tion in the same manner as the mechanism usually invoked to explain nitrogen hyperfine splittings in the esr spectra of aromatic free radicals.[31] Alternatively, an exchange polarization interaction between the unpaired e_g spins and the filled t_{2g} electrons[19] could cause some unpairing which must lead to a delocalization of a net negative spin density into the ligand π system. In view of the lack of sensitivity of the observed[4,7] "π" shifts to the reduced ligand symmetry, although the π shifts in the Cr(II) and Fe(III) chelates were the most sensitive to methyl substitution, the former mechanism may be dominant, since this does not necessitate postulating any metal–ligand π bonding at all.[32]

Acknowledgments.—We are indebted to Dr. E. E. Genser for attempting to obtain esr spectra of some of the Cr(II) chelates.

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(31) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 6.

(32) NOTE ADDED IN PROOF.—Recent theoretical considerations (R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, in press) have shown that the dipolar shift is related to the magnetic susceptibility anisotropy and is thus *independent* of the signs of the components of the g tensor. Thus DeSimone and Drago[7] overestimated the dipolar shifts for their Fe(III) chelates by 55% using the wrong signs. The correct calculation reduced the dipolar contribution so that the contact shifts at only the 4,4′ position exhibit the sign reversal between proton and methyl group; these contact shifts are therefore inconsistent with π-spin density alone. Similarly, the dipolar shifts in our Table V are also reduced by 55% and are thus secondary to contact shifts at all positions. Moreover, as pointed out by Horrocks[24] and McGarvey (private communication), second-order Zeeman, SOZ, contributions to the dipolar shift must also be included since they are of comparable magnitude, though perhaps of opposite sign, to the first-order terms, on which basis eq 9 in ref 7 is based. Thus Horrocks (private communication) has shown that for the isoelectronic d^5 $Fe(CN)_6^{3-}$ chromophore, inclusion of SOZ terms reduces the calculated dipolar shifts to one-fifth their value obtained on the basis of eq 9 in ref 7. This same situation is very likely to obtain in the present d^5 Fe(III)–bipy chelates.[7] Pending a more detailed and correct analysis of the dipolar shifts in these Fe(III) chelates, DeSimone and Drago's conclusions on the relative importance of dipolar shifts and the unimportance of σ-spin delocalization cannot be considered even qualitatively valid. On the other hand, a possible overestimation of the dipolar shifts for the Fe(III) chelates does not affect the necessarily qualitative conclusions of the present article.

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The Effect of Ring Size on the Stability of Polyamine Complexes Containing Linked Consecutive Rings

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Equilibrium constants are determined for the protonation and metal complexation of N,N-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) and N-(2-aminoethyl)-1,3-propanediamine (2,3-tri). In the 1:1 complexes the 5,6,5-membered chelate ring system forms more stable complexes than 5,5,5-membered rings by factors of $10^{3.8}$, $10^{2.0}$, and $10^{0.7}$ for Cu(II), Ni(II), and Zn(II), respectively. The 5,6-membered chelate ring system forms 1:1 complexes with nickel of the same stability as 5,5-membered rings. The log K values for the protonation constants are 10.25, 9.50, 7.28, and 6.02 for 2,3,2-tet and are 10.03, 9.11, and 6.18 for 2,3-tri (25.0° and $\mu = 0.5\ M$). The formation constants for the complexes $M(2,3,2\text{-tet})^{2+}$ (M = Ni, Cu, Zn) are log K = 16.4, 23.9, and 12.8, respectively. Nickel also forms a complex $Ni(2,3,2\text{-tet})_2{}^{2+}$ with log $\beta_2 = 20.1$. The formation constants for the nickel complexes of 2,3-tri are log $K_1 = 10.7$ and log $\beta_2 = 17.8$.

Introduction

Recently a number of investigators[2–4] have reported complexes of the quadridentate ligand N,N′-bis-(2-aminoethyl)-1,3-propanediamine (2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$). The complexes of this ligand with metal ions exhibit striking differences in properties compared to the well-known trien, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, complexes. These differences have been attributed to steric constraints in the three linked 5-membered rings of trien which are relieved by the presence of a 6-membered ring in the 2,3,2-tet complexes. It was of interest to see how the balance between the relief of ring strain and the unfavorable effects due to the presence of a 6-membered ring would be reflected in the stability constants of the 2,3,2-tet complexes.

