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PROGRESS IN THE THERMODYNAMICS OF COPPER(II) POLYAMINE COMPLEXES

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The stability of transition metal complexes with aliphatic multidentate ligands is dependent, to a large extent, on the size of the chelate rings, and it is well known that complexes containing five-membered rings are more stable than analogous complexes with six-membered rings

Such difference in stability is currently explained in terms of a higher strain in the six-membered than in five-membered rings[1]. Attempts to quantify the different effects which define the conformations of the chelate rings were first made by Corey and Bailar[2], and have been further developed by Gollogly and Hawkins[3] in their investigation of metal–diamine systems Two of the more important terms which influence the stability of the metal diamine cycle are the angle bending energy and the bond length distortion energy, which depend on the deviation from the normal undistorted parameters Examination of crystallographic data allows us to carry out an a posteriori analysis of the relative energies and stabilities of metal complexes containing five- or six-membered rings Figure 1 reports some structural parameters of the complexes $[Cu(en)_2]^{2+}$ (ref 4) and $[Cu(tn)_2]^{2+}$ (ref. 5) (en = ethylenediamine, tn = trimethylethylenediamine), with their thermodynamic functions

It can be seen that in the bis(ethylenediamine) complex, containing five-membered rings, there is no appreciable distortion of the angle and bond lengths in the aliphatic chain

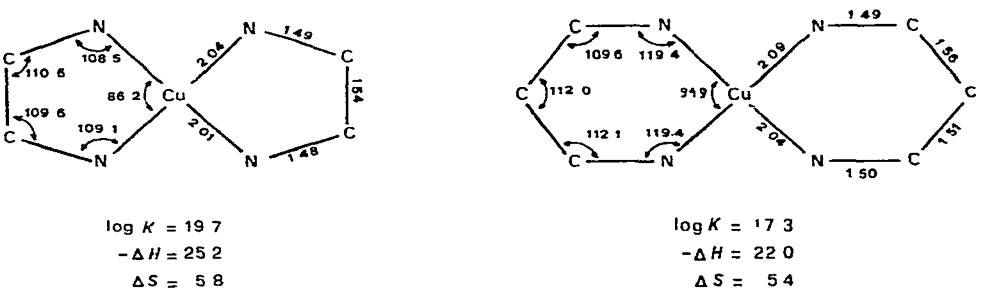

Fig 1 Thermodynamic and structural parameters for the complexes $[Cu(en)_2]^{2+}$ and $[Cu(tn)_2]^{2+}$ (Thermodynamic data from refs 6 and 7, structural data for $[Cu(en)_2](NO_3)_2$ from ref 4 and for $[Cu(tn)_2](NO_3)_2$ from ref 5)

and the angles CNCu and NCuN are only slightly distorted from the normal values of 109.5° and 90°. On the other hand, in the bistrimethylenediamine complex, involving six-membered metal diamine rings, there are appreciable distortions of the angles from the expected values. The energy terms mentioned above which affect the stability of a chelate complex are of course enthalpies. In fact, the higher thermodynamic stability of complexes having five-membered rings measured by log K values is entirely due to a more favourable enthalpy term (Fig. 1).

A. COMPLEXES CONTAINING LINKED CONSECUTIVE CHELATE RINGS

(i) Terdentate ligands

When two or more rings are fused, further steric constraints are introduced and a decrease of the heat of formation is expected. For example, the 1:2 complex formed by nickel(II) with the terdentate ligand 2,2'-diaminodiethylamine (den)[8], which contains two linked consecutive five-membered rings, exhibits a lower heat of formation than the analogous complex $[Ni(en)_3]^{2+}$ (ref. 7), which has individual five-membered rings (25.3 and 27.9 kcal mole^{-1}, respectively). Similarly $[Ni(dpt)_2]^{2+}$ (dpt = 3,3'-diaminodipropylamine)[9] which has two six-membered fused rings, has a lower heat of formation than $[Ni(tn)_3]^{2+}$ (ref. 7) (17.6 and 21.7 kcal mole^{-1}).

