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Chelating Properties of Linear Aliphatic Tetraamines with Some Bivalent Transition Metal Ions. 1,5,8,12-Tetraazadodecane (3,2,3-tet)

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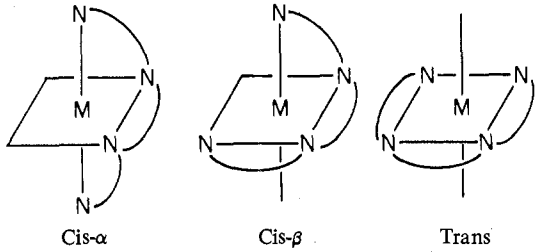
The basicity constants of 1,5,8,12-tetraazadodecane (3,2,3-tet) were determined potentiometrically in 0.5 *M* KNO_3 at 25.0°. The equilibria between 3,2,3-tet and Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were investigated under similar conditions. The basicity constants of 3,2,3-tet are compared with those of the other tetramines previously investigated. The order found of the stepwise basicity constants is related to the inductive effect of the constituent groups in the molecule. Two complexes are found with both nickel(II) and copper(II): the 1:1 complex $[ML]^{2+}$ and a protonated species $[MHL]^{3+}$. In addition to these two complexes zinc(II) gives at high pH the hydroxo complex $[ZnLOH]^{+}$. The stability order for the tetramines is $[M(2,3,2\text{-tet})]^{2+} > [M(3,2,3\text{-tet})]^{2+} > [M(2,2,2\text{-tet})]^{2+} > [M(3,3,3\text{-tet})]^{2+}$ for Ni^{2+} and Cu^{2+} ions. It can be deduced that an alternating sequence of five- and six-membered rings increases complex stability.

Introduction

The ligand 1,4,8,11-tetraazaundecane (2,3,2-tet) forms metal complexes having three chelate rings alternating in size, two being five-membered and one six-membered. These complexes are particularly stable,[1] more stable in fact than those formed with the tetramine 1,4,7,10-tetraazadecane[2] (2,2,2-tet) which contains an arrangement of three consecutive five-membered rings. The expansion of the middle chelate ring favors coordination owing to the alleviation of the strain in the equatorial ring system.[3] In fact reference to molecular models and to the X-ray structures shows that with 2,3,2-tet the nitrogen atoms can be arranged in a strain-free configuration while with 2,2,2-tet there is difficulty in reaching the four coordination sites.[4] [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.]

The quadridentate ligands can assume different arrangements around the central ion, both the various ring sizes and the metal ion can affect the ligand's ability to adopt the structures



The 2,2,2-tet ligand, for example, forms the octahedral species $[Ni(trien)(H_2O_2)]^{2+}$ which is, in solution, a cis-trans mixture.[5] The 2,3,2-tet ligand, on the contrary, forms the trans isomer with octahedral metal ions.[6]

It therefore seemed of interest to us to study the tetramine 1,5,8,12-tetraazadodecane (3,2,3-tet)

$H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

in order to establish both the kinds of the complexes formed and their order of stability, relative to those of the other tetramines which have already been studied, *i.e.*, 3,3,3-tet[7] which involves all six-membered rings, 2,2,2-tet[2] with all five-membered rings, and 2,3,2-tet[1] with a 5,6,5 ring size sequence. Therefore we have studied the equilibria between the ligand 3,2,3-tet and the ions H^+, Ni^{2+}, Cu^{2+}, and Zn^{2+} in aqueous solution (0.5 *M* KNO_3) at 25° using a potentiometric method.