In the present work the formation constants of the 2,3,2-tet complexes of Ni(II), Cu(II), and Zn(II) and the N-(2-aminoethyl)-1,3-propanediamine (2,3-tri), $H_2N(CH_2)_2NH(CH_2)_3NH_2$, complexes of Ni(II) were measured. The 2,3,2-tet complexes are more stable than the corresponding trien complexes and the 1:1 2,3-tri complex has the same stability as the 1:1 dien, $H_2N(CH_2)_2NH(CH_2)_2NH_2$, complex, but the 2:1 complex is less stable than the corresponding dien complex.

Experimental Section

Reagents.—Nickel sulfate (reagent grade) was recrystallized twice from water and standardized by the addition of excess *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate and back-titration with standard calcium chloride solution using methyl thymol blue indicator. Copper perchlorate was prepared from copper carbonate and perchloric acid and was recrystallized before use. Zinc perchlorate was recrystallized three times from water and standardized by EDTA titration using Erio-

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(1) Address correspondence to this author.

(2) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, 1331 (1966).

(3) H. G. Hamilton and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).

(4) A. T. Philip, Ph.D. Thesis, University of Sydney, 1964, p 34.

chrome Black T. The 2,3,2-tet (Eastman Organic Chemicals) was purified by distillation under reduced pressure. The 2,3-tri (Aldrich Chemical Co.) was purified by preparation of the hydrochloride and recrystallization three times from ethanol.

Potentiometric Measurements.—The potentiometric titrations were carried out in a glass cell under an atmosphere of nitrogen at 25.0° with a Beckman Research Model 1016 pH meter. The meter was calibrated with NBS standard buffers. The value of $-\log [H^+]$ was estimated by subtracting 0.12 unit from the measured pH.[5] Solutions were titrated manually with 0.1 M NaOH prepared in carbonate-free water. The amount of base added did not significantly affect the ionic strength. The protonation and metal ion stability constants were determined using the concentration conditions given in Table I. At least 40 data points were used for each titration and each titration was performed in duplicate. Equilibrium was attained almost instantaneously in all systems except in the case of nickel where in the pH range 3.5–7.5 it was necessary to wait 3–4 min after the addition of base before a stable reading was obtained. The protonation and formation constants were calculated using a Hewlett-Packard 2115A computer.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE POTENTIOMETRIC TITRATIONS[a]

Cation	$[M]_{initial}$, M	$[Ligand]_{initial}$, M	$[HCl]_{initial}$, M	Range of $-\log [H^+]$
		Ligand = 2,3-tri		
H^+		0.00193	0.0110	3.8–10.6
Ni^{2+}	0.00105	0.00206	0.00472	2.2–11.0
		Ligand = 2,3,2-tet		
H^+		0.00611	0.0249	4.7–10.3
		0.00434	0.0147	6.1–10.8
		0.00138	0.0120	2.4–11.25
Ni^{2+}	0.000722	0.00131	0.0110	2.2–11.2
	0.000722	0.00131	0.00550	4.6–11.2
	0.00123	0.00131	0.0135	2.0–11.2
Cu^{2+}	0.00125	0.00142	0.00643	3.0–10.2
Zn^{2+}	0.00535	0.00639	0.0130	3.0–10.5

[a] Temperature 25.0°; $\mu = 0.5$ M KCl; titrated with 0.1 M NaOH.

The protonation constants were determined from values of $\bar{p}$, the average number of protons bound to each ligand molecule, using the ranges 3.8–3.2, 2.8–2.2, 1.8–1.2, and 0.8–0.2 for K_4, K_3, K_2, and K_1, respectively. The values of the first two protonation constants, which overlapped, were obtained from the slope and intercept of the least-squares fit to eq 1. For 2,3,2-tet the third

$$\frac{\bar{p}}{(\bar{p} - 1)[H^+]} = K_1K_2 \left\{ \frac{(2 - \bar{p})[H^+]}{(\bar{p} - 1)} \right\} - K_1 \qquad (1)$$

and fourth protonation constants were separated by a similar equation. The formation constants of the metal complexes were calculated for $\bar{n}$ values between 0.2 and 0.8 and 1.2 and 1.8. The general equations of Hearon and Gilbert[6] were used to calculate $\bar{n}$. The formation constant of $Ni(2,3,2\text{-tet})_2^{2+}$ also was calculated using the program SCOGS[7] on a CDC 6500 computer. This program calculates the formation constants of species in solution from potentiometric data by minimizing the sums of the squares of the differences between computed and experimental titers using estimates of unknown constants and the experimental value of the pH. The program was modified so that the protonation constants used were stoichiometric constants based on the concentrations of all the species rather than Brønsted or mixed constants.[8] The four protonation constants of 2,3,2-tet and the formation constant for $Ni(2,3,2\text{-tet})^{2+}$ were held constant. Attempts to include such species as $Ni(2,3,2\text{-tet})_2H^{3+}$ and $Ni_2(2,3,2\text{-tet})_3^{4+}$ indicated that such species were not present in solution in significant concentrations (less than 1%) under the conditions used.

