Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Colgate Research Council for their support. We are also grateful to Mr. Jeffrey B. Kessler, a Colgate student, for his assistance with the compound preparations.

Registry No. $(+)[Mn^{III}((-)\text{-}5,14\text{-}[14]aneN_4)Cl_2]PF_6$, 53228-45-8; $(+)[Mn^{III}((-)\text{-}5,14\text{-}[14]aneN_4)Br_2]PF_6$, 53228-47-0; $(+)[Cu^{II}((-)\text{-}5,14\text{-}[14]aneN_4)](ClO_4)_2$, 53447-11-3; $(+)[Ni^{II}((-)\text{-}5,14\text{-}[14]aneN_4)](ClO_4)_2$, 52553-45-4; $(+)[Ni^{II}((-)\text{-}5,14\text{-}[14]aneN_4)(d\text{-}tart)]$, 53166-27-1; $(-)\text{-}5,14\text{-}[14]aneN_4$, 53187-81-8.

References and Notes

(1) (a) Colgate University. (b) Syracuse University.
(2) P. S. Bryan and J. C. Dabrowiak, *Inorg. Chem.*, preceding article.
(3) For nomenclature abbreviation see J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, *Inorg. Chem.*, **11**, 1979 (1972).
(4) R. Dingle, *Acta Chem. Scand.*, **20**, 33 (1966).
(5) T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).
(6) R. Dingle, *Inorg. Chem.*, **4**, 1287 (1965).
(7) L. G. Warner and D. H. Busch, "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 1.
(8) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).
(9) O. Schnepp, S. Allen, and E. Pearson, *Rev. Sci. Instrum.*, **41**, 1136 (1970).
(10) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(11) V. Katovic, L. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).
(12) N. F. Curtis, Y. M. Curtis, and H. K. Powell, *J. Chem. Soc.*, 1015 (1966).
(13) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, **6**, 700 (1967).
(14) E. K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972).
(15) Tentative rules on nomenclature, *Inorg. Chem.*, **9**, 1 (1970).
(16) E. Brackett and C. E. Pfluger, unpublished results.
(17) L. J. Boucher and D. R. Herrington, *Inorg. Chem.*, **13**, 1105 (1974).
(18) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. **100**, 44 (1971).
(19) A. B. P. Lever, "Inorganic Electronic Spectroscopy," American Elsevier, New York, N. Y., 1968, pp 355–362.
(20) Reference 19, pp 333–348.

Contribution from the Istituto di Chimica Generale ed Inorganica dell'Universita and
Laboratorio del CNR, 50132 Florence, Italy

Stability of Some Transition Metal Ion Complexes with a Linear Aliphatic Triamine Potentially Forming a Five-Membered Chelate Ring Fused with a Seven-Membered Chelate Ring: 1,4,9-Triazanonane (2,4-tri). II[1]

R. BARBUCCI, P. PAOLETTI,* and A. VACCA

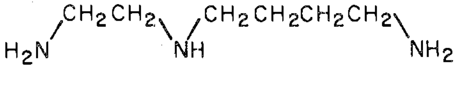
Received June 4, 1974 AIC40358I

The triamine $H_2N(CH_2)_2NH(CH_2)_4NH_2$ (2,4-tri) has been investigated as chelating agent for copper(II), nickel(II), and zinc(II) ions. These divalent metal ions form a large number of complexes with 2,4-tri in aqueous solution. The relative stability constants were determined potentiometrically in 0.5 *M* KNO_3 at 25°. Five complexes having the formulas ML, MHL, ML_2, $M(HL)_2$, and MHL_2 (where L = 2,4-tri) are common to all the three metal ions. In addition to the simple and protonated complexes, Cu^{2+} and Zn^{2+} give the hydroxo complexes $[Cu(OH)L]^+$, $[Zn(OH)L]^+$, and $[Zn(OH)_2L]$. With regard to the simple complex ML, the amine acts as a bidentate chelate agent toward Ni^{2+} and Zn^{2+} while it acts as a tridentate chelate toward Cu^{2+}, the latter forming two fused chelate rings, one five-membered and the other seven-membered. The ML_2 complexes contain only two five-membered chelate rings, both the molecules of 2,4-tri acting as bidentates. The protonation constants have been measured and compared with those of some other triamines previously investigated.