The effect on the basicity of the four nitrogen atoms of the progressive and systematic expansion of the aliphatic chain in going from 2,2,2-tet to 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet has also been investigated. The only data which have previously been reported in the literature are the overall constant for protonation and two stability constants for the Cu(II) species $[CuHL]^{3+}$ and $[CuL]^{2+}$.[8]

Experimental Section

Materials. Preparation of 3,2,3-tet. The procedure used is based on Van Alphen's general method of preparation for tetramines.[9] A 300-g sample of K_2CO_3 was added to 250 g of 1,3-diaminopropane dissolved in 500 ml of ethanol. To the cooled, stirred solution 500 g of 1,2-dibromoethane was added in small portions. When all the 1,2-dibromoethane had been added the solution was refluxed for 3 hr. After filtration of the KBr formed in the reaction and of unreacted K_2CO_3, the remaining 1,3-diaminopropane, 1,2-dibromoethane, and ethanol were distilled off using a rotary evaporator. The resulting solution was cooled and filtered and then distilled twice under vacuum. The middle fraction (170° and 4 mm) was purified as the hydrochloride obtained by adding hydrochloric acid to an alcoholic solution of the amine. This product was recrystallized twice from an ethanol-water mixture and dried *in vacuo* at 60°. *Anal.* Calcd for $C_8H_{26}N_4Cl_4$: Cl, 44.3. Found: Cl, 44.1.

Emf Measurements. The potentiometric technique has already been described.[10] The protonation constants were obtained using 209 data points from three titrations. The calculations were performed using an appropriate program (LG/3) on an IBM 1130 computer. This program is a FORTRAN IV version of that (LG/2) already described.[11] The formation constants of the Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes were calculated from 244, 234, and 214 data points, with the program LEAST.[12]

(1) D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 9, 1557 (1970).
(2) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961).
(3) L. Fabbrizzi, R. Barbucci, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1529 (1972).
(4) A. McPherson, M. G. Rossman, D. W. Margerum, and M. R. Jones, *J. Coord. Chem.*, 1, 39 (1971).
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(6) B. Bosnich, R. D. G. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).
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(8) G. R. Hedwing, J. L. Love, and H. K. J. Powell, *Aust. J. Chem.*, 23, 981 (1970).
(9) J. Van Alphen, *Recl. Trav. Chim. Pays-Bas*, 55, 835 (1936).
(10) E. Arenare, P. Paoletti, A. Dei, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 736 (1972).
(11) A. Dei, P. Paoletti, and A. Vacca, *Inorg. Chem.*, 7, 865 (1968).
(12) A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1693 (1972).

Table I. Experimental Details of the Potentiometric Measurements

Cation	L:M	Analytical concn × 10^2, *M* C_{ligand}	C_{metal}	C_{acid}	pH range
H^+		0.6460		2.8774	2.6–10.8
		0.6475		2.7943	2.8–10.8
		0.7733		3.3871	2.6–10.8
Ni^{2+}	1:0.5	0.7844	0.4279	3.3346	2.8–10.8
	1:0.6	0.7644	0.4470	3.2604	2.8–10.8
	1:0.2	0.7771	0.1852	3.3140	2.7–10.7
	1:0.2	0.8509	0.1874	3.6067	2.7–10.7
Cu^{2+}	1:0.2	0.6230	0.1685	2.6877	2.9–10.8
	1:0.3	0.8265	0.2584	3.5058	2.9–10.8
	1:0.7	0.6273	0.4222	2.6315	3.1–10.8
Zn^{2+}	1:0.4	0.8034	0.3292	3.4013	2.8–10.8
	1:0.9	0.7775	0.6822	3.3071	2.8–10.8
	1:0.3	0.8227	0.2455	3.4970	2.8–10.8
	1:0.2	0.5203	0.0972	2.2871	2.8–10.8

The details of the potentiometric measurements together with the appropriate range of pH are shown in the Table I.[13]

For the calculation of the stability constants of the metal ions the four protonation constants and the ionic product of water were kept constant.

