in a solid-state film the $MnBr_2PPhMe_2$ complex decomposes rapidly in competition with evacuation of the complexed dioxygen. Whether the reaction scheme proposed in Figure 2 is valid for this complex could not be determined in this work.

Conclusions

The interaction of dioxygen with tertiary phosphine complexes of $MnBr_2$ for solid-state films is markedly dependent upon the nature of the tertiary phosphine ligand employed. The $MnBr_2PMe_3$ complex is quite stable toward decomposition to $MnBr_2OPMe_3$ upon exposure to dioxygen, but it also shows little tendency toward reversibility during dioxygenation/evacuation cycles. In fact the blue color cannot be removed by prolonged evacuation, and it only disappears following decomposition. On the other hand, cycles of color/colorless can be obtained for $MnBr_2PEt_3$ and $MnBr_2PPhMe_2$ upon dioxygenation/evacuation, but these complexes decompose (especially $MnBr_2PPhMe_2$) competitively to the phosphine oxide complexes. The $MnBr_2PEt_3$ complex film was the only one in this study that exhibited an infrared band that clearly cycles in intensity upon dioxygenation/evacuation cycles. Finally, it should be noted that recent work here has demonstrated that the chloride analogues of the three complex films discussed in this work behave similarly to the bromide complex films.[19]

Acknowledgment. The authors are grateful to the Office of Naval Research, the National Science Foundation (through Grant CHE-7920825), the Research Corp., and the Auburn University Energy Grant-in-Aid program for partial support of this work.

Registry No. $MnBr_2PMe_3$, 85883-29-0; $MnBr_2PEt_3$, 82758-64-3; $MnBr_2PPhMe_2$, 71957-10-3; $MnBr_2PMe_3{\cdot}O_2$, 85893-33-0; $MnBr_2PMe_2OMe$, 92816-97-2; $MnBr_2OPMe_3$, 85883-30-3; $MnBr_2OPMe_2OMe$, 92816-98-3; $MnBr_2PEt_3{\cdot}O_2$, 92816-99-4; $MnBr_2OPEt_3$, 92817-00-0; $MnBr_2PPhMe_2{\cdot}{}^{16}O_2$, 72910-33-9; $MnBr_2{}^{16}OPPhMe_2$, 92817-01-1.

---

[19] Newberry, V. F.; Hill, W. E.; Worley, S. D., unpublished data.

Contribution from the Dipartimento di Chimica Generale,
Università di Pavia, 27100 Pavia, Italy

Ring-Size Effects on the Formation of Dicopper(II) and Dicopper(III) Complexes with Bimacrocycles Containing 13- and 14-Membered Tetraaza Subunits

ARMANDO BUTTAFAVA, LUIGI FABBRIZZI,* ANGELO PEROTTI, ANTONIO POGGI, and BARBARA SEGHI

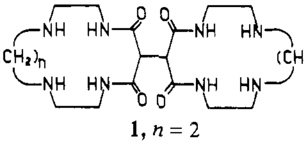
Received February 6, 1984

The double-ring macrocycle **1**, having 13-membered subunits, incorporates two Cu^{II} ions in aqueous solution according to three pH-controlled steps, which involve progressive deprotonation of the coordinated amido groups of the ligand. The fully deprotonated neutral dicopper(II) complex undergoes a reversible oxidation process to the dicopper(III) species according to two one-electron redox changes separated by 100 mV. This behavior is compared with that of the corresponding bimacrocyclic ligand having 14-membered subunits **2** as well as with the single-ring reference systems **3** and **4**. The 14-membered subunit forms the more stable complexes with Cu^{II} ion, whereas the 13-membered cavity favors the access to the trivalent state, with both single- and double-ring systems.

Introduction

Bimacrocycles are molecules in which two potentially chelating macrocyclic subunits are linked together. Each ring may coordinate a metal ion, and the two metal centers may display independent or mutually dependent behavior depending upon the length of the bridge joining the two subunits. The most favorable coordination of transition cations is that one containing four nitrogen atoms in the donor set, and some double-ring molecules with tetraaza subunits have been developed in the past years. All the reported bimacrocycles originated from metal template syntheses or from reactions involving preformed monocyclic metal complexes.[1-3] As a consequence, macrocyclic subunits of fixed ring size were obtained, preferably the 14-membered ones.

