ions, which have a square-pyramidal structure as a result of coordination with two cyclam nitrogen atoms and two nitrogen atoms of the pendant aminoethyl groups. The halogen atom at the vertex is able to complete the building of the square-pyramid in the Cu^{2+} complexes of chain-like structure. The addition constants for halide ion to the $[Cu_2L]$ complex have been found[112,120]

$$[Cu_2L]^{4+} + X^- = [Cu_2LX]^{3+},\ K_{st} = [Cu_2LX]^{3+}/[Cu_2L]^{4+}[X^-],$$

and are 2.6–5.1 for the ions F^-, Cl^-, Br^-, N_3^-, CN^-, OH^- and I^-.

Scheme 3



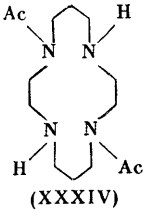
$[M_2L(X)]^{3+}$;
$M = Co^{2+}$, Cu^{2+};
$X = OH^-$ (for Co^{2+}),
$X = F^-$, I^-, NO_3^-,
N_3^-, NCO^- (for Cu^{2+}).

According to XSA data the complexes of Cu^{2+} [121] and Co^{2+} [122] with the ligand (XXXIII, 3) of composition $[M_2L(X)].(ClO_4)_3$ are of a similar structure in which each metal ion has a square-pyramidal environment (Scheme 3). Two ring nitrogen atoms and two pendant aminoethyl group nitrogen atoms are at the base of each pyramid. The X^- anion is at the vertex of the pyramid, common to both metal atoms.

X-Ray structural analysis has been carried out on the complex $[Ni_2LCl].Cl_3.H_2O$.[109] The Ni^{2+} atoms in this complex are not equivalent. One has square-planar coordination with two nitrogen atoms from the cyclam and two from the pendant aminoethyl groups. The second Ni^{2+} ion in the complex has a square-pyramidal environment with a Cl^- ion in the apical position.

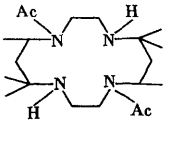
Lengthening the pendant groups leads to a change in complex-formation. The complex of (XXXIII, 6) with Ni^{2+} has a square-pyramidal structure. Four ring nitrogen atoms lie at the base of the pyramid and an amino group from a pendant aminopropyl group is in the apical position.[112]

Hay and Bembi[113] synthesised and investigated the complex of the Cu^{2+} ion with ligand (XXXIII, 7). In the $[CuL(NCS)].(NCS)$ complex the Cu^{2+} ion has a square-pyramidal environment. The four cyclam nitrogen atoms are at the base of the pyramid and the NCS group is in the apical position. The pendant cyanoethyl groups do not participate in the coordination. Complexes of composition $[Cu_2LBr_2].(ClO_4)_2$ [123] and $[Ru(HL)].(ClO_4)_3.H_2O$ [124] have been obtained for ligand (XXXIII, 8) and investigated by XSA. In the first complex the Cu^{2+} ion is coordinated with two nitrogen atoms of the pendant α-pyridylmethyl groups and with a bromine atom located on the axis perpendicular to the plane of the square in the corners of which lie nitrogen atoms. In the second complex the Ru^{2+} ion has a distorted octahedral environment with three ring nitrogen atoms and three nitrogen atoms of the α-pyridylmethyl groups. One pendant group in this complex is protonated and does not participate in coordination.

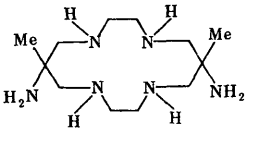


(XXXIV)

Ligand (XXXIV) has not been isolated in the free form since it is slowly converted into the corresponding lactam. However a crystalline complex of composition $[Cu^{2+}(L)]$ has been successfully obtained, XSA of which shows that it has an octahedral structure.[125] Four ring nitrogen atoms are located in the square plane and two oxygen atoms of the pendant groups are in the perpendicular positions.



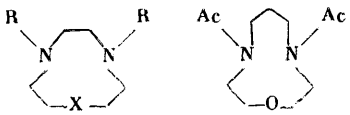
(XXXV)



(XXXVI)

The Ni^{2+} ion in the complex of composition $[Ni(L)].HBr.H_2O$ is coordinated (regular octahedron) with six donor atoms of the ligand (XXXV) (XSA data).[126] The complex-formation of ligand (XXXVI) with Co^{3+}, Ni^{2+} and Cu^{2+} ions has been investigated. According to XSA data the pendant NH_2 groups do not participate in coordination in the complex with Cu^{2+}.[148] The complex of Co^{3+} with this ligand is almost a regular octahedron with very short coordinate bond lengths at 1.94 to 1.95 Å due to chelation of the nitrogen atoms of the ring and pendant groups. The complex of the Ni^{2+} ion is also octahedral but with a large tetragonal distortion. On protonation, the pendant NH_2 groups add on protons and stop participating in coordination. The octahedral complexes of Co^{3+} and Ni^{2+} are converted by this into square-planar or into a *trans*-diaqua cation.

6. Unsymmetrical polyazamacrocyclic cyclopendants



(XXXVII) (XXXVIII)

1. R = CH_2COOH, X = NH; 2. R = CH_2COOH, X = O;
3. R = $CH_2CH_2NH_2$, X = NH; 4. R = $CH_2CH_2NH_2$, X = S;
5. R = $CH_2CH_2NEt_2$, X = O; 6. R = $CH_2CH_2CH_2NEt_2$, X = O.