Basicity Constants

The basicity constants for 3,2,3-tet are shown in Table II. The value of the constant for each successive stage is less than that of the previous stage as might have been expected on the basis of both 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. For the purpose of comparison the corresponding values for the protonation of the homologous linear tetramines 2,2,2-tet, 2,3,2-tet, and 3,3,3-tet are also shown in the table. For each of the first three stages of neutralization the constants lie in the order 3,3,3-tet ≈ 3,2,3-tet > 2,3,2-tet > 2,2,2-tet. In fact the first basicity constant for 3,2,3-tet is larger than that of 3,3,3-tet by 0.05 logarithmic unit but a difference of this order is not significant especially when account is taken of the fact that the two amines were studied in different ionic media (μ 0.5 *M* KNO_3 for 3,2,3-tet and μ 0.1 *M* $NaNO_3$ for 3,3,3-tet). An increase in ionic strength mainly affects the first stage of protonation and favors ion-dipole association. The sequence found for the four tetramines can be related to the inductive effect of the constituent groups in the molecule.

When there are two different basic sites in a polyamine molecule, it has been shown that an equilibrium is set up between two tautomeric forms,[14] one of the tautomeric forms having the primary nitrogen protonated and the other having the secondary nitrogen protonated.[15] The position of such an equilibrium will depend on the tetramine.

$$H_3\overset{+}{N}(CH_2)_nNH(CH_2)_mNH(CH_2)_pNH_2 \rightleftarrows$$

I

$$H_2N(CH_2)_n\overset{+}{N}H_2(CH_2)_mNH(CH_2)_pNH_2$$

II

(13) 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. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth 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 INORG-73-1861.

(14) 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.

(15) M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, **65**, 1224 (1961); P. Paoletti, M. Ciampolini, and A. Vacca, *ibid.*, **67**, 1065 (1963).

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

Ion	Reaction	3,2,3-tet[a]	2,3,2-tet[b]	2,2,2-tet[c]	3,3,3-tet[d]
H^+	$H^+ + L \rightleftarrows HL^+$	10.665 (1)	10.25	9.95	10.61
	$H^+ + HL^+ \rightleftarrows H_2L^{2+}$	9.956 (2)	9.50	9.31	9.98
	$H^+ + H_2L^{2+} \rightleftarrows H_3L^{3+}$	8.536 (3)	7.28	6.86	8.69
	$H^+ + H_3L^{3+} \rightleftarrows H_4L^{4+}$	5.837 (4)	6.02	3.66	7.35
Ni^{2+}	$Ni^{2+} + HL^+ \rightleftarrows NiHL^{3+}$	9.75 (1)			
	$Ni^{2+} + L \rightleftarrows NiL^{2+}$	14.693 (5)	16.4	14.1	10.70
Cu^{2+}	$Cu^{2+} + HL^+ \rightleftarrows CuHL^{3+}$	14.76		14.1	
	$Cu^{2+} + L \rightleftarrows CuL^{2+}$	21.839 (6)	23.9	20.2	17.3
Zn^{2+}	$Zn^{2+} + HL^+ \rightleftarrows ZnHL^{3+}$	7.18 (1)			
	$Zn^{2+} + L \rightleftarrows ZnL^{2+}$	11.259 (5)	12.8	12.1	9.4
	$ZnL^{2+} + OH^- \rightleftarrows ZnLOH^+$	4.05 (1)			

[a] In 0.5 *M* KNO_3; the values in parentheses are the standard deviations. [b] Reference 1; in 0.5 *M* KCl. [c] Reference 2; in 0.1 *M* KCl. [d] Reference 7; in 0.1 *M* $NaNO_3$.

Table III. Percentage of Tautomeric Species for the Tetramines

Amine	Form	%	Amine	Form	%
2,2,2-tet	I	69.4	3,2,3-tet	I	74.7
	II	30.6		II	25.3
3,3,3-tet	I	51.1	2,3,2-tet	I	48.3
	II	48.9		II	51.7

The values of the basicity microconstants can be evaluated from Clark and Perrin's[16] method and this allows us to determine the percentages of the two forms (see Table III).

It will be noticed that for 3,3,3-tet and 2,3,2-tet the percentages of protonated primary and secondary nitrogens are almost equal while for 3,2,3-tet and 2,2,2-tet the equilibrium is displaced considerably toward I. The shorter central chain has a negative effect on the basicity of the secondary nitrogen.