Introduction

Recently it has been clearly demonstrated that the coordinating power of ligands which form complexes with a sequence of alternating five- and six-membered rings is greater than that of ligands forming complexes with all five-membered or all six-membered chelate rings. This has been verified both for linear aliphatic tetramines[2] and for linear aliphatic triamines.[3] This enhanced coordinating power is made evident by the thermodynamic functions $\Delta G°$ and $\Delta H°$ relative to the reaction of complex formation in aqueous solution.[4]

In order to determine the coordinating properties of the 1,4,9-triazanonane ligand (2,4-tri)[5] in aqueous solution



$H_2NCH_2CH_2NHCH_2CH_2CH_2CH_2NH_2$

we have measured the stability constants of its complexes with copper(II), nickel(II), and zinc(II). The full coordination of the three nitrogen atoms would give rise to the formation of a five-membered chelate ring fused with a seven-membered chelate ring. A chelate ring of such size is unusual, especially in aqueous solution. The equilibria between the ligand 2,4-tri and the ions have been studied in aqueous solution (0.5 *M* KNO_3) at 25° using a potentiometric method.

Also the protonation constants have been measured and the effect on the three nitrogens' basicity of the progressive and systematic extension of one aliphatic chain in going from 2,2-tri[6] to 2,3-tri[3] to 2,4-tri has been investigated.

Table I. Experimental Details of the Potentiometric Measurements (Initial Concentrations, $M \times 10^2$)

Cation	L:M ratio	[L]	$[M^{2+}]$	$[H^+]$	pH range
H^+		0.2641		0.943	3.5–11.6
		0.2885		1.032	3.5–11.1
		0.2799		1.003	3.5–11.2
Ni^{2+}	1:0.14	0.4169	0.0599	1.491	3.3–10.9
	1:0.40	0.3681	0.1454	1.317	3.4–11.1
	1:0.23	0.3724	0.0855	1.329	3.4–10.8
Cu^{2+}	1:0.26	0.4287	0.1127	1.532	3.6–11.2
	1:0.14	0.4244	0.0598	1.518	3.6–11.2
	1:0.70	0.4036	0.2812	1.443	3.7–11.2
Zn^{2+}	1:0.27	0.4263	0.1151	1.520	3.5–10.8
	1:0.43	0.4088	0.1758	1.457	3.4–8.4
	1:0.22	0.4206	0.0934	1.504	3.4–11.1

Experimental Section

Materials. 2,4-tri is commercially available (Eastman Organic Chemicals). The product was purified as the hydrochloride which was recrystallized twice from ethanol and dried *in vacuo* at 60°. *Anal.* Calcd for $C_6H_{20}N_3Cl_3$: Cl, 44.2. Found: Cl, 44.2.

The potassium hydroxide solution (≃0.5 *M*) was prepared from KOH pellets. The pellets were washed with twice distilled and decarbonated H_2O (under a N_2 flow); the last addition of water was

Table II. Basicity Constants of Linear Aliphatic Triamines and Stability Constants of Their Metal Complexes at 25°

