Contribution from the Istituto di Chimica Generale ed Inorganica dell'Università and Laboratorio del CNR, via I. Nardi 39, Firenze, Italy

Size of the Chelate Rings and Stability of Some Transition Metal^{II} Ion Complexes with Linear Aliphatic Triamines: 1,4,8-triazaoctane(2,3-tri)

R. Barbucci, L. Fabbrizzi, and P. Paoletti

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The basicity constants of 1,4,8-triazaoctane (2,3-tri) were determined in 0.5 M *KNO_3 at 25.0° C potentiometrically, using a glass electrode. The equilibria between (2,3-tri) and Ni^{2+}, Cu^{2+}, Zn^{2+} ions were investigated under similar conditions. The stability constants show that the complexes ML^{2+} with this unsymmetrical ligand are more stable than the complexes with the symmetrical ligands: 1,4,7 triazaeptane (2,2-tri) and 1,5,9 triazanonane (3,3-tri). This behaviour seems to be due to the alleviation of the strain present in the complexes of the last two ligands. In addition to the simple complexes ML^{2+} and ML_2^{2+}, Cu^{2+} and Zn^{2+} give at high pH hydroxo complexes $MLOH^+$. Cu^{2+} and Ni^{2+} also form protonated complexes $CuHL_2^{3+}$, $CuHL^{3+}$ and $NiHL^{3+}$.*

Introduction

It has been clearly demonstrated that the stability of the complexes formed from metal ions and linear aliphatic tetramines is greater when the three chelate rings are 5-membered than when they are 6-membered. One might therefore have expected that complexes with a ligand such as (2,3,2-tet),[*] which contain a sequence of 5,6,5 membered rings, would have a stability intermediate between those of (2,2,2-tet) (this ligand is also known as trien) and (3,3,3-tet). The fact is, however, that (2,3,2-tet) forms stronger complexes with Ni^{2+} and Cu^{2+} than does (2,2,2-tet).[1] This result has been ascribed to the effects due to the introduction of the extra methylene group upon the strain within the coordinated ligand. It was thought, therefore, that a similar difference in stability in favour of complexes containing alternating 5- and 6-membered rings might also be encountered in the complexes of the tridentate ligand (2,3-tri). A partial investigation of this unsymmetrical ligand[2] appeared to show that the complex $[Ni(2,3\text{-tri})]^{2+}$ had the same formation constant as the complex $[Ni(2,2\text{-tri})]^{2+}$. This seemed strange since X-ray structure determinations have shown that both the Ni^{2+}[3] and Cu^{2+}[4] complexes with (2,2-tri) are rather strained and some relief of this strain might be expected when one of the polymethylene chains is lengthened.

Thus, we have remeasured the formation constants of the complexes of (2,3-tri) with Ni^{2+}, and have also measured the formation constants of the Cu^{2+} and Zn^{2+} complexes.

Experimental Section

(2,3-tri) (Aldrich Co.) was purified as the hydrochloride, which was recrystallized from ethanol and dried to constant weight at 60°C, in vacuo (Found: Cl 46.8%, $C_5H_{16}N_3Cl$ requires 46.9%). Solutions of potassium hydroxide, nitric acid and metal nitrate were obtained and standardised as previously described.[5,6] The potentiometric titrations were performed using a Radiometer PHM5 digital potentiometer, a Radiometer G 2025/B glass electrode, a 0.1 *M* calomel electrode and a salt bridge containing 0.5 *M* KNO_3 solution, following the procedure previously described.[6] All the potentiometric experiments were carried out at 25.0°C in 0.5 *M* KNO_3.