(ii) Quadridentate ligands

In the case of complex formation with quadridentate ligands which have three fused rings, the difficulty in occupying the coordination sites becomes greater and an increase of the steric constraints in the ring system is expected. The crystal structure of the nickel(II) complex with the linear triethylenetetramine (trien)[10] shows the difficulty of the ligand in spanning the square planar coordinative positions, the four nitrogen atoms are coplanar but deformed towards a trapezoidal arrangement and the central five-membered ring is present in an eclipsed rather than in the normal *gauche* form. The steric constraints imposed in this ligand in the square planar coordination reflect in the enthalpy of complex formation. The complex $[Cu(trien)]^{2+}$ (ref. 11), for example, has a heat of formation rather lower than the reference complex $[Cu(en)_2]^{2+}$ (ref. 6), with separated five-membered rings (Table 1). Similarly the complex $[Cu(3,3,3)\text{-tet}]^{2+}$ (ref. 12) (3,3,3-tet = *N,N'*-bis(3-aminopropyl)-1,3-propanediamine), with three consecutive six-membered rings, has a heat of formation lower than that of $[Cu(tn)_2]^{2+}$ (ref. 7), with separated rings (Table 1).

The progressive linking of chelate rings involves a decrease in the heat of complex formation, as we have seen, but this is only true when the consecutive rings have the same number of atoms, i.e. either all five-membered or all six-membered. The copper complex with the tetramine (2,3,2)-tet (2,3,2-tet = *N,N'*-bis(2-aminoethyl)-1,3-propanediamine), which has two external five-membered rings and a central six-membered ring, is much more stable[13] than the corresponding complexes with the homologous tetramine trien and this is

TABLE 1

Reactions of copper(II) ion with linear aliphatic four-coordinate polyamines in aqueous solution at 25°C thermodynamic functions ΔG, ΔH and ΔS

Reaction	$-\Delta G$ (kcal mole^{-1})	$-\Delta H$ (kcal mole^{-1})	ΔS (cal mole^{-1} deg^{-1})
Cu^{2+} + trien $\rightleftarrows$ $[Cu(trien)]^{2+}$ [a]	27.4	21.6	19.5
Cu^{2+} + (3,3,3)-tet $\rightleftarrows$ $[Cu(3,3,3)\text{-tet}]^{2+}$ [b]	23.3	19.5	12.8
Cu^{2+} + (2,3,2)-tet $\rightleftarrows$ $[Cu(2,3,2)\text{-tet}]^{2+}$	32.6 [c]	27.7 [d]	16.5 [d]
Cu^{2+} + 2 en $\rightleftarrows$ $[Cu(en)_2]^{2+}$ [e]	26.9	25.2	5.8
Cu^{2+} + 2 tn $\rightleftarrows$ $[Cu(tn)_2]^{2+}$ [f]	23.6	22.0	5.4

[a] Ref. 11 (0.1 *M* KCl), [b] ref. 12 (0.1 *M* $NaNO_3$), [c] ref. 13 (0.5 *M* KCl), [d] this work (0.5 *M* KCl), [e] ref. 6 (0.5 *M* KNO_3), [f] ref. 7 (0.3 *M* $NaClO_4$)

due to an exceptionally high heat of reaction (Table 1). The complex $[Cu(trien)]^{2+}$ could be considered as derived from $[Cu(en)_2]^{2+}$ by joining two nitrogens with an ethylenic chain. Introducing this ethylenic chain leads to steric strain in the external five-membered rings, which we shall call girdle strain, this unfavourable steric effect is reflected, as shown above, in a decrease in the heat of formation. However, the introduction of a methylene group in the central chain, as occurs in the complex $[Cu(2,3,2)\text{-tet}]^{2+}$, removes the girdle strain and the other steric constraints generated by it, so that the heat of formation and hence the stability of this complex are increased relative to trien complex (Table 1).

However, it is apparently surprising that the complex $[Cu(2,3,2)\text{-tet}]^{2+}$ has a larger heat of formation than $[Cu(en)_2]^{2+}$ itself. Thus we have a case where the formation of a complex with linked rings has a greater thermal effect than the formation of a complex with separated rings, which we have previously considered to be the more favourable case because it is the less sterically hindered. The difference in the enthalpy values parallels the increase of the strength of the ligand field (the visible absorption maxima in aqueous solution of the complexes $[Cu(en)_2]^{2+}$ and $[Cu(2,3,2)\text{-tet}]^{2+}$ are 18.2 and 19.0 kK, respectively)[14]. Probably the increase of the heat of reaction reflects the crystal field stabilisation of the copper(II) ground state owing to a more enhanced tetragonal distortion.