Ion	Reaction	2,4-tri[a]	2,3-tri[b]	2,2-tri[c]	3,3-tri[d]
H^+	$H^+ + L \rightleftarrows HL^+$	10.669 (2)	10.437	9.79	10.65
	$H^+ + HL \rightleftarrows H_2L^{2+}$	9.592 (4)	9.356	8.98	9.57
	$H^+ + H_2L^{2+} \rightleftarrows H_3L^{3+}$	6.984 (6)	6.374	4.25	7.72
	$3H^+ + L \rightleftarrows H_3L^{3+}$	27.25	26.17	23.02	27.94
Ni^{2+}	$Ni^{2+} + HL^+ \rightleftarrows [NiHL]^{3+}$	6.026 (6)	5.86		
	$Ni^{2+} + L \rightleftarrows [NiL]^{2+}$	7.81 (17)	11.234	10.60	9.19
	$Ni^{2+} + 2HL \rightleftarrows [Ni(HL)_2]^{4+}$	10.60 (2)			
	$Ni^{2+} + HL + L \rightleftarrows [NiHL_2]^{3+}$	11.62 (2)			
	$[NiL]^{2+} + L \rightleftarrows [NiL_2]^{2+}$	4.04 (8)	7.06	7.99	3.55
Cu^{2+}	$Cu^{2+} + HL^+ \rightleftarrows [CuHL]^{3+}$	9.190 (3)	9.02		
	$Cu^{2+} + L \rightleftarrows [CuL]^{2+}$	13.05 (1)	16.601	15.80	14.20
	$Cu^{2+} + 2HL^+ \rightleftarrows [Cu(HL)_2]^{4+}$	16.593 (8)			
	$Cu^{2+} + HL^+ + L \rightleftarrows [CuHL_2]^{3+}$	17.43 (1)	19.11		
	$[CuL]^{2+} + L \rightleftarrows [CuL_2]^{2+}$	4.61 (2)	3.28	5.21	
	$[CuL]^{2+} + OH^- \rightleftarrows [Cu(OH)L]^+$	4.36 (1)	4.72	4.50	4.1
Zn^{2+}	$Zn^{2+} + HL^+ \rightleftarrows [ZnHL]^{3+}$	4.36 (1)			
	$Zn^{2+} + L \rightleftarrows [ZnL]^{2+}$	6.34 (14)	8.770	8.80	7.92
	$Zn^{2+} + 2HL^+ \rightleftarrows [Zn(HL)_2]^{4+}$	8.31 (6)			
	$Zn^{2+} + L + HL^+ \rightleftarrows [ZnHL_2]^{3+}$	9.72 (7)			
	$[ZnL]^{2+} + L \rightleftarrows [ZnL_2]^{2+}$	4.12 (19)	3.80	7.44	
	$[ZnL]^{2+} + OH^- \rightleftarrows [Zn(OH)L]^+$	5.48 (2)	4.99		5.2
	$[ZnL]^{2+} + 2OH^- \rightleftarrows [Zn(OH)_2L]$	8.29 (2)			

[a] In 0.5 *M* KNO_3; the values in parentheses are the standard deviations. [b] In 0.5 *M* KNO_3.[3] [c] In 0.1 *M* KCl.[6] [d] In 0.1 *M* KCl.[11]

used to prepare the KOH solution. The absence of CO_2 in the KOH solution was tested by Gran's method[7] and by K_w measurements. Nitric acid and metal nitrates were obtained and standardized as previously described.[8]

Emf Measurements. The potentiometric titrations were performed using an Orion digital potentiometer, an Orion 91-01-00 glass electrode, a 0.1 *M* calomel electrode, and a salt bridge containing 0.5 *M* KNO_3 solution, following the procedure previously described.[8] All the potentiometric measurements were carried out at 25° in 0.5 *M* KNO_3. The protonation constants were derived from 102 data points obtained from three titrations. For the Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes 108, 144, and 90 data points, respectively, were used.[9] The concentration conditions used are given in Table I. The ligand:metal ratios varied between 1:0.7 and 1:0.2. The program MINIQUAD which was used to calculate the constants has been described elsewhere.[10] The protonation constants and the experimentally measured ionic product of water were held constant during the calculation of the complex formation constants.

Results and Discussion

The basicity constants of the ligand 2,4-tri are shown in Table II with those of the other 2,2-tri, 2,3-tri, and 3,3-tri[11] triamines previously reported. A large number of complexes is formed with the metal ions Ni^{2+}, Cu^{2+}, and Zn^{2+} in aqueous solution: five complexes have been found to be present in the Ni^{2+}–2,4-tri system, six in the Cu^{2+}–2,4-tri system, and seven in the Zn^{2+}–2,4-tri system (Table II). It will be noticed that the five species MH(2,4-tri), M(2,4-tri), M(H-2,4-tri)$_2$, MH(2,4-tri)$_2$, and M(2,4-tri)$_2$ are common to all the three systems. Copper(II) and zinc(II) also give the hydroxo complexes $[Cu(OH)(2,4\text{-tri})]^+$, $[Zn(OH)(2,4\text{-tri})]^+$, and $[Zn(OH)_2(2,4\text{-tri})]$. Taking into consideration the structure of the amine, the absence of polymer species (at least in the conditions investigated by us) is surprising. The stability constant of the complexes are given in Table II. Also reported in Table II are the constants obtained with the other homologous triamines. The distribution curves for all three metals are given in Figures 1–3. It is to be noted that the simple complex M(2,4-tri) is little represented, while the protonated complexes are formed in large amounts. This behavior is opposed to that of other systems investigated (as an example M^{2+}–2,3-tri).[3]