The protonation constants were derived from 172 data points obtained in three titrations. For the metal complexes 210 (Cu^{2+}), 200 (Ni^{2+}) and 151 (Zn^{2+}) data points were used. The concentration conditions are given in Table I. The ligand/metal ratios varied between 1:1 and 1:0.2. The program LEAST which was used to calculate the constants has been described elsewhere,[7] and may be obtained as there described. Species introduced into the calculations, but later rejected for lack of computational evidence to support them were: Cu_3L_2, $Cu_2L_2(OH)_2$, Ni_2L_3, $NiHL_2$ and $NiL(OH)$. Rejection of other species always gave a significantly poorer fit of the experimental data, and higher standard deviations for the formation constants. The three protonation constants and

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(*) Linear aliphatic tetramines of the type $H_2N(CH_2)_nNH(CH_2)_mNH(CH_2)_pNH_2$ are denoted by the symbol (n, m, p-tet). Triamines of the type $H_2N(CH_2)_nNH(CH_2)_mNH_2$ are denoted by the symbol (n, m-tri).

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Table I. Experimental details of the potentiometric measurements. Initial concentrations $(\text{mol l}^{-1}\times 10^{2})$

Cation	L:M ration	[L]	$[M^{2+}]$	$[H^{+}]$	pH range
Zn^{2+}		1.2736		3.9570	3.0-10.9
H^{+}		1.2996		4.0350	3.0-10.8
		1.0451		3.1350	4.6-10.9
—	1:1	0.8983	0.8170	2.8402	2.9-10.8
Cu^{2+}	1:0.5	0.9030	0.3912	2.8627	3.0-10.8
	1:0.5	1.0533	0.4286	3.3100	3.0-10.8
	1:0.25	1.1038	0.2863	3.3620	3.6-10.8
	1:0.5	0.9076	0.4737	2.9283	2.9-10.8
	1:0.5	0.8400	0.4906	2.6767	3.C-10.8
	1:0.2	1.0282	0.2061	3.2877	2.9-10.9
	1:0.2	1.0048	0.1846	3.1806	3.0-10.8
Ni^{2+}	1:0.5	0.9261	0.3847	2.9176	3.0-10.8
	1:1	0.9171	0.7414	2.9022	3.1-10.8
	1:0.2	1.0416	0.1651	3.2886	2.9-10.8
	1:0.5	1.0530	0.5031	3.3069	3.1-10.9

Table II. Tipycal Computer Output containing three points of the 1:1 Curve for the system Ni^{II}/(2,3)-tri in Table I.

1	2	3	4	5	6	7	8	9	10
72	2.70	—88.1	0.134×10^{-9}	0.0000045	—0.0000098	0.0000041	8.5	48.8	0.0
73	2.90	—90.9	0.189×10^{-10}	0.0000015	—0.0000038	0.0000019	8.4	53.9	0.0
74	3.10	—93.9	0.432×10^{-10}	0.0000036	0.0000046	—0.0000029	8.2	59.2	0.0

Column Number: 1) Order Number; 2) Volume (ml) of KOH standard solution added; 3) Value of the potential (mV) of the glass electrode; 4) Value of partial U;[6] 5) Value of ΔT_{H};[6] 6) Value of the ΔT_{M};[6] 7) Value of ΔT_{L};[6] 2) Percentage of the $[NiHL]^{3+}$ species; 9) Percentage of $[NiL]^{2+}$ species; 10) Percentage of $[NiL_2]^{2+}$ species.

Table III. Basicity constants of linear altiphatic triamines and stability constants of their metal complexes at 25°C.

Ion	Reaction	2,3 tri [a]	2,2-tri [b]	3,3-tri [c]
H^{+}	$H^{+}+L\leftrightarrows HL^{+}$	10.437(2)	9.79	10.65
	$H^{+}+HL^{+}\leftrightarrows H_2L^{2+}$	9.356(6)	8.98	9.57
	$H^{+}+H_2L^{2+}\leftrightarrows H_3L^{3+}$	6.374(8)	4.25	7.72
Ni^{2+}	$Ni^{2+}+HL^{+}\leftrightarrows NiHL^{3+}$	5.86 (3)		
	$Ni^{2+}+L\leftrightarrows NiL^{2+}$	11.234(4)	10.60	9.19
	$NiL^{2+}+L\leftrightarrows NiL_2^{2+}$	7.06 (1)	7.99	3.55
Cu^{2+}	$Cu^{2+}+HL^{+}\leftrightarrows CuHL^{3+}$	9.02 (2)		
	$Cu^{2+}+L\leftrightarrows CuL^{2+}$	16.601(3)	15.80	14.20
	$CuL^{2+}+L\leftrightarrows CuL_2^{2+}$	3.28 (2)	5.21	
	$CuL^{2+}+HL^{+}\leftrightarrows CuHL_2^{3+}$	2.51 (2)		
	$CuL^{2+}+OH^{-}\leftrightarrows CuLOH^{+}$	4.72 (1)	4.50	4.1
Zn^{2+}	$Zn^{2+}+L\leftrightarrows ZnL^{2+}$	8.770(8)	8.80	7.92
	$ZnL^{2+}+L\leftrightarrows ZnL_2^{2+}$	3.80 (3)	7.44	
	$ZnL^{2+}+OH^{-}\leftrightarrows ZnLOH^{+}$	4.99 (1)		5.2