Even the reversal of the order of 3,2,3-tet and 2,3,2-tet for the fourth protonation constant (Table II) becomes comprehensible when we take account of the fact that this last stage involves the protonation of a secondary nitrogen. The different aliphatic chain length sequence makes the secondary nitrogen in 2,3,2-tet more basic than that of 3,2,3-tet. The values of the basicity microconstants of the secondary nitrogen calculated using Clark and Perrin's formula are 1.38×10^{10} for 2,3,2-tet and 1.23×10^{10} for 3,2,3-tet.

Ni^{2+} Complexes. Two complexes are found to be present in the Ni^{2+}-3,2,3-tet system: the 1:1 complex $[NiL]^{2+}$ and the protonated species $[NiHL]^{3+}$. Their formation constants are shown in Table II. The distribution curves relative to the ionic species present in solution at equilibrium are shown in the Figure 1. Although the two species are competitive, the percentage of the protonated one is very low. For pH >6 its percentage decreases rapidly while at pH 8 the species has disappeared completely. The fact that the two complexes start to form at pH 5 shows that the concentration of the species $[H_4L]^{4+}$ is not affected by complex formation. The stability constants for Ni(II) with the other tetramines are also shown in the table and it will be noticed that 3,2,3-tet is unique among the four ligands in forming a protonated complex. It is assumed this protonation involves the opening of one of the two six-membered[17] rings which are less stable than the five-membered rings. Thus the protonated nitrogen is the one at the outside end of the trimethylene chain. Measurements of rates of dissociation indicate that, in Ni(II) complexes

(16) J. Clark and D. D. Perrin, *Quart. Rev., Chem. Soc.*, 18, 295 (1964).

(17) R. Barbucci, L. Fabbrizzi, and P. Paoletti, submitted for publication.

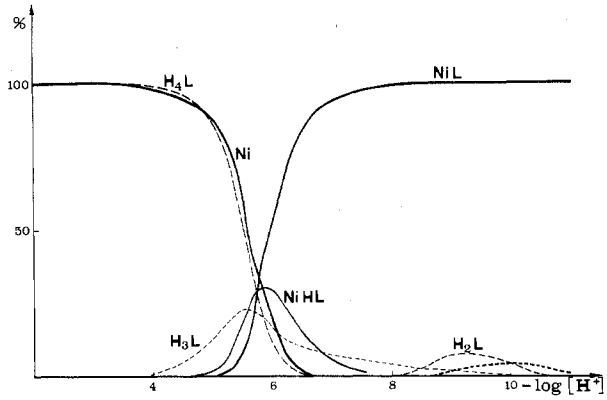
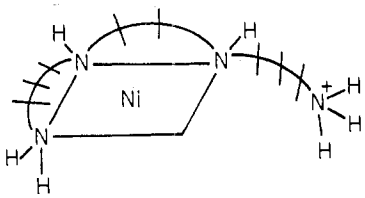


Figure 1. Distribution diagram for the system Ni^{2+}–3,2,3-tet. The percentages have been calculated from the data of the curve with a 1:0.6 L:M ratio in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

with linear aliphatic polyamines, it is easier to remove the terminal NH_2 groups than the central NH.[18]



The stability of the complex $[NiH(3,2,3\text{-tet})]^{3+}$ is lower than that of the complex $[Ni(2,3\text{-tri})]^{2+}$,[17] having the same ring size sequence. That lower stability is presumably due to the repulsion of the charged nitrogen atom on the metal ion.

The complex $[Ni(3,2,3\text{-tet})]^{2+}$ is more stable than $[Ni(2,2,2\text{-tet})]^{2+}$ but less stable than $[Ni(2,3,2\text{-tet})]^{2+}$. The stability order is $[Ni(2,3,2\text{-tet})]^{2+} > [Ni(3,2,3\text{-tet})]^{2+} > [Ni(2,2,2\text{-tet})] > [Ni(3,3,3\text{-tet})]^{2+}$ so that it can be deduced that an alternating sequence of five- and six-membered rings increases complex stability. However for two complexes having chelate rings of alternating size the one with the larger number of five-membered rings is the more stable.