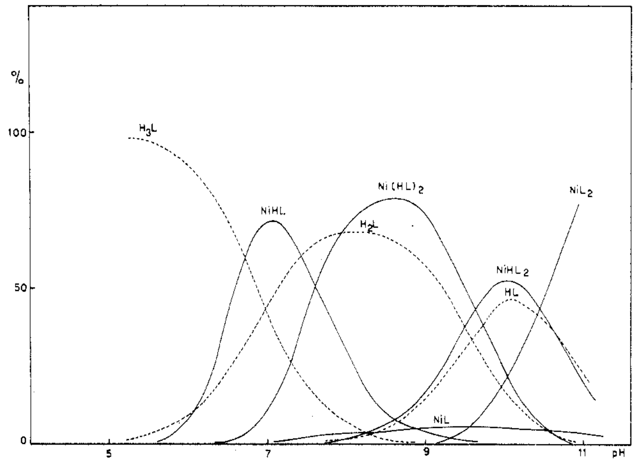


Figure 1. Distribution diagram for the system Ni^{2+}–2,4-tri. The percentages have been calculated from the data of the curve with a 1:0.14 L:M ratio in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

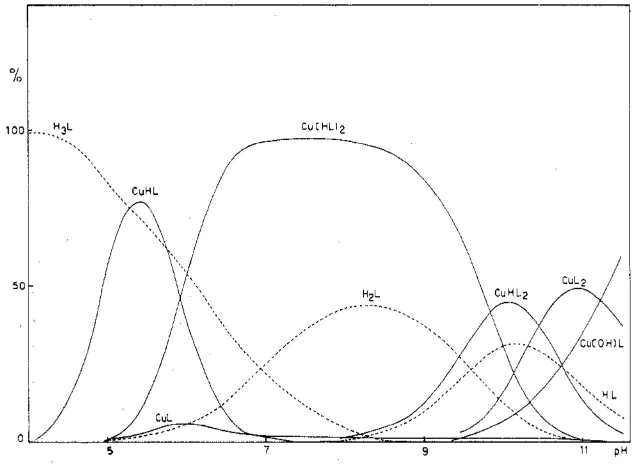


Figure 2. Distribution diagram for the system Cu^{2+}–2,4-tri. The percentages have been calculated from the data of the curve with a 1:0.26 L:M ratio in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

Basicity of the Free Ligand. That the value of the constant for each stage is less than that of the previous stage might have been expected on the bases both of statistical factors and of electrostatic repulsion between the hydrogen ion and the ligand molecule which in successive stages of protonation becomes progressively more positively charged. If we consider the basicity constants of the other triamines in Table II, we note that for each of the three stages of neutralization the constants lie in the order 2,4-tri > 2,3-tri > 2,2-tri. The sequence found can be related to the progressive lengthening of the aliphatic chain, because of the existence, at least in the first two stages,

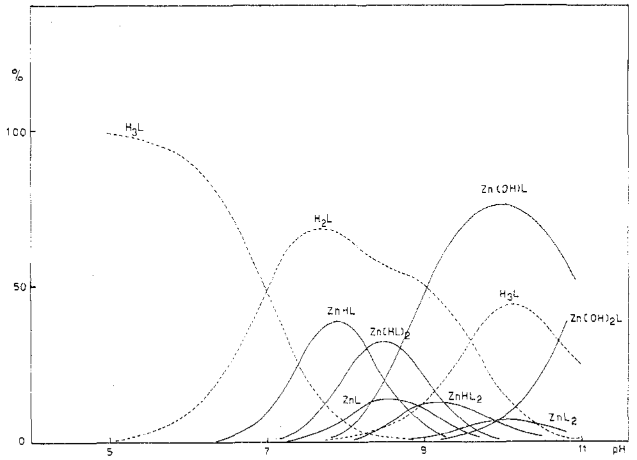


Figure 3. Distribution diagram for the system Zn^{2+}–2,4-tri. The percentages have been calculated from the data of the curve with a 1:0.27 L:M ratio in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