[a] in 0.5 *M* KNO_3, the values in parentheses are the standard deviations. [b] Ref. 8 in 0.1 *M* KCl. [c] Ref. 9 in 0.1 *M* KCl.

the experimenally measured ionic product of water were held constant during the calculation of the complex formation constants. A tipycal computer output of the 1:1 curve in the system Ni^{2+}/(2,3-tri) is given in Table II. The data relating to all the 733 data points can be obtained on request to the authors.

Results and Discussion

Protonation. The basicity constants of (2,3-tri) are shown in Table III. The agreement with the values obtained by Margerum at 25°C in 0.5 *M* KCl[2] is not very satisfactory: our values are up to 0.4 log units higher. This difference cannot be simply due to the different inert salt used to maintain the ionic strength. Our values for (2,3-tri) are intermediate between those of (2,2-tri)[8] and (3,3-tri),[9] with the biggest difference in the constant relating to the attachment of the third proton. In the latter process the most important factor is the electrostatic repulsion between the positively charged groups, in that the third proton must approach a molecule rendered somewhat less flexible by the repulsion between the two positively charged nitrogen atoms. Schwarzenbach's effective dielectric constant, ε_{eff} must therefore be small.[10] The flexibility of the molecule, and therefore ε_{eff}, increases considerably as the distance between the charges increases, that is as the aliphatic chain lengthens from (2,2-tri) to (2,3-tri) to (3,3-tri).

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Complex Formation. The complexes which we have ascertained to be present at some point in the titrations are: $CuHL^{3+}$, CuL^{2+}, CuL_2^{2+}, $CuHL_2^{3+}$, $CuL(OH)^+$; ZnL^{2+}, ZnL_2^{2+}, $ZnL(OH)^+$; $NiHL^{3+}$, NiL^{2+} and NiL_2^{2+}. The complex $NiHL^{3+}$ was not characterised by Margerum.[2] The distribution curves for all three metals are given in Figure 1, 2, and 3.

MHL^{3+} Complexes. This type of complex has been characterised for nickel and for copper in low pH regions. The equilibrium constant for the reaction $ML^{2+}+H^+\leftrightarrows MHL^{3+}$ varies, when M = Ni, in the order Me_7(2,2,2,2tetra)[11] > penten[12] > ptetraen[13] > (2,3-tri) > (2,2,2,2-tetra)[14] while when M = Cu the order is different, ptetraen > penten > Me_7(2,2,2,-tetra) > (2,2,2,2-tetra), (2,2,2-tri)[15] > (2,3-tri), where Me_7-(2,2,2,2-tetra) = tetraethylenepentamine eptametylated, penten = N,N,N′,N′-tetra(2-aminoethyl)ethylenediamine, ptetraen = N,N,N′,N′-tetra(2-aminoethylpropylenediamine). The amine Me_7(2,2,2-tetra) (otherwise known as Me_7-tetren) forms only weak complexes because of the steric hindrance to coordination produced by the N-methyl groups. It is therefore logical that Me_7-tetren should form the most easily protonated complex. With copper, however, one nitrogen atom of ptetraen[13] or penten[12] is not coordinated at all, and therefore the copper complexes of these ligands protonate the most easily. Complexes of (2,3-tri) with both metals are weakly protonated, which would seem to indicate that they are particularly stable. It is strange, however, that (2,3-tri), which forms stronger 1:1 complexes with Ni and Cu than do (2,2-tri) and (3,3-tri) should also form more strongly protonated 1:1 complexes (Table II). This apparent disparity can be explained by considering in more detail the protonation process. The proton may attack any one of three different sites leading to the formation of three different protonated 1:1 complexes of (2,3-tri), because of the unsymmetrical nature of the ligand. (2,2-tri) and (3,3-tri) can form only two isomeric protonated complexes. There are four factors which can determine which protonated form is predominant in MH(2,3-tri):