It is remarkable that the addition of another six-membered ring to the complex $[Cu(2,3,2)]^{2+}$ increases the stability even more. Thus the stability constant of the Cu^{II} complex with the cyclic tetramine tet-a (tet-a = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azocyclotetradecane)[15] is about 4 log units larger than the (2,3,2)-tet complex. In order to underline the exceptional stability of these complexes the term *macrocyclic effect* has been introduced. Because of the kinetic inertness of these compounds a full thermodynamic investigation is not possible. However, we can state that the macrocyclic effect is not a more extensive chelate effect, i.e. due to a favourable change in the translational entropy, but is due primarily to the enthalpy term.

(iii) Hexadentate ligands

The stabilizing effect of a central trimethylenic chain on the formation of linear aliphatic tetramine complexes does not occur in the formation of complexes with the aliphatic hexamine penten (*N,N,N′,N′*-tetra-(2-aminoethyl)-ethylenediamine) and p-tetraen[16] (*N,N,N′,N′*-tetra-(2-aminoethyl)-trimethylenediamine). These polyamines behave as hexadentate ligands with their donor atoms arranged at the corners of an octahedron. The resulting complexes have three linked chelate rings in the equatorial plane, as also occurs in the complexes with the tetradentate ligands, considered above (trien and its homologues), plus two rings in a plane containing the axial bonds. Unlike the case of the tetramines, the introduction of a methylenic group in the central equatorial ring causes a decrease in the stability of the complexes. In fact all the complexes formed by metal ions of the first transition series with p-tetraen, which has the sequence 5,6,5 in the equatorial rings, are less stable than the corresponding penten complexes in which all the rings are five-membered. Once again this decrease in stability is due to a less exothermic heat of formation as can be seen by comparing the respective ΔH values, for example, for $[\mathrm{Ni(penten)}]^{2+}$, $\log K = 19.16$, $-\Delta H = 19.65$ kcal mole^{-1}, $\Delta S = 21.5$ cal·mole^{-1} deg^{-1}, for $[\mathrm{Ni(p\text{-}tetraen)}]^{2+}$, $\log K = 18.46$, $-\Delta H = 19.29$ kcal mole^{-1}, $\Delta S = 19.8$ cal mole^{-1} deg^{-1}. It should be pointed out that these complexes are susceptible to electrophilic attack, and that the $\mathrm{Co^{III}}$ complexes in particular are also susceptible to nucleophilic attack by hydroxide ion.

An examination of the crystal structures of the nickel(II) complex with the analogous hexadentate ligand EDTA, $\mathrm{Ni(H_2EDTA)}$ (ref. 17) and $[\mathrm{Co(OH)penten}]\mathrm{I_2}$ (ref. 16) shows that in both cases these reactions lead to the opening of five-membered equatorial rings. The p-tetraen complexes are more resistant to attack by protons or hydroxide ion than the corresponding penten compounds, and $\mathrm{Co(p\text{-}tetraen)^{3+}}$ in particular is stable even in strongly alkaline solutions. The apparently surprising fact that the thermodynamically more stable penten complexes are more susceptible to electrophilic or nucleophilic attack than the less stable p-tetraen complexes must be attributed, once again, to the different effects of the steric strain. The crystal structure of the compound $[\mathrm{Co(penten)}]\,\mathrm{Co(CN)_6}\cdot 2\mathrm{H_2O}$ (ref. 18) has been reported and it was found that the external equatorial rings are the more sterically strained. This explains the opening of one of the equatorial rings in the reactions with protons and the hydroxide ion. The greater resistance of the p-tetraen complexes to electrophilic and nucleophilic attack can be explained by the reduction of strain in the external equatorial rings following the introduction of a methylenic group in the central equatorial ring. However, the expansion of the central equatorial ring probably gives rise to steric strain in the axial rings, sufficient to overcome the enthalpic gain due to the removal of the strain in the equatorial ring system. In the $\mathrm{Cu^{II}}$ complexes with these two hexamines only five of the nitrogen atoms are coordinated to the central metal ion. (For Cu(penten), $\log K = 22.15$, $-\Delta H = 24.5$ kcal mole^{-1}, $\Delta S = 19.0$ cal mole^{-1} deg^{-1}, for Cu(p-tetraen), $\log K = 21.10$, $-\Delta H = 22.73$ kcal mole^{-1}, $\Delta S = 20.7$ cal·deg^{-1} mole^{-1}.)