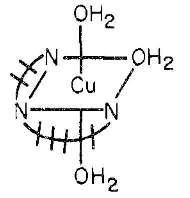
Table III. Protonation of the Coordinated Ligand (2,4-tri) at 25° and in 0.5 *M* KNO_3

	log *K*		
Reaction	Ni	Cu	Zn
$ML^{2+} + H^+ \rightleftarrows MHL^{3+}$	8.9	6.8	8.7
$ML_2{}^{2+} + H^+ \rightleftarrows MHL_2{}^{3+}$	10.4	10.4	9.9
$MHL_2{}^{3+} + H^+ \rightleftarrows M(HL)_2{}^{4+}$	9.7	9.9	9.3

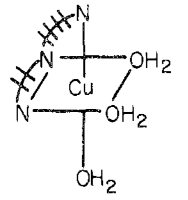
of different tautomeric forms. When there are two or more different basic sites in a polyamine molecule, it has often been shown that an equilibrium is set up between two or more tautomeric forms and that the position of such an equilibrium depends on the polyamine.[12] A comparison between the overall constants will be more meaningful. The basicity order is always 2,4-tri > 2,3-tri > 2,2-tri. The progressive addition of a methylene group causes an increase of the mean basicity of each nitrogen. A remarkable increase is observed from 2,2-tri to 2,3-tri but a lower one from 2,3-tri to 2,4-tri. However the overall equilibrium constant of 2,4-tri is very similar to that of 3,3-tri containing the same number of methylene groups, so that the sequence found must be mainly due to the inductive effect of the constituent groups in the molecule.

Basicity of the Coordinated Ligand. All the systems Ni^{2+}–, Cu^{2+}–, and Zn^{2+}–2,4-tri have the same number and same types of protonated complexes. The existence of these types of complexes is due to the favorable structure of the ligand. It is possible to consider three factors which are responsible for the formation of these protonated species: (1) the high basicity of the nitrogen bonded to the tetramethylenic chain, (2) the hindering to coordination of the two nitrogens extreme to that chain (a seven-membered chelate ring would thus be formed), and (3) the existence of a particularly stable five-membered chelate ring which holds the complex in solution.

If we suppose that the formation of the protonated complexes occurs *via* protonation of the normal complex M(2,4-tri) or $M(2,4\text{-tri})_2$, it is clear that the protonation of the coordinated ligand depends on the thermodynamic stability of the normal complex. It is logical to suppose that ligands which are not coordinated to the metal ion through all their donor atoms should be the easiest to protonate. If we examine the first reaction as written in Table III, we see that the Ni^{2+} and Zn^{2+} constants are similar and lie between the first and the second protonation constants of the free ligand (Table II). The copper(II) constant is lower than those of nickel(II) and zinc(II) and lower than the lowest basicity constant of the amine. That means that the nitrogen atom to be protonated was coordinated to the metal atom in the case of the Cu(2,4-tri) complex and was free in both the Ni(2,4-tri) and Zn(2,4-tri) complexes. Thus the structure of the Cu(2,4-tri) complex contains two chelate rings, one five-membered and the other seven-membered. It is the first time that a saturated chelate ring of such a size is formed in a complex. Also noteworthy is that this complex is stable in aqueous solution where the ligand capacity of the amine nitrogen is lowered, owing to the competition of the H_2O ligand.[13] Either the three nitrogen atoms of the complex Cu(2,4-tri) can be placed in the same plane containing the copper(II) ion (meridional isomer) or one nitrogen can be placed in the apical position and two nitrogens in the equatorial plane (facial isomer). The second hypothesis is the more likely because copper(II) complexes with these polyamines generally have a distorted octahedral structure and the nitrogen atom bonded to the longer chain, *i.e.*, tetramethylenic chain, can be placed in the farther position, *i.e.*, apical.