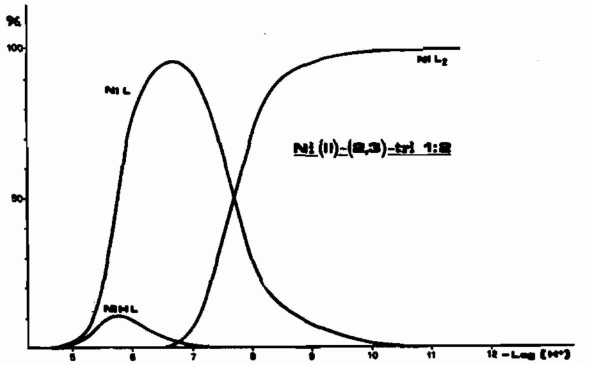

Figure 1. Distribution curves of Ni^{II}(2,3-tri) complexes. Ligand: metal ratio 1:0.5. The curves of the free Ni^{2+}ion was not reported.

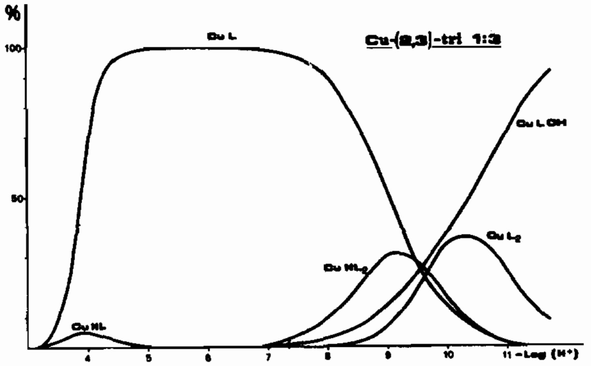

Figure 2. Distribution curves of Cu^{II}(2,3-tri) complexes. Ligand: metal ratio 1:0.25. The curves of the free Cu^{2+}ion was not reported.

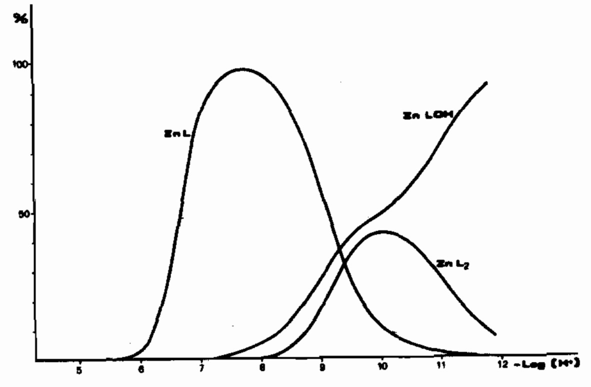

Figure 3. Distribution curves of Zn^{II}(2,3-tri) complexes. Ligand: metal ratio 1:0.5. The distribution curve of the free Zn^{2+}ion was not reported.

(i) The nitrogen atom at the end of the trimethylene chain has a pK value of 10.27 (obtained from the formula of Clark and Perrin[16] which gives the pK for individual nitrogen atoms) and is therefore more basic than the central nitrogen atom (pK 9.95) and the other terminal nitrogen atom (pK 9.82).

(ii) The protonation of the nitrogen atom at the end of the trimethylene chain opens the least stable six-membered chelate ring and leaves the five-membered ring intact.

(iii) The ammonium group so formed is at the greatest possible distance from the positive charge on the central metal ion.

(iv) The protonation of the central nitrogen atom would give rise to an unstable 9-membered chelate ring.

