Thermodynamic Behaviour of Complexes with 5,6-Membered Condensed Chelate Rings: 1,4,8-Triazaoctane

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The enthalpies of the reactions, in 0·5M-KNO$_3$ at 25 °C, between the linear tri-amine 1,4,8-triazaoctane (2,3-tri) and nickel(II), copper(II), and zinc(II) ions have been determined by means of direct calorimetric titrations. By using the $\Delta G°$ values reported elsewhere the corresponding $\Delta S°$ values have been calculated. The ML complexes of (2,3-tri) which contain a system of condensed chelate rings with a 5,6-ring size sequence, have heats of formation higher than those of the corresponding complexes of (2,2-tri) (5,5-ring size sequence) and of (3,3-tri) (6,6-sequence). An analogous trend has already been observed in tetra-amine complexes. The importance of steric factors in the formation of the ML$_2$ complexes is discussed.

THE co-ordinating properties of quadridentate polyamines have been extensively studied by thermodynamic investigations.[1] In particular, the study of complexes with 5- and 6-membered alternating rings with tetra-amines has increased.[2] The great stability of these compounds in aqueous solution is mainly due to the enthalpy term whilst the high heat of formation originates in the ease with which these ligands co-ordinate to the metal ion in a strain-free configuration.[2]

In the work described here we have turned our attention to the triamine ligand 1,4,8-triazaoctane (2,3-tri),[†] in order to establish whether the formation of complexes containing an alternate sequence of only two, one penta and one exatomic, chelate rings is able to produce a higher enthalpy effect than that obtained from the analogous complexes with the (2,2-tri)[3] or (3,3-tri)[4] (elsewhere known as den and dpt) ligands which form only penta- or hexa-atomic rings. A previous potentiometric investigation[5] has shown that (2,3-tri) forms with Ni^{II}, Cu^{II}, Zn^{II} a higher number of complexes than that formed by the other two ligands (2,2-tri) and (3,3-tri) and that both copper(II) and nickel(II) complexes with (2,3-tri) are more stable than those with the analogous triamine ligands. A complete thermodynamic investigation allows for reliable conjecture on both the reasons why some complexes are formed and their stoicheiometries.

EXPERIMENTAL

Calorimetric Measurements.—The measurements were carried out with a LKB 8700/2 titration calorimeter. In order to study the formation of complexes with copper(II) and zinc(II), standard KOH was added to a

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[†] For convenient reference, linear triamines of the type NH$_2$[CH$_2$]$_n$NH[CH$_2$]$_m$NH$_2$ are denoted by the symbol (*n,m*-tri), tetra-amines of the type NH$_2$[CH$_2$]$_n$NH[CH$_2$]$_m$NH[CH$_2$]$_l$NH$_2$ by the symbol (*n,m,l*-tet).

[1] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta Rev.*, 1973, **7**, 43.

[2] (*a*) D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557; (*b*) L. Fabbrizzi, R. Barbucci, and P. Paoletti, *J.C.S. Dalton*, 1972, 1529; (*c*) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, 1973, **12**, 1861; (*d*) R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1973, 1763; (*e*) D. B. Gabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540; P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, 1973, **8**, 1962.

[3] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1961, 2994.

[4] P. Paoletti, F. Nuzzi, and A. Vacca, *J. Chem. Soc. (A)*, 1966, 1385.

[5] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, 1973, **7**, 157.

0·5M-KNO_3 solution containing the amine hydrochloride and the metal nitrate. The heats of formation of nickel(II) complexes were determined by an indirect method: the calorimetric vessel contained *ca.* 90 ml of a 0·5M-KNO_3 solution of the complex prepared 24 h earlier. The complexes were destroyed by adding an excess of nitric acid. Calorimetric data are reported in Table 1. The method of calculation has been already described.[2d] The stepwise heats of protonation used to calculate the enthalpies of complex formation are: $-\Delta H_1 = 12{\cdot}18$, $-\Delta H_2 = 12{\cdot}14$, $-\Delta H_3 = 9{\cdot}95$ kcal mol^{-1}. The details of the protonation results will be reported elsewhere.