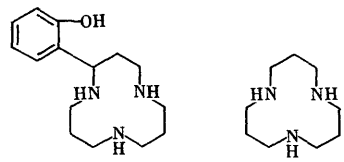
The thermodynamic parameters for complex-formation have been determined for ligand (XXXVII, 2) and (XXXVIII).[85] The increase in size of the cyclic fragment on transfering from (XXXVII, 2) to (XXXVIII) leads to a reduction in the stability of the complexes of the cations investigated, viz. Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.

For the potentially pentadentate ligands (XXXVII, 1 and 2) complexes $[VO(L)].H_2O$, where L = 1 and $[VO(L)]$ where L = 2 have been obtained in which vanadium is tetravalent. A third complex was obtained by the oxidation of the first complex and in this $[VO_2(L)H].2H_2O$ vanadium is pentavalent.[128] It was shown by XSA that the first and third complexes have a distorted octahedral structure.

The environment of the VO^{2+} ion is square-pyramidal. At the apex of the pyramid is a nitrogen atom with coordinate bond length 2.31 Å. Two nitrogen and two oxygen atoms lie at the base of the pyramid. In the third complex one protonated pendant CH_2CH_2COOH group does not participate in coordination with the VO_2^+ ion. The short lengths for V=O bonds (1.61 Å in the first, 1.63 and 1.64 in the third complex) are characteristic of the double bond in vanadyl ions.

Complexes of composition $[Co^{3+}LCl].(ClO_4)_2$ were obtained by oxidation of the corresponding complexes of Co^{2+} with ligands (XXXVII, 3 and 4). It was shown that the complexes of Co^{3+} with these ligands exist as two isomers in which the chlorine atom occupies either an equatorial or an apical position.[129] On coordination of ligands (XXXVII, 3 and 4) with VO^{2+} and Co^{3+} ions one ring nitrogen atom occupies the apical position, i.e. the disposition of all three ring nitrogen atoms in one plane seemingly encounters steric difficulties, which is also observed for complexes of Cu^{2+} with ligands (XXX, 2), (I) and (XXX, 9) based on 1,4,7-triazacyclononane. The VO^{2+} ion has a coordination number of five since on coordination with ligand(I) one dentate position of this complexone proved to be unused. Ligands (XXXVII, 5 and 6) show a physiological effect on the central nervous system of mice.[130] The complex-forming properties of these compounds have not been studied.

The stability constants of the complexes of compounds (XXXIX) and (XL) with the TM have been determined (Table 12).



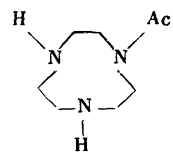
(XXXIX) (XL)

Protonation of complexes of ligand (XXXIX), when the oxygen atom of the pendant hydroxyphenyl group ceases to participate in coordination, shows that this group participates actively in the binding of cations. Ligand (XXXIX) forms far more stable complexes than the free amine. According to XSA data, the complex of this ligand with the Zn^{2+} ion has a trigonal-bipyramidal structure.[82] Two ring nitrogen atoms and the oxygen atom of the phenolic hydroxyl are located in the equatorial plane (triangle) with very short coordinate bond lengths (which shows the strong bonding). A ring nitrogen atom and a molecule of water are located in the apical positions with large bond lengths.

Table 12. Values of $\lg K_{st}$ complexes [ML] (T = 25 °C, μ = 0.1).

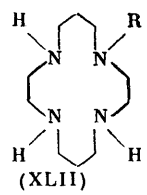
Cation	(XXXIX) [79]	(XL) [80]
Co^{2+}	11.4	–
Ni^{2+}	14.0	10.93
Cu^{2+}	18.4	12.63
Zn^{2+}	12.6	8.75

The ligand (XLI) has been synthesised.[131] Its complex-forming properties were not studied.

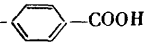


(XLI)

The complexes of Ni^{2+} and Cu^{2+} with the following ligands have been investigated.

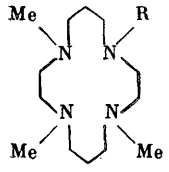


(XLII)

1. R = H; 2. R = CH_2COOH; 3. R = CH_2CH_2COOH;
4. R = $(CH_2)_3COOH$; 5. R = CH_2–;
6. R = CH_2––COOH [131].

The pendant carboxyl groups of ligands (XLII, 2 and 5) participate in coordination. The pendant groups of ligands (XLII, 3, 4 and 6) do not participate in coordination. On reducing the pH the carboxylate groups COO^- are protonated and cease participation in complex-formation with M^{2+}.

Complexes of Ni^{2+} and Cu^{2+} with ligands (XLIII, 1–8) have been synthesised.[133]



(XLIII)

1. R = H; 2. R = CH_2CN; 3. R = $CH_2CH_2NH_2$; 4. R = CH_2CH_2CN;
5. R = $(CH_2)_3NH_2$; 6. R = $CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$; 7. R = $CH_2CH_2\overset{\overset{O}{\|}}{C}OMe$;
8. R = CH_2CH_2COOH; 9. R = Me; 10. R = CH_2COOMe;
11. R = CH_2COOEt; 12. R = CH_2CH_2COOEt; 13. R = $CH_2C(O)NMe_2$;
14. R = $CH_2CH_2P(O)(OEt)_2$; 15. R = $CH_2CH_2P(O)(OEt)(OH)$;
16. R = CH_2COOH; 17. R = $CH_2C(O)NH_2$; 18. R = CH_2CH_2SH;
19. R = $CH_2CH_2NMe_2$.