Cu^{2+} Complexes. In this case too there are two complexes present in solution, the protonated $[CuHL]^{3+}$ and the 1:1 complex $[CuL]^{2+}$ (see Figure 2). However they start to form at lower pH than in the case of nickel and there is an area of overlap with the range of existence of the species $[H_4L]^{4+}$. Once again the two complexes are competitive and at no stage is there a big percentage of the protonated species. As in the case of Ni^{2+} the formation constant of the protonated species is lower than that for the complex formed with the neutral ligand 2,3-tri.[17] Again the stability of $[Cu(3,2,3\text{-tet})]^{2+}$ lies between those of $[Cu(2,3,2\text{-tet})]^{2+}$ and $[Cu(2,2,2\text{-tet})]^{2+}$.

Zn^{2+} Complexes. Zinc forms three complexes: a protonated species, a 1:1 complex, and a hydroxy species $[Zn(3,2,3\text{-tet})OH]^{+}$. The constants are shown in Table II while the distribution curves for the three complexes are shown in Figure 3. As might have been expected the existence of the hydroxy species restricts the range in which the simple complex exists. The existence of a protonated complex is rather unusual for Zn^{2+} and analogous behavior is

(18) G. A. Nelson and R. G. Wilkins, *J. Chem. Soc.*, 2662 (1963).

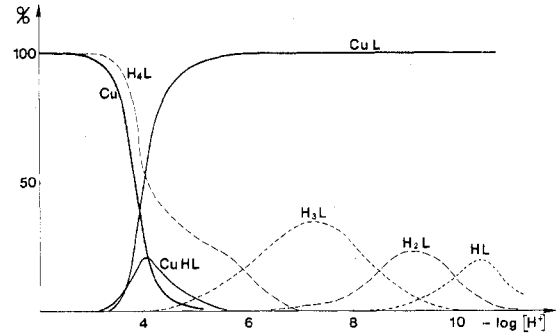


Figure 2. Distribution diagram for the system Cu^{2+}–3,2,3-tet. The percentages have been calculated from the data of the curve with a 1:0.7 L:M ratio in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

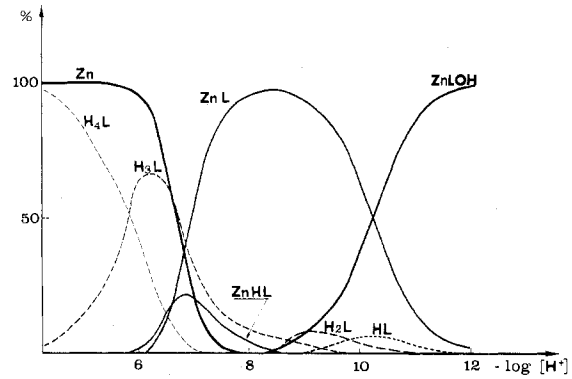


Figure 3. Distribution diagram for the system Zn^{2+}–3,2,3-tet. The percentages have been calculated from the data of the curve with a 1:0.9 L:M ratio in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

only found with the hexadentate amines penten and ptetraen[19] which, however, when coordinated to Zn^{2+}, only use five of the six available nitrogen donor atoms.

The stabilities of the zinc complexes with the four tetramines lie in the order $[Zn(2,3,2\text{-tet})]^{2+} > [Zn(2,2,2\text{-tet})]^{2+} > [Zn(3,2,3\text{-tet})]^{2+} > [Zn(3,3,3\text{-tet})]^{2+}$. The sequence is different from that found for the ions Cu^{2+} and Ni^{2+} inasmuch as the constant for $[Zn(2,2,2\text{-tet})]^{2+}$ lies between those for $[Zn(2,3,2\text{-tet})]^{2+}$ and $[Zn(3,2,3\text{-tet})]^{2+}$. The greater stability of this complex is due to the different way in which 2,2,2-tet is arranged around the metal ion. In fact the complex $[Zn(2,2,2\text{-tet})]^{2+}$ appears not to be octahedral.[2]