The type of protonated complex formed is determined by all four factors. With (2,2-tri) the complex MHL^{3+} is not formed on account of factor (iii), that is, because of electrostatic repulsion between the ammonium group and the central metal cation, whereas with (3,3-tri) protonation of a terminal nitrogen atom would leave the complex with only one relatively unstable six-membered ring.

If one compares the reaction of Ni^{2+} and Cu^{2+} with

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the bidentate ligands (2,3-triH)$^+$ or with ethylene diamine[17,18] the constant for the formation of the former complexes is 1.7 log units lower for both metals, showing that the electrostatic effects operative in this reaction are the same for both metals.

ML^{2+} Complexes. All three ligands (2,2-tri), (2,3-tri) and (3,3-tri) form 1:1 complexes with Ni^{2+}, Cu^{2+} and Zn^{2+}. The stability of the complexes follows the usual order Cu>Ni>Zn (Table III). The ligand stability order for the copper and nickel complexes is (2,3-tri)>(2,2-tri)>(3,3-tri). This shows that a sequence of 5- and 6-membered connected chelate rings is more stable than two 5-membered rings. Thus, the results obtained with tridentate ligands are analogous to those obained[1,15,19] with the tetradentate ligands described in the introduction, in that complexes with mixed 5- and 6-membered rings are more stable than complexes with only 5- or only 6-membered rings.

The stability of the Zn^{2+} complexes follows the order Zn(2,2-tri) ≃ Zn(2,3-tri) > Zn(3,3) and this trend is similar to the one found with the tetrammines Zn-(2,3,2-tet)[1] ≃ Zn(2,2,2-tet)[15] > Zn(3,3,3-tet).[19] The difference in the order of ligands compared to the copper and nickel cases has been explained on the basis that the zinc complexes have a tetrahedral stereochemistry.

ML_2^{2+} Complexes. The equilibrium constants for the reaction $ML^{2+} + L \leftrightarrows ML_2^{2+}$ are given in Table III. The complexes $Zn(2,3\text{-tri})_2$ and $Cu(2,3\text{-tri})_2$ have a small range of existence, as shown in Figures 2 and 3, because of competition with the formation of the hydrolyzed complex $ML(OH)^+$. The fact that the hydrolyzed complex is formed at the expense of 1:2 complex clearly shows that the 1:1 complex can accept a hydroxyl group more easily than a second polyamine ligand. Steric factors must play an important role in the formation of these complexes. This can also be seen in the fact that the step-wise formation constants for the addition of the second ligand (K_2) decrease in the order (2,2-tri)>(2,3-tri)>(3,3-tri), that is, they decrease with the increasing bulk of the ligands. The trend in K_2 is different from the trend in K_1.

K_2 for the copper complex is very small, and the difference (K_2-K_1) is the greatest in the copper complexes. This is consistent with the hypothesis that not all the nitrogen atoms are coordinated in the 1:2 complex. The presence of a protonated complex $CuHL_2^{3+}$ which is formed in the more acid region seems to confirm this hypothesis. The deprotonation of $CuHL_2^{3+}$ in the regions of higher pH would give the 1:2 complex CuL_2^{2+} in which the formerly protonated nitrogen atom remains uncoordinated. It is to be noted that the equilibrium constant for the reaction $CuL^{2+} + L \leftrightarrows CuL_2^{2+}$ is not very different from the constant for the equilibrium $CuL^{2+} + HL^+ \leftrightarrows CuHL_2^{3+}$, especially when one considers that in the second reaction two positively charged groups come together.

Hydroxy-complexes $ML(OH)^+$. The stability of the hydroxy complex is virtually independent of the steric effects of the polyamine bound to the metal ion, so that the formation constants of the hydroxy complexes $CuL(OH)^+$ and $ZnL(OH)^+$ are roughly the same when L = (2,2-tri), (2,3-tri) or (3,3-tri). Nor is the stability of the hydroxy-complex changed much for the N-methyl or N-ethyl derivatives of (2,2-tri).[20] It seems probable, therefore, that the complex $CuL(OH)^+$ has a square-planar structure, as this is the only structure in which there is no steric interference from the polyamine ligand.

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