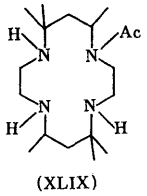
In the complexes of Ni^{2+} and Cu^{2+} ions with ligands (XLIII, 1–8) of composition $[ML].(ClO_4)_2$ the pendant group participates in coordination since, according to spectral data, these cations are pentacoordinated. The cyanoethyl pendant group and the protonated ethyl- and propylamino groups do not participate in complex-formation with Ni^{2+} and Cu^{2+}.

Finally, ligands with the same general formula but with other pendant substituents (XLIII, 9–19) have been obtained and investigated.[134]

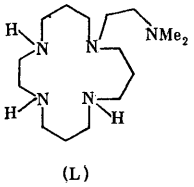
It was established spectroscopically that the pendant groups of ligands (XLIII, 10–18) coordinate the Cu^{2+} ion in the axial position (at the apex of a square pyramid).

X-Ray structural analysis of complexes of composition $[HL.H_2O].2Br$, $[NiL(H_2O)].Br$ and $[NiL(NCS)].H_2O$ showed that the Ni^{2+} ion in these complexes is coordinated (octahedral environment) with five donor atoms of ligand (XLIX) and one water molecule or NCS group.[135]

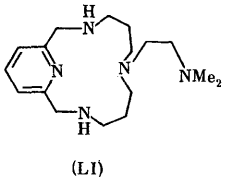
The complexes of Ni^{2+} and Cu^{2+} with ligands (L) and (LI), also containing one pendant group, were obtained by Alcock and collaborators.[136]



(XLIX)



(L)



(LI)

The complexes of ligands (L) and (LI) with Ni^{2+} and Cu^{2+} ions have a trigonal-bipyramidal structure in neutral media which is transformed into square-planar at low pH. The pendant group is protonated by this and stops participating in coordination. The XSA of complex $[Ni(L)].(ClO_4)_2$ showed that it has a trigonal-bipyramidal structure.[136]

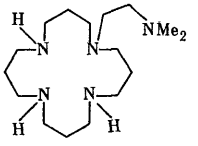
Complexes of Ni^{2+} of composition $[Ni(L)(NCS)].(ClO_4)$ and $[Ni(LH)(NCS)_2].(ClO_4)$ have been obtained and investigated.[137]

One or two (when the pendant group is protonated and does not participate in coordination) NCS^- groups occupy apical positions in hexacoordinated complexes of Ni^{2+}. The thermodynamic parameters have been calculated for the protonation of the complex of Cu^{2+} with ligand (L).

$$[Cu(L)]^{2+}+H^+ \rightleftharpoons [Cu(HL)]^{3+} \quad (L=(L)).$$

Complexes of ligands (L) and (LI) with the Zn^{2+} ion of composition $[Zn(L)].(NO_3)_2$ have also been synthesised. It was shown that the pendant dimethylaminoethyl group participates in coordination in the complexes of ligands with Zn^{2+}.

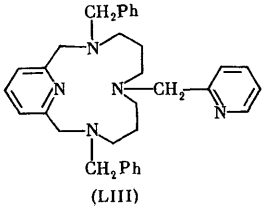
Alcock and collaborators[138] have synthesised and studied the complex-forming properties of ligand (LII) in relation to Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}.



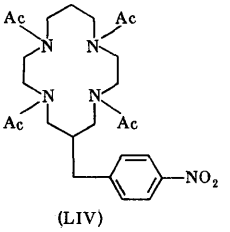
(LII)

It was established that the ions of Ni^{2+}, Co^{2+} and Cu^{2+} were pentacoordinated, i.e. the pendant group participates in coordination. The problem of the participation of the pendant group of ligand (LII) in coordination with Zn^{2+} and Cd^{2+} ions remains unresolved. On acidification, the complex $[Ni(L)].(ClO_4)_2$ is decomposed completely. The square-pyramidal complex $[Cu(L)].(ClO_4)_2$ is transformed on acidification with $HClO_4$ into the square-planar $[Cu(HL)].(ClO_4)_3$ in which the protonated pendant group has ceased participating in coordination [L = (LII)].

The same authors have synthesised and investigated ligand (LIII) having a pendant α-pyridylmethyl group.[139] It was discovered that the pendant group participates in coordination in the complexes $[M(L)].(ClO_4)_2$ (M = Ni^{2+} and Zn^{2+}). Acidification of the blue pentacoordinated complex of (LIII) with Ni^{2+} leads to the yellow $[NiHL].(ClO_4)_3$ complex in which the protonated pendant group does not participate in coordination.



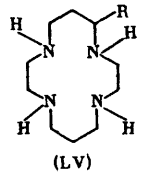
(LIII)



(LIV)

The complex of Cu^{2+} with ligand (LIV) has been studied by XSA.[140] In this complex the Cu^{2+} ion has an octahedral environment due to the ring nitrogen atoms and the two pendant carboxyl groups. The ring nitrogen atoms do not lie in one plane as was observed previously for the complex $[Cu(H_2L)]$ with ligand (II).[102]

Kimura and collaborators have synthesised and investigated the complexes of ligands (LV, 1–4).



(LV)

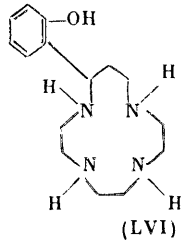
1. R =  [140, 141];
2. R =  [142];
3. R =  [143];
4. R = CH_2OH [144].

The stability constants have been found for the complexes of Fe^{2+} and Fe^{3+} with the ligand (LV, 1).[140] The XSA of the complex with the Ni^{2+} ion shows that Ni^{2+} is in a plane of four ring nitrogen atoms.[141] The oxygen atom of the phenolic hydroxyl is at the vertex of a square pyramid and in this complex occupies an axial position with a very short coordinate bond length. At pH > 6 the phenolic oxygen atom is protonated and ceases to participate in coordination.