The hydrolysis constant for the equilibrium $[Zn(3,2,3\text{-tet})]^{2+} + OH^- \rightleftharpoons [Zn(3,2,3\text{-tet})OH]^{+}$ is similar to those previously found for complexes with other tridentate polyamine ligands, *e.g.*, $[Zn(2,2\text{-tri})]^{2+}$ [20] and $[Zn(3,3\text{-tri})]^{2+}$.[21] This leads us to believe that in the case of the tetramine 3,2,3-tet the coordination of the hydroxy group does not lead to the breaking of a Zn–N bond.

General Discussion

The particular configuration of this tetramine makes it possible for a protonated complex to be formed with all

(19) P. Paoletti, R. Walser, A. Vacca, and G. Schwarzenbach, *Helv. Chim. Acta*, 54, 243 (1971).

(20) J. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 33, 985 (1950).

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

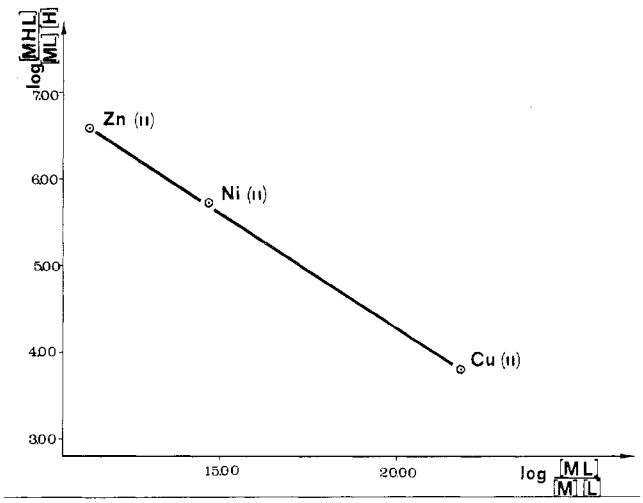


Figure 4. Plot of the basicity constant of the complex against the $[M(3,2,3\text{-tet})]^{2+}$ stability constant.

three metal ions. If we assume that the formation of the protonated complex involves the equilibrium $[M(3,2,3\text{-tet})]^{2+} + H^+ \rightleftharpoons [MH(3,2,3\text{-tet})]^{3+}$, we notice that the basicity of the complex varies in the order $Zn^{2+} > Ni^{2+} > Cu^{2+}$ which is the reverse of the Irving-Williams order found for the 1:1 complexes. Plotting the basicity constant defined in this way as ordinate and the stability constant for the complex $[M(3,2,3\text{-tet})]^{2+}$ as abscissa we obtain a straight-line relationship (Figure 4). As a consequence we can assume (1) the protonation of the nitrogen involves the same process for all three complexes, (2) the inverse proportionality between the constants of protonation and of complex formation provides evidence that the attachment of a proton involves the opening of a chelate ring, and (3) the stereochemistry of these complexes both in the protonated and in the nonprotonated forms does not vary with the metal ion, even if the problem of the type and the number of isomers remains unsolved. It is worthwhile that the Zn^{2+} ion forms with this ligand an octahedral complex in aqueous solution.

Table IV. Stability constants of Nickel(II), Copper(II), and Zinc(II) Complexes of Linear Aliphatic Polyamines