TABLE 1

Calorimetric results for the metal complex formation of (2,3-tri) in 0·5M-KNO_3 at 25 °C

	Calorimetric vessel				Titrant added HNO_3		
Metal	H^+ mmol	M^{2+} mmol	(2,3-tri) mmol	Vol. mol	ml	mmol	Q [a] cal
Ni^{2+}	0·0418	0·9035	0·9400	89·40	10·00	4·4909	19·147
	0·0413	0·8933	0·9294	88·39	10·00	4·4909	19·110
	0·0414	0·8959	0·9321	88·65	10·00	4·4909	19·126
	0·0681	0·3869	0·9468	88·48	10·00	4·4909	21·235
	0·0683	0·3881	0·9504	88·81	10·10	4·5090	21·209
	0·0688	0·3909	0·9572	89·46	10·00	4·4909	21·265
	0·9282	0·8715	0·9244	90·18	10·00	4·4909	13·022
	0·9038	0·8486	0·9001	87·81	10·00	4·4909	12·740
	0·9081	0·8528	0·9046	88·25	10·00	4·4909	12·765
					KOH		
Cu^{2+}	3·0506	0·3454	1·0169	87·95	4·00	2·3224	13·327
	0·7282	0·3454	1·0169	91·95	4·00	2·3224	0·843
	3·0900	0·3248	1·0300	89·20	4·00	2·3224	12·906
	0·7676	0·3248	1·0300	93·20	4·00	2·3224	0·776
	1·5831	0·4745	0·5277	91·90	2·50	1·4515	12·404
	0·1316	0·4745	0·5277	94·40	2·50	1·4515	1·286
	1·5209	0·1072	0·5070	93·03	1·50	0·9290	4·752
	1·8605	0·1139	0·6202	90·36	2·00	1·1612	5·590
	0·6149	0·2415	0·5383	90·69	2·50	1·4515	8·436
	1·7560	0·2368	0·5853	89·96	2·50	1·4515	8·503
	3·3033	1·0199	1·1011	93·39	2·10	1·1313	9·825
	2·1720	1·0199	1·1011	95·49	2·10	1·1313	9·624
	3·4781	0·3831	1·1594	91·05	1·70	0·9158	7·947
	2·5623	0·3831	1·1594	92·75	4·20	2·2625	7·831
	3·2967	0·5498	1·0989	91·56	2·00	1·0774	9·298
	2·2193	0·5498	1·0989	93·56	4·30	2·3164	9·919
	3·0981	0·2768	1·0327	94·01	6·00	3·2322	12·711
	1·5930	0·4904	0·5310	89·55	2·50	1·4515	12·616
	0·1415	0·4904	0·5310	93·05	2·50	1·4515	1·678
	1·6341	0·5091	0·5447	89·23	2·50	1·4515	12·615
Zn^{2+}	3·0677	0·5071	1·0226	91·73	4·10	2·2087	9·774
	0·8590	0·5071	1·0226	95·83	4·10	1·5880	1·588
	3·0610	0·2843	1·0203	94·02	5·00	2·6935	9·609
	0·3675	0·2843	1·0203	99·02	4·00	2·1538	−0·562
	3·2398	0·9376	1·0799	90·84	6·00	3·2322	14·678
	3·1670	0·3099	1·0557	91·39	7·50	4·0403	9·738
	3·2676	0·5700	1·0892	90·52	7·50	4·0403	12·670

[a] Corrected for the heat of dilution of the titrant in 0·5M-KNO_3.

TABLE 2

Thermodynamic functions for the formation of metal complexes with three-co-ordinating polyamines in aqueous solution at 25 °C

	(2,3-tri) [a]			(2,2-tri) [b]			(3,3-tri) [c]		
Reaction	$-\Delta G°$ kcal mol^{-1}	$\Delta H°$ kcal mol^{-1}	$\Delta S°$ cal mol^{-1} K^{-1}	$-\Delta G°$ kcal mol^{-1}	$-\Delta H°$ kcal mol^{-1}	$\Delta S°$ cal mol^{-1} K^{-1}	$-\Delta G°$ kcal mol^{-1}	$-\Delta H°$ kcal mol^{-1}	$\Delta S°$ cal mol^{-1} K^{-1}
$Ni^{2+} + HL^+ \rightleftharpoons [NiHL]^{3+}$	7·99 (4)	7·79 (79)	0·7 (2·8)						
$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}$	15·320 (5)	13·54 (6)	5·9 (2)	14·45	11·85	8·5	12·53	10·56	6·6
$[NiL]^{2+} + L \rightleftharpoons [NiL_2]^{2+}$	9·63 (1)	13·73 (12)	−13·7 (4)	10·90	13·45	8·5	4·84	7·08	−7·5
$Cu^{2+} + HL^+ \rightleftharpoons [CuHL]^{3+}$	12·30 (3)	11·5 (1·5)	2·7 (5·0)						
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	22·639 (4)	19·22 (6)	11·5 (2)	21·55	18·00	12·0	19·38	16·09	11·0
$[CuL]^{2+} + L \rightleftharpoons [CuL_2]^{2+}$	4·47 (3)	6·1 (3)	−5·5 (1·1)	7·10	8·15	−3·5			
$[CuL]^{2+} + HL^+ \rightleftharpoons [CuHL_2]^{3+}$	3·42 (3)	5·9 (4)	−8·3 (1)4						
$[CuL]^{2+} + OH^- \rightleftharpoons [Cu(OH)L]^+$	6·44 (1)	2·28 (8)	13·9 (3)	6·14	2·70	11·5	5·65	2·28	11·3
$Zn^{2+} + L \rightleftharpoons [ZnL]^{2+}$	11·96 (1)	8·41 (7)	12·1 (3)	12·00	6·45	18·5	10·80	5·44	18·0
$[ZnL]^{2+} + L \rightleftharpoons [ZnL_2]^{2+}$	5·18 (4)	8·45 (28)	−10·9 (1·1)	7·50	10·15	−9·0			
$[ZnL]^{2+} + OH^- \rightleftharpoons [Zn(OH)L]^+$	6·80 (1)	0·05 (18)	22·6 (6)				7·10	3·77	11·2