According to XSA data the conformation of the complex of Cu^{2+} ion with ligand (LV, 2) is square-pyramidal. Four ring nitrogen atoms are located in the plane of the pyramid and the oxygen atom of the phenolic group is at the vertex. The $K_{st}[CuL] = 1 \times 10^{32}$ M^{-1}, but for the protonated complex with the pendant group not participating in coordination $K_{st}[CuHL] = 2.5 \times 10^{29}$ M^{-1}. It is evident from this that the pendant 2-hydroxyphenyl group makes a contribution to the stability of the resulting complex.[145]

For ligand (XXXIX) based on triazacyclododecane the difference in the values of $\lg K_{st}$ of the complexes [CuL] and [CuHL] was 5.8 with the 2-hydroxyphenyl pendant group not participating in coordination.[79]

A reduction in the size of the ring in ligand (LVI) compared with (LV, 1) leads to a change in the structure of the complex formed with the Ni^{2+} ion.



(LVI)

The octahedral Ni^{2+} complex has the following structure. At the vertices of the square cross section are three ring nitrogen atoms and a water molecule. Perpendicular to this square are a ring nitrogen atom and the oxygen atom of the phenolic group. On reducing the pH the protonated pendant group ceases to participate in coordination and the blue high-spin octahedral Ni^{2+} complex is transformed into the yellow square-planar low-spin complex.[147]

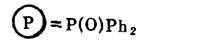
The complex of the Ni^{2+} ion with ligand (LV, 2), with a pyridine substituent, of composition $[Ni(L)H_2O].(ClO_4)_2$ has been studied. According to XSA data the high-spin complex has an octahedral structure.[142] Four cyclam nitrogen atoms are at the vertices of the square and the nitrogen atom of the pyridine ring and a water molecule are on the perpendicular axis. The XSA data on the complexes with the ligands described have been reported.[132] An XSA was carried out on the complex of the Ni^{2+} ion with ligand (LV, 3) which has an imidazole substituent in the molecule.[143] In this complex the Ni^{2+} ion has an octahedral environment. Four nitrogen atoms are found at the vertices of the square and the imidazole nitrogen and an oxygen of the ClO_4^- group are on the perpendicular axis.

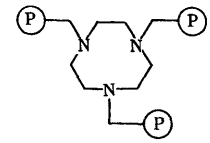
The stability constants of the [NiL] complex of ligand (LV, 2) have been determined.[147]

It was established that in the complex of ligand (LV, 4) with $NiCl_2$ four ring nitrogen atoms and the pendant hydroxymethyl group participate in coordination with the Ni^{2+} ion.[146]

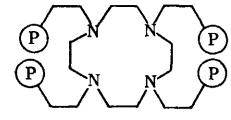
7. Polyazacyclopendants with diphenylphosphoryl pendant groups

Ligands (XXX, 10), (XXXII, 6), (XXXIII, 9) and (XXXIII, 10) contain cyclic polyalkylene-polyamine fragments considered above and pendant diphenylphosphoryl-methyl and -ethyl groups. These ligands form complexes with ions of the alkali, alkaline earth and transition metals in non-aqueous media by participation of the nitrogen atoms of the cyclic fragment and the oxygen atoms of the pendant groups in coordination.

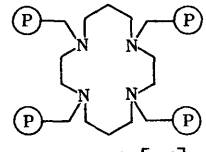




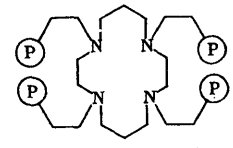
(XXX. 10) [64–66]



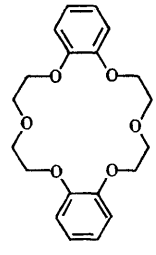
(XXXII. 6) [149]



(XXXIII. 9) [116]



(XXXIII. 10) [116]



(XIX. 1) [149]

Stability constants are given in Table 13 for complexes of these ligands and also (for comparison) for dibenzo-18-crown-6 (XIX, 1) with alkali metals. The selectivity of the ligands with diphenylphosphoryl pendant groups was reduced with the reduction in the conformational rigidity.

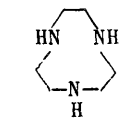
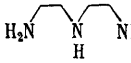
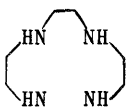
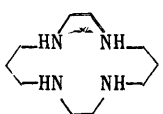
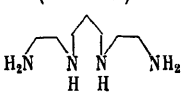
Compounds (XXX, 10), (XXXII, 6) and (XXXIII, 10) form complexes with the Li^+ ion exceeding in stability the complexes with all the ligands known until 1988.[150]

It was established that the ring nitrogen atoms and the oxygen of the pendant $P(O)Ph_2$ groups take part in the formation of complexes of the ligands represented with ions of the alkali metals, AEM and TM.[64, 65,151] In contrast to (XXX, 2) with its phosphonic acid pendant groups, the ligand (XXX, 10) is not specific complex-forming agent for the Mg^{2+} ion. It forms a more stable complex with Ca^{2+} than with Mg^{2+}.[64] In complexes of $Co(SCN)_2$ with the ligands (XXX, 10) and (XXXIII, 10) either all or only a portion of the donor atoms of these ligands, depending on the composition, participate in coordination with the Co^{2+} ion.[65,151]

Table 13. Values of $\lg K_{st}$ for complexes $[ML]^+$ (T = 25 °C, THF:$CHCl_3$ 4:1) and A and S of complex-formation for the set Li^+, Na^+, K^+ and Cs^+.[149]

Cation A, S	(XXX.10)	(XXXII.6)	(XXXIII.9)	(XXXIII.10)	(XIX.1)
Li^+	5.6	5.91	4.7	6.2	4.06
Na^+	4.5	6.29	3.8	5.9	5.60
K^+	3.2	5.04	3.0	4.9	4.66
Cs^+	2.2	3.60	2.3	4.1	3.30
A	3.9	5.21	3.5	5.3	4.41
S	1.9	1.49	1.3	1.2	1.25

Table 14. Values of pK_a of cyclic amines and their linear analogues.