Results

Protonation Constants.—The protonation constants obtained for 2,3,2-tet and 2,3-tri are given in Table II together with the constants for trien,[9] 3,3,3-tet,[10] dien,[11] and 3,3′-diaminodipropylamine (3,3-tri).[12] Comparison of the values of log K_1 shows that 2,3,2-tet is slightly more basic than trien, and the ligand 3,3,3-tet is even more basic. Also 2,3-tri is intermediate in basicity between dien and 3,3-tri. This behavior has been attributed to an inductive effect due to the larger number of methylene groups.[10] The large increase in the values of log K_3 and log K_4 with additional methylene groups is attributed to reduced electrostatic repulsion between the NH^+ groups.

TABLE II

PROTONATION CONSTANTS OF 2,3-tri AND 2,3,2-tet IN 0.5 M KCl AT 25.0°

Ligand	Log K_1	Log K_2	Log K_3	Log K_4
2,3-tri[a]	10.03 ± 0.03	9.11 ± 0.06	6.18 ± 0.03	
2,3,2-tet[a]	10.25 ± 0.02	9.50 ± 0.05	7.28 ± 0.02	6.02 ± 0.02
trien[b]	9.95 ± 0.02	9.31 ± 0.02	6.86 ± 0.02	3.66 ± 0.03
3,3,3-tet[c]	10.61	9.98	8.69	7.35
dien[d]	9.94	9.13	4.34	
3,3-tri[e]	10.70	9.70	8.02	

[a] This work. [b] Reference 9; $\mu = 0.5$ M (KCl), 25.0°. [c] Reference 10; $\mu = 0.1$ M ($NaNO_3$), 20.0°. [d] Reference 11; $\mu = 0.1$ M (KCl), 20.0°. [e] Reference 12; $\mu = 1.0$ M (KNO_3), 30.0°.

TABLE III

FORMATION CONSTANTS OF METAL COMPLEXES WITH POLYAMINES

Ligand	Metal	Log K_1	Log β_2	Log β_{23}
dien[a]	Ni^{2+}	10.6	18.6	
2,3-tri[b]	Ni^{2+}	10.7 ± 0.1	17.8 ± 0.1	
3,3-tri[c]	Ni^{2+}	9.09	...	
trien	Ni^{2+} [d]	14.4 ± 0.1	18.6 ± 0.3	36.9 ± 0.5
	Cu^{2+} [e]	20.2		
	Zn^{2+} [e]	12.1		
2,3,2-tet[b]	Ni^{2+}	16.4 ± 0.1	20.1 ± 0.1	...
	Cu^{2+}	23.9 ± 0.1		
	Zn^{2+}	12.8 ± 0.1		
3,3,3-tet[f]	Ni^{2+}	10.65	...	
	Cu^{2+}	17.3	...	
	Zn^{2+}	9.41	...	

[a] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 2994 (1961); $\mu = 0.1$ M (KCl), 25.0°. [b] This work. [c] Reference 12; $\mu = 1$ M (KNO_3), 20.0°. [d] Reference 9; $\mu = 0.5$ M (KCl), 25.0°. [e] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961); $\mu = 0.1$ M (KCl), 25.0°. [f] Reference 10; $\mu = 0.1$ ($NaNO_3$), 20.0°.

Metal Stability Constants.—The formation constants of the metal complexes of 2,3,2-tet, 2,3-tri, trien, 3,3,3-tet, 3,3-tri, and dien are given in Table III. The potentiometric data for $Ni(2,3,2\text{-tet})^{2+}$ indicate the presence of only two complexes in solution, Ni-

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(5) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964, p 74.

(6) J. Z. Hearon and J. B. Gilbert, *J. Am. Chem. Soc.*, **77**, 2594 (1955).

(7) I. G. Sayce, *Talanta*, **15**, 1397 (1968).

(8) F. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 27.

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$(2,3,2\text{-tet})^{2+}$ and $Ni(2,3,2\text{-tet})_2{}^{2+}$. This behavior is in contrast to that of trien which also forms $Ni_2(\text{trien})_3{}^{4+}$ in solution. Solid complexes of the type $[Ni_2(2,3,2\text{-tet})_3]X_4$ have been isolated,[2,4] but they reportedly disproportionate in solution. No attempt was made to measure the stability constants of possible bis complexes of copper and zinc.