[a] Values in parentheses are the standard deviations. [b] Ref. 3. [c] Ref. 4.

Materials.—The hydrochloride of the triamine (2,3-tri) was prepared as described elsewhere.[5] Solutions of potassium hydroxide, nitric acid, and metal nitrate were obtained and standardized as described.[6]

Complexes of Nickel(II).—Nickel(II) forms three complexes

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[6] A. Dei, P. Paoletti, and A. Vacca, *Inorg. Chem.*, 1968, **7**, 865.

of formula $[NiHL]^{3+}$, $[NiL]^{2+}$, and $[NiL_2]^{2+}$ with the ligand (2,3-tri) [5] and their enthalpies were all measured (Table 2). The $\Delta H°$ value of the reaction $Ni^{2+} + HL^{+} \rightleftharpoons [NiHL]^{3+}$ is lower than that obtained in the formation of the complex $[Ni(en)]^{2+}$ (8·90 kcal mol^{-1}) [7] but higher than that with the ligand propane-1,3-diamine: $[Ni(tn)]^{2+}$ (7·24 kcal mol^{-1}).[8] This comparison supports our previous suggestion [5] that the chelate ring in this complex is the 5-membered one.

By comparison of the thermodynamic functions relative to the reaction $Ni^{2+} + HL^{+} \rightleftharpoons [NiHL]^{3+}$ with those of the reaction $Ni^{2+} + L \rightleftharpoons [NiL]^{2+}$ (Table 2), we can deduce that the simple complex $[NiL]^{2+}$ possesses the full co-ordination of the nitrogen atoms of the ligand (2,3-tri). The higher heat evolved in the second reaction is indicative of a larger number of co-ordinated nitrogen atoms. Furthermore the reaction $Ni^{2+} + L \rightleftharpoons [NiL]^{2+}$ relative to the ligand (2,3-tri) exhibits a higher thermal effect than that relative to the analogous complexes $[Ni(den)]^{2+}$ and $[Ni(dpt)]^{2+}$: the formation of a complex with alternating 5,6-membered rings causes an increase of the enthalpy term with respect to the formation of complexes containing only 6,6- and even 5,5-membered rings: the presence of two alternate chelate 5,6-membered rings decreases the cumulative ring strain.[1] This behaviour had been already proved in complexes containing quadridentate ligands [2] and now, for the first time, it is verified with a ligand exhibiting lower denticity.

The addition of a second molecule of ligand, in the reaction

$$[Ni(2,3\text{-tri})]^{2+} + (2,3\text{-tri}) \rightleftharpoons [Ni(2,3\text{-tri})_2]^{2+}$$

takes place with $\Delta H°$ value equal, within the standard deviations, to that obtained in the first step (Table 2). This behaviour is in contrast with that obtained either with analogous ligands as den or with lower denticity ligands as ethylenediamine: [7] the addition of a second molecule of ligand usually gives rise to a higher $\Delta H°$ value. This was explained by assuming that the second molecule of ligand co-ordinates with release of a lower number of water molecules than that released during the first step. This lower desolvation (endothermic) process yields $-\Delta H_2 > -\Delta H_1$.