Compound	pK_1	pK_2	pK_3	pK_4	Reference
 (XXX.1)	<2	6.82	10.42	-	[83]
	4.23	9.02	9.84	-	[73]
 (XXXII.1)	<1	<2	9.7	10.7	[152]
	3.25	6.56	9.08	9.74	[73]
 (XXXIII.1)	1.0	1.7	10.2	11.5	[152]
	6.02	7.28	9.50	10.25	[73]

VI. Acid dissociation of cyclopendant complexones: derivatives of polyazamacrocycles

The mechanism of the acid dissociation has been investigated for phosphonyl- and carboxyl-containing complexones in the molecules of which there are the cyclic polyalkylene-polyamine fragments of triazacyclononane, cyclene and cyclam. In contrast to linear polyamines with highly basic nitrogen atoms, the basicity of the nitrogen atoms in the cyclic fragment of cyclopendant complexones varies within very wide limits and a zwitterionic structure exists involving only some of the nitrogen atoms.

Values of pK_a of some cyclic amines and their linear analogues are shown in Table 14.

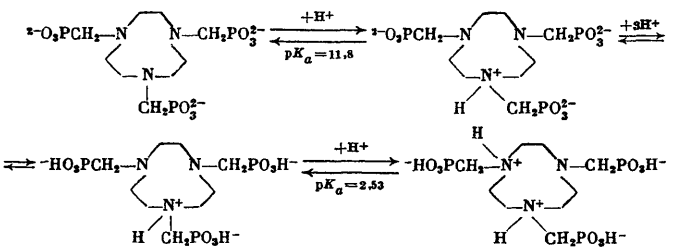
The fission of protons on acid dissociation of cyclopendant complexones with cyclic polyalkylene-polyamines in the molecule may occur both from acid (PO_3H_2 or COOH) groups or from ammonium nitrogen atoms of the cyclic fragment since they have closely similar pK_a values.

Complexones with phosphonoalkyl pendant groups have a different scheme for acid dissociation from that of compounds with carboxyl groups. The phosphonic acid group has two dissociation stages. The size of pK_1 ($PO_3H_2 \rightarrow PO_3H^- + H^+$) is less and of pK_2 ($PO_3H^- \rightarrow PO_3^{2-} + H^+$) is greater than the pK_a of a carboxyl group.[98,153] The phosphonic acid group exerts a different electronic effect on the nitrogen atoms of the cyclic fragment of complexones during the dissociation process.

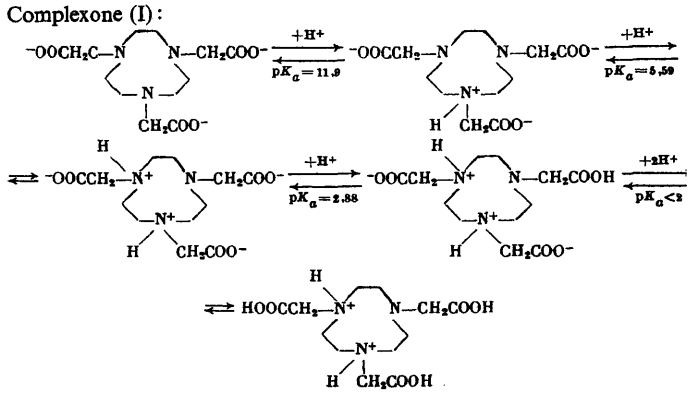
The dissociation sequence of the organophosphorus complexones (XXX, 2), (XXXII, 2) and (XXVIII, 2) has been studied by IR spectroscopy in water and in heavy water.[56,155] Complexones (XXX, 3) and (XXXII, 3) were investigated by ^{31}P NMR spectroscopy in water. ^1H NMR and IR (in D_2O) spectroscopy[154] and ^1H and ^{13}C NMR spectroscopy[156] have been used to study the protonation of the carboxyl-containing complexones (I), (II) and (IV).

The following protonation schemes are proposed.

Complexone (XXX, 2)

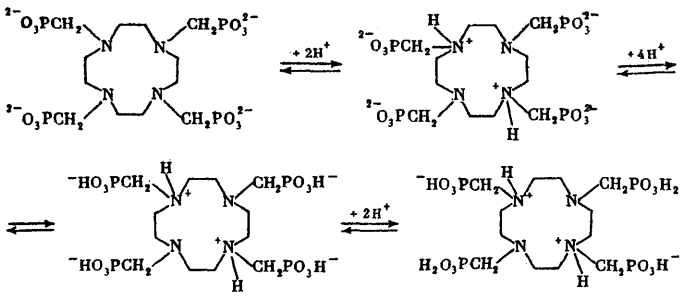


Complexone (I):



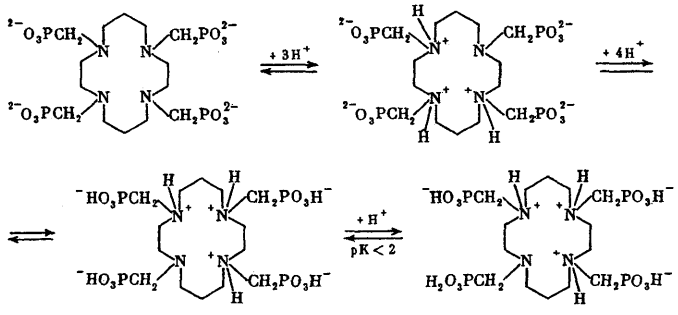
The ring nitrogen atoms of ligand (I) are protonated only at very low pH.