meridional isomer

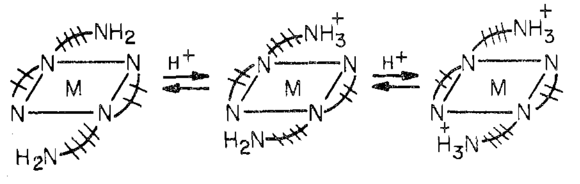


facial isomer

Unfortunately these 1:1 complexes are difficult to isolate; only small traces are formed in solution and always in the presence of other complexes.

The constants for the first protonation of the $M(2,4\text{-tri})_2$ complexes are similar for all the three metal ions and higher than those obtained for the protonation of the Ni(2,4-tri) and Zn(2,4-tri) complexes. This similarity of constants means that the nitrogen atom to be protonated is a noncoordinated nitrogen, and the higher values are probably closely bound up with the presence of two free nitrogens in the complex $M(2,4\text{-tri})_2$ instead of one nitrogen as in the Ni(2,4-tri) and Zn(2,4-tri) complexes. This hypothesis is strengthened by the values for the second protonation reaction of the complex $M(2,4\text{-tri})_2$. Once again the values of the constants are similar for all the three metal ions and lower than those of the previous stage. Thus the protonation reaction of the $M(2,4\text{-tri})_2$ complex goes on according to Scheme I. It is also possible that the $Zn(2,4\text{-tri})_2$ complex does not have the same configuration of the analogous Ni^{2+} and Cu^{2+} complexes.

Scheme I



$[M(2,4\text{-tri})_2]^{2+}$ $[MH(2,4\text{-tri})_2]^{3+}$ $[M(H\text{-}2,4\text{-tri})_2]^{4+}$

Reaction of Complex Formation. The constants relative to the complex formation with the 2,4-tri ligand are shown in Table II. A comparison between the stability constants of the M(2,4-tri) complexes and those of M(en) complexes (for en = ethylenediamine) shows that both Ni(2,4-tri) and Zn(2,4-tri) complexes have constants similar to those of the Ni(en) and Zn(en) complexes[14] while Cu(2,4-tri) has a constant higher than that of Cu(en)[15] by about 3 log units. This is in agreement with the hypothesis previously considered of the existence of a chelate ring five membered in both Zn(2,4-tri) and Ni(2,4-tri) complexes and of two chelate rings, one five membered and one seven membered, in the case of the Cu(2,4-tri) complex.

A comparison of the copper(II) complexes with the homologous triamines 2,2-tri, 2,3-tri, and 3,3-tri shows the sequence Cu(2,3-tri) > Cu(2,2-tri) > Cu(3,3-tri) > Cu(2,4-tri). This order proves that the complex with two alternating five- and seven-membered rings is the least stable in the series considered, even less stable than the compound with two six-membered rings Cu(3,3-tri).

The stability constants of the reaction M(2,4-tri) + 2,4-tri $\rightleftarrows$ $M(2,4\text{-tri})_2$ are similar for all the three metal ions and are lower than those relative to the equilibrium[16]

$$\mathrm{M(propylen) + propylen \rightleftarrows M(propylen)_2}$$

(propylen = *N*-*n*-propylethylenediamine, $CH_3CH_2CH_2NHCH_2CH_2NH_2$). This unexpected behavior could be explained by considering the different possibility of formation of hydrogen bonds, for example with the solvent, of the two complexes.

The stability constants relative to the reaction M + H-2,4-tri $\rightleftarrows$ M(H-2,4-tri) follow the usual order $Cu^{2+} > Ni^{2+} > Zn^{2+}$. The values are slightly higher than those of 2,3-tri analogous complexes,[3] the increase in stability being 0.17 log unit for both nickel and copper. The fact that in both cases (2,4-tri and 2,3-tri) a five-membered chelate ring is formed clearly shows that the difference in the values is due to the character of the free protonated arm. We must consider two factors to understand this behavior.