As has been explained, the open ring must be one of the external equatorial ones

Therefore the introduction of a methylene group in the central aliphatic ring is no longer able to remove the strain in the equatorial rings, with the resulting enthalpic gain, whilst the destabilizing effect of the axial rings remains This explains why in going from penten to p-tetraen, there is a larger decrease in the heat of formation of the five-coordinate Cu^{II} complex (1 8 kcal mole^{-1}) than in the formation of the corresponding hexacoordinate Ni^{II} complex (0 4 kcal mole^{-1})

B REACTIONS OF POLYAMINE COMPLEXES WITH SOME INORGANIC ANIONS

Copper(II) complexes of aliphatic tetraamines can coordinate a further anion to give five-coordinate species A crystallographic study of the solid compound [Cu(trien)(SCN)] (CNS) (ref 19) has shown it to have a square pyramidal structure with the Cu^{II} ion about 0 4 Å above the plane containing the four nitrogens of the organic ligand, and the fifth, apical, position occupied by the sulphur atom of a thiocyanate group Furthermore, the bond distances and bond angles of the tetramine molecule do not differ from those reported for Cu^{II} bis(ethylenediamine) complexes The elevation of the copper ion above the basal plane seems to remove the strain in the polyamine molecule, stretched to achieve a square-planar coordination In methanolic solution the solvent may cause this removal of the strain by the displacement of one of the two axial groups in 4 + 2 complexes of Cu^{II} ion and formation of a five-coordinate adduct[20] In some copper(II) bis(thiocyanate) complexes this effect also causes isomerization of the remaining thiocyanate group from being S- to N-bonded The same effect may also be obtained by substituting one thiocyanate group in the solid compound by a weakly coordinating group such as perchlorate[20] In order to determine which energy terms play an important role in the formation of pentacoordinate complexes, we have carried out a thermodynamic study of the equilibria of adduct formation in methanolic solution between square planar polyamine complexes and inorganic anions, according to the reaction

$$CuL^{2+} + X^{-} \rightleftharpoons CuLX^{+}$$

The polyamines considered were L = 2en, 2tn, (3,3,3-tet) and (2,3,2-tet), and X = iodide, thiocyanate and azide anions It can be seen that the enthalpies of formation are all positive or only slightly negative, and this is due to the endothermic desolvation process accompanying the reaction (Table 2) This unfavourable enthalpy contribution more than compensates for the much smaller contribution arising from the formation of the Cu–X bond However, these adduct formation reactions, whether they be considerably or only slightly endothermic, occur because of the favourable change in entropy which accompanies all reactions involving neutralization or partial neutralization of electric charge Thus the energy terms useful to explain the formation of pentacoordinate adducts in solution are exclusively entropy terms In general, the reactions involving the addition of thiocyanate ion are less endothermic and more entropic than those involving the iodide ion which in turn are less endothermic and more entropic than those involving the azide ion

TABLE 2

Adducts of copper(II) polyamine complexes with inorganic anions Thermodynamic functions ΔG, ΔH and ΔS for the reaction $[\mathrm{CuL}]^{2+} + \mathrm{X}^- \rightleftarrows [\mathrm{CuLX}]^+$ in methanolic solution at 25°C

CuL	X^-	ΔG (kcal mole^{-1})	ΔH (kcal mole^{-1})	ΔS (cal mole$^{-1}\cdot$deg^{-1})
$[\mathrm{Cu(en)_2}]^{2+}$	SCN^-	−3.0	1.8	15.9
	N_3^-	−3.5	3.5	23.5
	I^-	−2.5	2.8	17.9
$[\mathrm{Cu(tn)_2}]^{2+}$	SCN^-	−3.8	0.0	12.7
	N_3^-	−3.6	2.4	20.3
	I^-	−3.6	0.5	13.7
$[\mathrm{Cu(3,3,3)tet}]^{2+}$	SCN^-	−4.8	−0.7	13.8
	N_3^-	−4.3	1.6	19.6
	I^-	−4.4	−0.4	13.5
$[\mathrm{Cu(2,3,2)tet}]^{2+}$	SCN^-	−3.9	−0.8	15.7
	N_3^-	−3.5	3.3	22.9
	I^-	−3.6	1.2	16.0

The larger positive values of ΔS and ΔH for the complex formation with the N_3^- ion are in agreement with the fact that this ligand has a hydration sphere bulkier than iodide or thiocyanate ion[21] However, the thiocyanate ion has an entropy value similar to that of the iodide ion in all the series considered This agrees with the hypothesis that in solution all these complexes have the thiocyanate group bonded with the same S or N atom The different bonding atom would be expected to give different enthalpy and especially entropy effects, in fact, coordination involving the sulphur atom, the most probable site of the negative charge[22], would result in more effective neutralization of charge in the formation of the complex and a more positive ΔS

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