Complexone (XXXII, 2)

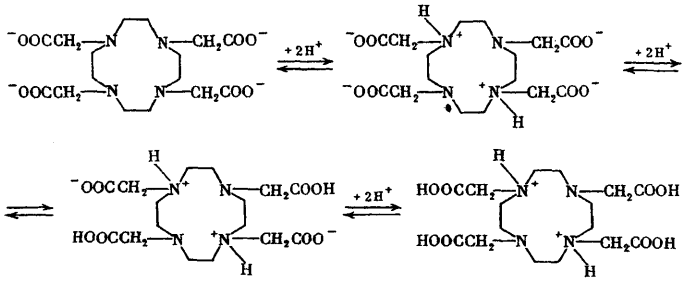


Complexone (XXXII, 2) therefore has a double zwitterion structure in solution. The nitrogen protons dissociate finally at high pH values (pK_7 and pK_8 in Table 15).

Complexone (XXXIII, 2)



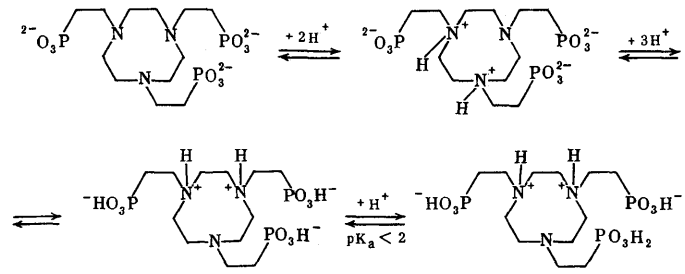
Complexone (XXXIII, 2) has a triple zwitterion structure in solution. All the nitrogen protons are finally split off in one buffer region at very high pH (pK_6, pK_7, pK_8 in Table 15). In the case of the carboxyl-containing complexones (II) and (IV) the size of the cyclic fragment has little effect on the dissociation. Complexones based on cyclene and cyclam have the same dissociation mechanism and the protonation scheme below applies to both (II) and (IV).



With increasing acidity two nitrogen atoms are protonated first and then the two carboxyl groups bound to the unprotonated nitrogen atoms. The remaining carboxyl groups are then protonated. Complexones (II) and (IV) protonate the acid groups first since the nitrogen atoms are less basic than the COOH groups in these molecules.[154]

The mechanism of the acid dissociation of complexones (XXX, 3) and (XXXII, 3) has been investigated by $^{31}P-\{^1H\}$ NMR spectroscopy in water. In the dissociation of the aminophosphonic acids the fission of protons from the PO_3H_2 group is accompanied by an insignificant reduction in the size of the chemical shift (δ) in the ^{31}P NMR spectra.[157] Dissociation of the proton from a nitrogen atom leads, on the other hand, to an increase in δ. This is explained[158] by the fundamental difference in the hybridisation of the nitrogen atoms on going from ammonium to amine and consequently by a change in the shielding of the phosphorus atom. A sharp increase in δ (shift to low field) on fission of the proton bound to the nitrogen atom is observed on dissociation of nitrilotris(methylphosphonic acid) (NTP)[159] and iminobis(methylphosphonic acid).[160]

The sequence of protonation of complexone (XXX, 3) is represented as follows.



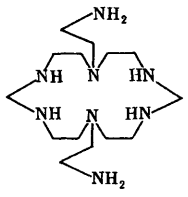
The replacement of the phosphonomethyl pendant groups by phosphonoethyl leads to a definite change in the dissociation mechanism of complexone (XXX, 3) compared with (XXX, 2). The former has the structure of a double zwitterion and the protons bound to the ring nitrogen atoms are split off last.

As is seen the acid dissociation of cyclopendant polyphosphonic complexones (like the polyphosphonic complexones with an open chain) occurs over a very wide pK region, from <1 to 13.5. The formation of complexes within wide limits of acidity of the medium is a characteristic of these compounds. Stable "hydrogen" complexes are formed in acid medium with incomplete displacement of acid group protons by the metal cation. The formation of homo- and heteronuclear complexones (when some of the protons are displaced by one cation and some by another) is also characteristic.[161–171] All these are properties specific to the polyphosphonic complexes.

The complexone (XXXII, 2) has the same order of fission of protons as (XXXII, 3).