(1) The lengthening of the aliphatic chain causes a destabilization of the complex. In fact the stability constants of Cu(Etilen) (10.19) and Ni(Etilen) (6.78)[16] are lower than those of Cu(Meen)[15] (10.55) and Ni(Meen) (7.36)[16] (Etilen = *N*-ethylethylenediamine and Meen = *N*-methylethylenediamine).

(2) The removal of the charged NH_3^+ group from the complex causes a higher stability of the complex.

Therefore the stabilizing term (2) overcomes the destabilizing term (1) and the stability constants of the two complexes Ni(H-2,4-tri) and Cu(H-2,4-tri) can be higher than those of Ni(H-2,3-tri) and Cu(H-2,3-tri). In the second step M(H-2,4-tri) + (H-2,4-tri) $\rightleftarrows$ $M(H\text{-}2,4\text{-tri})_2$ the equilibrium constant is markedly lower than that of the first step, for nickel and copper complexes, but the stability constants of the two Zn(H-2,4-tri) and $Zn(H\text{-}2,4\text{-tri})_2$ complexes are similar. This can be explained on the basis that the zinc complexes may assume different stereochemistries, tetrahedral and octahedral being the most common.[13]

Hydrolysis Reaction. Hydroxy complexes of formulas Cu(OH)(2,4-tri), Zn(OH)(2,4-tri), and $Zn(OH)_2(2,4\text{-tri})$ are formed. Once again[13] the Ni^{2+} ion does not form hydroxy complexes. The two complexes $Zn(OH)_2(2,4\text{-tri})$ and Cu(OH)(2,4-tri) start to form at high pH and are the last complexes present in the pH range investigated. Their percentage is therefore low. The Zn(OH)(2,4-tri) complex is formed in large proportions. It starts to form together with the simple Zn(2,4-tri) and the protonated Zn(H-2,4-tri) complex. The simultaneous presence of both protonated and hydroxy complexes is unusual and this behavior is not in agreement with the Zn^{2+}–2,3-tri system.[3]

The two Zn(OH)(2,4-tri) and Cu(OH)(2,4-tri) complexes have constants very close to the analogous complexes with the other triamines. Neither a differing bulkiness of the polyamine nor a different number of coordination sites available for the OH^- ion causes a different behavior in the thermodynamic functions.

Finally the neutral complex $Zn(OH)_2(2,4\text{-tri})$ is not formed with the other aliphatic triamines, but it is present in the Zn^{2+}–Oden system (for Oden = β-aminoethyl ether) with a higher constant by 1.4 log units.[17]

Registry No. 2,4-tri, 35513-87-2; copper, 7440-50-8; nickel, 7440-02-0; zinc, 7440-66-6.

Supplementary Material Available. Listings of the final computer output with the data points will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40358I.

References and Notes

(1) Part I: R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, **7**, 157 (1973).

(2) (a) L. Fabbrizzi, R. Barbucci, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1529 (1972); (b) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, **12**, 1861 (1973); (c) R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1763 (1973).

(3) R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, 157 (1973).

(4) R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Coord. Chem. Rev.*, **8**, 31 (1972).

(5) Linear aliphatic triamines of the type $H_2N(CH_2)_nNH(CH_2)_mNH_2$ are denoted by the symbol (*n*,*m*-tri).

(6) M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, **65**, 1224 (1961).

(7) F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ.*, **7**, 377 (1965).

(8) E. Arenare, P. Paoletti, A. Dei, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 736 (1972).

(9) See paragraph at the end of paper regarding supplementary material.

(10) A. Sabatini, A. Vacca, and P. Gans., *Talanta*, **21**, 53 (1974).

(11) A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, **5**, 1384 (1966).

(12) E. J. King, "International Encyclopedia of Physical Chemistry and Chemical Physics," R. A. Robinson, Ed., McGraw-Hill, New York, N. Y., 1965, Topic 15, p 219.

(13) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta, Rev.*, **7**, 43 (1973).

(14) I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1406 (1955).

(15) R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 740 (1972).

(16) F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **74**, 5243 (1952).

(17) R. Barbucci and A. Vacca, *J. Chem. Soc., Dalton Trans.*, in press.