However the difference $(\Delta H_1 - \Delta H_2)$ relative to the nickel(II) complexes with the three ligands den, 2,3-tri, and dpt shows a decrease from den (1·60 kcal mol^{-1}) to 2,3-tri (0·19 kcal mol^{-1}) to dpt (-2·48 kcal mol^{-1}). This is indicative of steric hindrance between the two molecules of ligand, which increases with the length of the aliphatic chain. Moreover, we cannot exclude the possibility that the differences in the thermodynamic functions of the three complexes could also be attributed to different percentages of isomers of the complex $[NiL]^{2+}$ (where L is the triamine den, 2,3-tri, or dpt). Reilley *et al.* have recently shown [9] that den forms two different isomers with Ni^{II} ion in aqueous solution: facial and meridional; $-\Delta H°$ for the meridional $\rightleftharpoons$ facial reaction is almost zero, whilst $\Delta S°$ is positive.

Complexes of Copper(II).—There are five copper(II) complexes with the ligand (2,3-tri): $[CuHL]^{3+}$ and $[CuHL_2]^{3+}$, $[CuL]^{2+}$ and $[CuL_2]^{2+}$, and $[Cu(OH)L]^{+}$ the heats of formation for each of which we measured (Table 2). As for the Ni^{II} complexes, a comparison of $\Delta H°$ for the $[CuHL]^{3+}$ and $[CuL]^{2+}$ complexes accounts for the complete co-ordination of all three nitrogens in the simple complex.

Now let us consider the quadridentate ligand (3,2,3-tet): it forms two complexes with copper(II), $[Cu(3,2,3\text{-tet})]^{2+}$ and $[CuH(3,2,3\text{-tet})]^{3+}$.[2c] The difference of the enthalpies $\Delta H°(CuHL) - \Delta H°(CuL)$ (L = 3,2,3-tet or 2,3-tri) is the same, within experimental error, for the two ligands. The similarity of the values is confirmation that in the complex $[CuHL]^{3+}$ the nitrogen of the aliphatic chain belonging to the less-stable ring, *i.e.* the 6-membered one, is protonated. As for the Ni^{II} complex, the complex $[Cu(2,3\text{-tri})]^{2+}$ exhibits a higher enthalpy value than that of the two complexes $[Cu(den)]^{2+}$ and $[Cu(dpt)]^{2+}$ (Table 2). Then the enthalpy term is the one responsible for the higher stability constant of the complex with alternating 5,6-membered rings. The entropy term is practically constant along the series $[Cu(den)]^{2+}$, $[Cu(2,3\text{-tri})]^{2+}$, and $[Cu(dpt)].^{2+}$. Here the comparison of the thermodynamic functions is particularly significant since with this metal ion the tridentate ligand is equatorially disposed.[10] The unique isomer of the CuL complex is then the meridional one.

The heat of formation step for the second simple complex $[Cu(2,3\text{-tri})_2]^{2+}$ is lower than that for the corresponding complex $[Cu(den)_2]^{2+}$ for which an incomplete co-ordination of the second molecule has already been suggested (see Table 2).[3] This means that there is at least one free site of co-ordination in the $[Cu(2,3\text{-tri})_2]^{2+}$ complex. Moreover the overall heat of the reaction $Cu^{2+} + 2(2,3\text{-tri}) \rightleftharpoons [Cu(2,3\text{-tri})_2]^{2+}$ is higher than that relative to the formation of the complex $[Cu(Meen)_2]^{2+}$ (23·73 kcal mol^{-1}; Meen = *N*-methylethylenediamine) [11] where 4 nitrogen atoms are co-ordinated. This fact excludes the possibility that the complex $[Cu(2,3\text{-tri})_2]^{2+}$ has more than one free arm.

Together with the simple 1 : 2 complex, the complex $[CuH(2,3\text{-tri})_2]^{3+}$ is also formed. From a consideration of the relative thermodynamic functions for the two complexes two points can be made. (1) The enthalpy value of the reaction $[CuL]^{2+} + HL^{+} \rightleftharpoons [CuHL_2]^{3+}$ is very close to that obtained for the reaction $[CuL]^{2+} + L \rightleftharpoons [CuL_2]^{2+}$. This is confirmation that the second molecule of 2,3-tri is not completely co-ordinated to the Cu^{II} ion in the complex $[CuL_2]^{2+}$; further, it means that the presence of a charge on the non-co-ordinated amino-group does not affect the heat of formation of the other 5-membered ring. (2) The entropy value is lower. This is due both to the greater orientating power of the triply-charged $[CuHL_2]^{3+}$ complex toward the solvent molecules and to a greater rigidity of the aliphatic chain bonded to the protonated nitrogen.[12]

Finally the thermodynamic functions relative to the reaction

$$[Cu(2,3\text{-tri})]^{2+} + OH^{-} \rightleftharpoons [Cu(OH)(2,3\text{-tri})]^{+}$$

are very similar to those obtained for the analogous $[Cu(OH)(den)]^{+}$ and $[Cu(OH)(dpt)]^{+}$ complexes. A difference in bulkiness of the polyamine ligand should

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[7] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1960, 4453.