Effect of Adding a Six-Membered Ring to a Five-Membered Ring				
$[Ni\ en]^{2+}$ [a]		$[Ni(2,3\text{-tri})]^{2+}$ [b]		$[Ni(3,2,3\text{-tet})]^{2+}$
7.70	3.53	11.23	3.46	14.69
$[Cu\ en]^{2+}$ [a]		$[Cu(2,3\text{-tri})]^{2+}$ [b]		$[Cu(3,2,3\text{-tet})]^{2+}$
10.58	6.02	16.60	5.17	21.83
$[Zn\ en]^{2+}$ [a]		$[Zn(2,3\text{-tri})]^{2+}$ [b]		$[Zn(3,2,3\text{-tet})]^{2+}$
5.79	2.98	8.77	2.49	11.26
Effect of Adding a Five-Membered Ring to a Six-Membered Ring				
$[Ni\ tn]^{2+}$ [c]		$[Ni(2,3\text{-tri})]^{2+}$ [b]		$[Ni(2,3,2\text{-tet})]^{2+}$ [d]
6.91	4.32	11.23	5.53	16.4
$[Cu\ tn]^{2+}$ [c]		$[Cu(2,3\text{-tri})]^{2+}$ [b]		$[Cu(2,3,2\text{-tet})]^{2+}$ [d]
10.16	6.44	16.60	7.30	23.9

[a] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 4553 (1960). [b] Reference 17. [c] F. Holmes and R. Williams, *J. Chem. Soc. A*, 1702 (1967). [d] Reference 1.

Let us consider the relative stability constants for Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes with ligands of varying denticity (Table IV). Going from $[Men]^{2+}$ to $[M(2,3\text{-tri})]^{2+}$ and from $[M(2,3\text{-tri})]^{2+}$ to $[M(3,2,3\text{-tet})]^{2+}$ involves in both cases the addition of a six-membered ring, in the first case to a simple five-membered ring and in the second case to a five-membered ring attached to a six-membered ring. The differences between the stability constants indicate that this linking has a greater stabilizing effect in the first case. The opposite occurs when we consider the addition of a five-membered ring to an isolated six-membered ring tn[22] or to one linked to another five-membered ring 2,3-tri. Thus it would appear that the effect of the increased degree of crowding in the two cases is different, in one case facilitating the ability of the ligand to coordinate and in the other hindering it.

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Substitution Reactions of Sterically Hindered Gold(III) Complexes

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The complexes $[Au(Me_2dien\text{-}H)Cl]PF_6$, $[Au(Me_4dien\text{-}H)Cl]PF_6$, and $[Au(Et_2dien\text{-}H)Cl]PF_6$[1] have been synthesized and the dissociation constants of their conjugate acids measured. Kinetic studies reveal that the complexes containing the methylated ligands undergo bromide substitution by the usual two-path mechanism common to low-spin d^8 metal complexes. Substitution of $[Au(Et_2dien\text{-}H)Cl]^+$ is postulated to proceed *via* a ring-opening mechanism.

Introduction

Square-planar metal complexes generally undergo substitution at rates that are reagent dependent.[2] In particular such dependence has been observed for substitution by monoden-

(1) Abbreviations used in this paper: amine, any diethylenetriamine or substituted diethylenetriamine; amine-H, the conjugate base of amine; dien, $NH_2CH_2CH_2NHCH_2CH_2NH_2$; dien-H, $(NH_2CH_2CH_2NCH_2CH_2NH_2)^-$; Me_2dien, $(CH_3)_2NCH_2CH_2NHCH_2CH_2NH_2$; Me_2dien-H, $[(CH_3)_2NCH_2CH_2NCH_2CH_2NH_2]^-$; Me_4dien, $(CH_3)_2NCH_2CH_2NHCH_2CH_2N(CH_3)_2$; Me_4dien-H, $[(CH_3)_2NCH_2CH_2NCH_2CH_2N(CH_3)_2]^-$; Et_2dien, $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2NH_2$; Et_2dien-H, $[(C_2H_5)_2NCH_2CH_2NCH_2CH_2NH_2]^-$; Et_4dien, $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$; Et_4dien-H, $[(C_2H_5)_2NCH_2CH_2NCH_2CH_2N(C_2H_5)_2]^-$; Me_5dien, $(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$; $MeEt_4$dien, $(C_2H_5)_2NCH_2CH_2N(CH_3)CH_2CH_2N(C_2H_5)_2$.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.