Discussion

Bosnich, *et al.*,[2] have shown that while 2,3,2-tet can readily adopt either a *cis* or *trans* configuration around a metal ion, there is a general tendency for it to adopt the *trans* configuration. On the other hand, trien shows a marked tendency to adopt the *cis*-octahedral configuration. The crystal structure of the yellow square-planar form of $[Ni(\text{trien})](ClO_4)_2$ has recently been determined.[13] The bond distances and configuration of the ligand indicate that considerable strain is present in the ligand when nickel and the nitrogens are all in one plane. The visible spectrum of $Cu(\text{trien})^{2+}$ has been interpreted as indicating a marked destabilization of one of the copper–nitrogen bonds.[2] The large increase in the formation constant of $Cu(2,3,2\text{-tet})^{2+}$ ($\log K_1 = 23.9$) compared to $Cu(\text{trien})^{2+}$ ($\log K_1 = 20.1$) despite the presence of a 6-membered ring in the former can be attributed to a decrease in the steric constraints imposed on the ligand in the square-planar configuration. The steric constraints imposed on trien when it is able to adopt a *cis* configuration are somewhat less than in the square-planar configuration. At room temperature $Ni(\text{trien})^{2+}$ is predominantly *cis*-octahedral in solution,[14] but $Ni(2,3,2\text{-tet})^{2+}$ exists in both blue and yellow forms in solution, again indicating fewer steric constraints in the square-planar arrangement for 2,3,2-tet.

There is some evidence based on the ΔS of formation that $Zn(\text{trien})^{2+}$ is tetrahedral in solution.[15] Molecular models indicate that 2,3,2-tet should be able to coordinate metal ions in a tetrahedral manner with fewer steric constraints than trien. The formation constant of $Zn(2,3,2\text{-tet})^{2+}$ ($\log K_1 = 12.8$) is slightly higher than that of $Zn(\text{trien})^{2+}$ ($\log K_1 = 12.1$).[15] The quadridentate ligand 2,2′,2″-triaminotriethylamine (tren) which imposes a tetrahedral configuration on metal ions forms a Zn^{2+} complex with $\log K_1 = 14.5$.[16] The decrease in stability from tren to 2,3,2-tet may therefore be partly attributed to the presence of the 6-membered ring in 2,3,2-tet, although entropy effects built into the tren molecule must also be important. The small difference in stability constants of $Zn(2,3,2\text{-tet})^{2+}$ and $Zn(\text{trien})^{2+}$ suggests that in this case the increase in steric constraints with trien is almost equal to the decrease in stability due to the 6-membered ring. The formation constants of 3,3,3-tet with a number of metals have been measured[10] and a considerable decrease in stability compared to the corresponding trien constants was noted. A difference of almost 6 log units is observed between the formation constants of 3,3,3-tet and 2,3,2-tet with copper and nickel indicating considerable destabilization with the addition of two additional 6-membered rings.

Yamauchi, *et al.*,[17] have recently measured the stability constants of a series of copper dipeptides containing linked 5,5-, 5,6-, and 6,6-membered rings. They found that the linked 5,5- and 5,6-membered rings formed complexes of equal stability but there was a decrease in stability with 6,6-membered rings. These observations were in contrast to their earlier[18] qualitative observations on the stability of linked 5,5- and 5,6-membered rings in copper–Schiff base complexes which suggested that linked 5,6-membered rings were more stable than linked 5,5-membered rings. They attributed this behavior to the varied steric requirements of the different donor groups of the ligands. It was therefore of interest to compare the stability of complexes of 2,3-tri with the complexes of dien. The results for the nickel complex show that replacement of one 5-membered ring by a 6-membered ring does not lead to a decrease in stability. This suggests that two linked 5-membered rings are strained and that the relief of the strain by the addition of another methylene group is balanced by the decrease in stability due to the presence of a 6-membered ring. The decrease in stability of the $Ni(2,3\text{-tri})_2{}^{2+}$ complex compared to $Ni(\text{dien})_2{}^{2+}$ can be attributed to steric crowding by the more bulky ligand already bound to the nickel. The larger ligand 3,3-tri does not form a bis complex with nickel.[12]

These results show that a series of linked 5-membered rings become sterically constrained on coordination to a metal and that the replacement of a 5-membered ring by a 6-membered ring can reduce the steric constraints and lead to a considerable increase in the stability of the metal complex. The size of this increase depends upon the configurational requirements of the metal.

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