[8] F. Holmes and D. R. Williams, *J. Chem. Soc.* (*A*), 1967, 1702.

[9] R. F. Evilia, D. C. Young, and C. N. Reilley, *J. Co-ordination Chem.*, 1973, **3**, 17.

[10] F. Stephens, *J. Chem. Soc.* (*A*), 1969, 2233, 2493.

[11] R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1972, 740.

[12] D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc.* (*A*), 1952, **215**, 416.

not disturb the addition of a hydroxo-group to the CuL complex (see Figure 1).

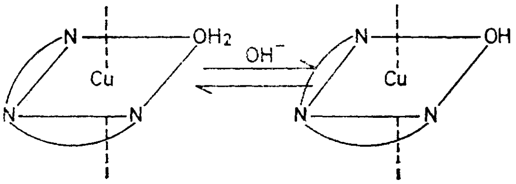

FIGURE 1

Complexes of Zinc(II).—The complex $[Zn(2,3\text{-tri})]^{2+}$ shows a higher $\Delta H°$ value than that for the corresponding $[Zn(den)]^{2+}$ and $[Zn(dpt)]^{2+}$ complexes (Table 2), behaviour analogous to that already seen for the Cu^{II} complexes; its entropy is however the lowest of the three complexes. This behaviour, which appears anomalous in comparison with that of the copper(II) complexes, suggests for $[Zn(2,3\text{-tri})]^{2+}$ a stereochemistry different from the tetrahedral one shown in both the $[Zn(den)]^{2+}$ [3] and $[Zn(dpt)]^{2+}$ [4] complexes in aqueous solution. Indeed a co-ordination number greater than 4 should account both for the smaller number of water molecules released during the reaction and the lower $\Delta S°$ value. It is then likely that the $[Zn(2,3\text{-tri})]^{2+}$ complex has an octahedral structure with water molecules completing the co-ordination sites. In this connection it is to be remembered that Zn^{II} complexes with alternating ring sequence 5,6,5 [2b] or 6,5,6 [2d] of quadridentate ligands exhibit, in aqueous solution, a co-ordination number greater than 4, with co-ordinated water molecules, whilst $[Zn(2,2,2\text{-tet})]^{2+}$ with three consecutive 5-membered rings, forms a tetrahedral complex.[13] The octahedral stereochemistry of $[Zn(2,3\text{-tri})]^{2+}$ is supported by the thermodynamic values of the $[Zn(OH)(2,3\text{-tri})]^{+}$ complex. Its enthalpy is lower than that of the analogous $[Zn(OH)(dpt)]^{+}$ complex, whilst the entropy is higher (Table 2).

The introduction of a charged group in the co-ordination sphere would give rise to a tetrahedral complex in both cases (see Figure 2).

As a matter of fact the process of OH addition is less exothermic and more entropic for the first than for the second complex. This is due to a greater release of solvent molecules for the $[Zn(OH)(2,3\text{-tri})]^{+}$ complex, as a consequence of the different stereochemistry of the original complex. Zinc(II) also bonds a second molecule of (2,3-tri), forming the complex $[Zn(2,3\text{-tri})_2]^{2+}$. Its enthalpy value is very similar to that obtained in the first step. Therefore the thermodynamic behaviour of this complex becomes equal to that of nickel(II), thus supporting the hypothesis of octahedral co-ordination.

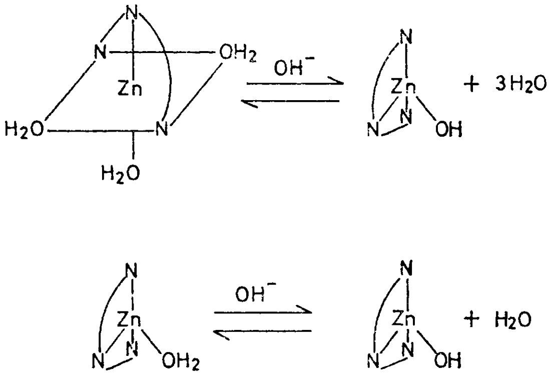

FIGURE 2

[4/064 *Received*, 15th *January*, 1974]

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[13] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115.