VII. Cyclopendants with a large cyclic fragment

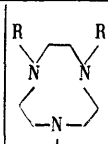
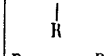
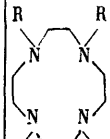
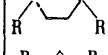
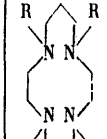
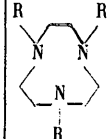
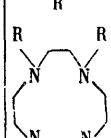
These ligands contain more than four nitrogen atoms in the cyclic fragment. The XSA of complexes (LVII) of composition $[La(L)(CF_3SO_3^-)_2]^+$ and $[Yb(L)(CF_3SO_3^-)]^+$ showed that the La^{3+} ion is decacoordinated with eight donor nitrogen atoms of the ligand and two oxygen atoms of the $CF_3SO_3^-$ group.[162]



(LVII)

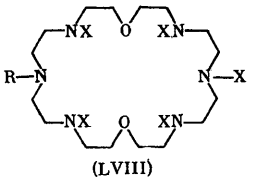
The Yb^{3+} ion complexed with this ligand is nonacoordinated. Eight sites are occupied by nitrogen atoms of the ligand and one by an oxygen atom of the $CF_3SO_3^-$ group. The mean length of the M–N-ring bonds is 2.5–2.6 Å and of the M–N-pendant groups is 2.5 Å, much greater than in cyclopendant complexes with transition metals. This was observed previously when studying the complex of Eu^{2+} with ligand (II).[101]

Table 15. Values of pK_a for the dissociation of phosphonyl- and carboxyl-containing cyclopendant complexones (T = 25 °C, μ = 1.0).[56,57,81,154,93]

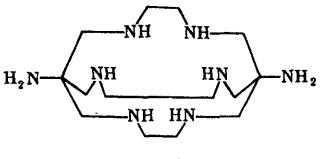
№	Complexone	R	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7	pK_8
1		$CH_2PO_3H_2$	<2	2.53	5.38	7.09	8.65	11.8	-	-
2		CH_2COOH	3.16	6.03	10.77	-	-	-	-	-
3		$CH_2PO_3H_2$	<1	<2	4.88	5.73	7.28	8.46	11.5	12.1
4		CH_2COOH	4.18	4.24	9.23	11.08	-	-	-	-
5		$CH_2PO_3H_2$	<2	4.96	6.27	7.67	9.16	11.8	12.8	13.5
6		CH_2COOH	3.38	4.05	10.18	11.56	-	-	-	-
7		$(CH_2)_2PO_3H_2$	<2	5.38	6.21	6.97	8.85	12.3	-	-
8		$(CH_2)_2PO_3H_2$	<2	2.30	6.21	6.84	7.63	8.34	11.2	12.4

Note. For complexones Nos. 2, 4 and 6 the values of pK_a found are for the addition of proton to the carboxylate group of the corresponding zwitterion.

Ligands (LVIII) have been synthesised and contain a cyclic fragment with donor atoms of nitrogen and oxygen and various pendant groups, such as CH_2CH_2CN, $(CH_2)_3NH_2$, PO_3H_2, etc. (X = H or Ts).[52,53]

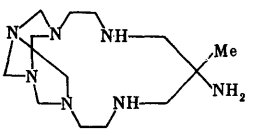


(LVIII)



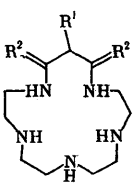
(LIX)

The pendant NH_2 groups of ligand (LIX) do not participate in coordination. The hexacoordinated complexes of Co^{3+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, etc. are formed with ring nitrogen atoms.[173] Complexes have been obtained with ligand (LX) and Ni^{2+} and Ni^{3+} ions.



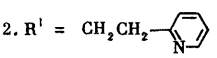
(LX)

Four ring nitrogen atoms participate in coordination and are located at the corners of a square. The fifth ring nitrogen atom and the pendant group NH_2 do not participate in coordination.[174] It was established that (LXI, 1) does not form complexes with Na^+, K^+, Mg^{2+} and Ca^{2+}.[175] The pendant group R^1 of the ligand (LXI, 2) participates in coordination with Ni^{2+}. The stability constant for the complex of Ni^{2+} with this ligand has been found.[176]

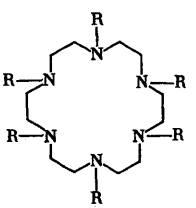


(LXI)

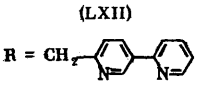
1. $R^1 = (CH_2)_4NH_2$, $R^2 = H_2$;

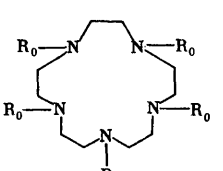
2. $R^1 =$ ; $R^2 = O$.

The complex-formation of ligands (LXII) and (LXIII), which contain bipyridinylmethyl and hydroxyethyl pendant groups in the molecule, has not been studied.[177,178] Martell and collaborators have investigated the complex-forming ability of ligands (LXIV, 1 and 2) with the Fe^{3+} ion.[172,179] The values of $\lg K_{st}$ for complexes [ML] [T = 25 °C, μ = 0.1 (KNO_3)] were 37.6 and 36.0 for (LXIV, 1) and (LXIV, 2) respectively.



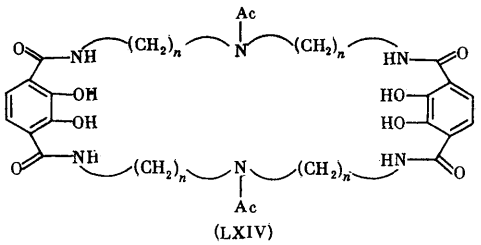
(LXII)

R = 



(LXIII)

$R_0 = CH_2CH_2OH$



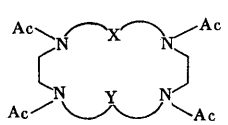
(LXIV)

1. $n = 2$
2. $n = 3$

VIII. Effect of the nature of the pendant groups and the structure of the cyclic fragment of cyclopendants on the efficiency and selectivity of complex-formation

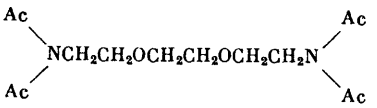
The majority of the ligands investigated contain as acids either phosphonic or carboxyl groups, consequently it is interesting to compare the efficiency and selectivity of complex-formation of the phosphoryl- and carboxyl-containing complexones having the same carbon skeleton. Such comparison were carried out previously but without using the *A* and *S* criteria.[180]

Values of *A* and *S* for complex-formation are given in Table 16 calculated from the stability constants of complexes.[67,69,105,180,181] In contrast to their carboxyl-containing analogues the organophosphorus complexones with two PO_3H_2 groups form low stability complexes with Mg^{2+} and the alkaline earth elements. For the transition metals the organophosphorus complexones exceed the carboxyl-containing in both efficiency and selectivity of complex-formation. There are few data for Mg^{2+} and the alkaline earth elements and it is difficult at present to draw conclusions on the superiority of the organophosphorus or of other complexones. On the whole the acyclic organophosphorus complexones surpass their carboxyl-containing analogues in selectivity by, on average, one order and the cyclopendants by two orders of magnitude.



(LXV)

The effect of change of size and conformational rigidity of the cyclic fragments is shown in the efficiency and selectivity of complex-formation of the cyclopendant complexones. The complex-formation of compounds (LXV, 1–8), having the same pendant groups and various cyclic fragments, has been studied.[94] Values of *A* and *S* are given in Table 17 for two sets of cations. The change in the size of the cyclic fragment has the most striking effect on *A* and *S*. On going from ligand 1 to 2 and 3, and also from 6 to 7 the efficiency falls sharply. The selectivity may increase or decrease during this. The introduction of alkyl substituents into the bridge shows up negatively on the selectivity of action in relation to the second group of cations, the efficiency of binding is reduced to the same extent. There are no such regularities when using the TM although here also an increase in the bulk of the alkyl substituent in the bridge reduces the efficiency of complex-formation (cf. ligands 4, 5 and 6 in Table 17). Complexones (LXV, 1–8) display interesting complex-forming properties. Complexone (LXV, 1) forms the most stable complex with the Ca^{2+} ion of the known complexones ($\lg K_{st} = 15.9$). Complexone (LXV, 3) has the maximal difference in stability constant for complexes with Mg^{2+} and Ca^{2+} (values of $\lg K_{st}$ for these complexes were 3.0 and 9.5 respectively). The best linear complexone in this respect (LXVI) forms complexes with Mg^{2+} and Ca^{2+} cations with $\lg K_{st}$ 5.21 and 10.97 respectively.[182]



(LXVI)

Table 16. Values of *A* and *S* of complex-formation of organophosphorus and carboxyl-containing complexones.

Complexone	X	*A* Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	*S* Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	*A* Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	*S* Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	*A* Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	*S* Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}
$XCH_2NCH_2CH_2NCH_2X$ (H, H)	PO_3H_2	see *	see *	12.2	4.6	–	–
	COOH	–	–	11.9	4.1	–	–
$XCNHCH_2CH_2NHCX$ (Me, Me)	PO_3H_2	see *	see *	12.8	5.4	–	–
	COOH	–	–	9.9	3.2	–	–
XCH_2 CH_2X NCH_2CH_2N XCH_2 CH_2X	PO_3H_2	–	–	17.6	4.7	–	–
	COOH	9.0	11.4	16.7	2.4	16.6	2.0
		6.9	0.6	14.2	3.9	–	–
XCH_2NCH_2X CH_2X	PO_3H_2	(7.1) **	(0.9) **				
	COOH	5.4	0.9	10.6	2.5	10.5	2.2
XCH_2–N N–CH_2X N CH_2X	PO_3H_2	6.8	3.5	20.4	3.7	20.7	3.4
	COOH	7.6	2.6	–	–	17.1	2.4
XCH_2–N N–CH_2X XCH_2–N N–CH_2X	PO_3H_2	9.1	1.7	21.4	4.6	22.4	3.7
	COOH	12.8	2.7	18.3	0.9	18.8	0.8
XCH_2–N N–CH_2X XCH_2–N N–CH_2X	PO_3H_2	see *	see *	17.2	6.8	17.1	5.8
	COOH	5.8	3.6	15.2	3.1	15.1	2.7

* $\lg K_{st}$ for complexes of Mg^{2+} and the alkaline earth elements < 2.
** Data.[144]

The increase in dentate number in the case of ligand 8 did not lead to an increase in the value of A but this compound forms a more stable complex with the Ba^{2+} ion than with Ca^{2+} and Sr^{2+}, which is also unusual for the classic (linear) complexones.

Table 17. Values of A and S of complex-formation of compounds (LXV, 1–8).

№ Ligand in (LXV)	X in (LXV)	Y in (LXV)	A	S	A	S
			Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}		Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	
1	CH_2CH_2	CH_2CH_2	12.8	2.7	19.0	0.6
2	CH_2CH_2	$CH_2CH_2CH_2$	8.1	2.2	15.8	1.5
3	$CH_2CH_2CH_2$	$CH_2CH_2CH_2$	5.8	3.6	15.9	1.7
4	CH_2CH_2	CH_2CHCH_2 (Me)	9.3	2.5	17.5	0.6
5	CH_2CH_2	CH_2CHCH_2 (Et)	6.8	1.2	13.8	1.8
6	CH_2CH_2	CH_2CCH_2 (Me, Me)	4.0	0.7	7.5	0.9
7	$CH_2CH_2CH_2$	CH_2CCH_2 (Me, Me)	2.8	0.4	7.5	1.8
8	$(CH_2CH_2)_2N$ (Ac)	$(CH_2CH_2)_2N$ (Ac)	7.4	1.5	15.2	0.7

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