We have recently developed a new synthetic strategy for the preparation of bimacrocycles containing tetraaza subunits, simply based on the condensation of a tetraester (tetraethyl 1,1,2,2-ethanetetracarboxylate) with a linear tetraamine in a 1:2 molar ratio.[4,5] In this way, the double-ring macrocycle, in which two dioxo tetraamine subunits are linked by a covalent bond between two atoms of the carbon backbones, is obtained as a free, uncomplexed molecule. Moreover, the method is particularly flexible, since when the length of the tetraamine fragment used in the condensation is modulated, bimacrocycles containing subunits of varying ring size can be obtained. In a previous report the coordinating behavior of a bimacrocycle with 14-membered rings, ([14-14]bisdioxocyclam (**2**)), has been described.[5] We report here the chelating tendencies of the 13-membered analogue, ([13-13]bisdioxocyclam (**1**)).



1, $n = 2$
2, $n = 3$

Dioxo tetraamine macrocycles and their metal complexes present some interesting properties. (*i*) The dioxo tetraamine ring can incorporate a divalent 3d cation (e.g., Cu^{II}) with a simultaneous extrusion of two hydrogen ions from the amido groups;[6] therefore, complexation is pH dependent and can be monitored through potentiometric titration. (ii) When en-

---

[1] Barefield, E. K.; Chueng, D.; Van Derveer, D.; Wagner, F. *J. Chem. Soc., Chem. Commun.* **1981**, 302-304.

[2] Murase, I.; Hamada, K.; Kida, S. *Inorg. Chim. Acta* **1981**, *54*, L171-172.

[3] Murase, I.; Hamada, K.; Ueno, S.; Kida, S. *Synth. React. Inorg. Met.-Org. Chem.* **1983**, *13*, 191-207.

[4] Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166-1167.

[5] Fabbrizzi, L.; Forlini, F.; Perotti, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 807-813.

[6] Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1979**, 325-329.

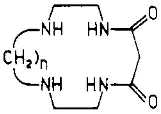
Table I. log *K* Values for the Stepwise Protonation Equilibria Involving Single- and Double-Ring Macrocycles (25 °C, in 0.1 M $NaClO_4$)[a]

	[13]-dioxo-cyclam	[13-13]-bisdioxo-cyclam	[14]-dioxo-cyclam[b]	[14-14]-bisdioxo-cyclam[b]
$L + H^+ \leftrightharpoons HL^+$	8.78 (2)	8.98 (2)	9.51	9.96
$HL^+ + H^+ \leftrightharpoons H_2L^{2+}$	4.12 (3)	8.51 (3)	5.80	9.45
$H_2L^{2+} + H^+ \leftrightharpoons H_3L^{3+}$		3.71 (4)		5.40
$H_3L^{3+} + H^+ \leftrightharpoons H_4L^{4+}$		2.78 (5)		4.62

[a] Uncertainties in the last figure are given in parentheses. [b] Values taken from ref 5.

circled by the doubly negative tetraaza ring, the Cu^{II} ion undergoes a one-electron reversible oxidation process to give a water-stable authentic Cu^{III} species.[7,8]

In this work we report an equilibrium study on the complexation of two Cu^{II} ions by [13-13]bisdioxocyclam (**1**) in aqueous solution and the electrochemical investigation on the two-electron oxidation of its copper(II) complex. For comparative purposes, the corresponding chemistry of the single-ring macrocycle, [13]dioxocyclam (**3**), has been considered.



3, $n = 2$
4, $n = 3$

The aim of the present work is to evaluate to what extent ring-to-ring effects in dimetallic complexes are influenced by variation of the ring size. In particular, the equilibrium constants for the incorporation of two Cu^{II} ions and the electrode potentials for the two consecutive Cu^{II}/Cu^{III} redox changes will be considered with regard to systems having 13-membered and 14-membered subunits. Contraction of the 14-membered ring to the 13-membered one has been shown to produce drastic variation in the thermodynamic solution stability of the metal complexes[9,10] and in its electronic properties[11,12] as far as single-ring systems are concerned.

Experimental Section

Synthesis of [13-13]Bisdioxocyclam (1). The bimacrocycle was obtained through aminolytic condensation of tetraethyl 1,1,2,2-ethantetracarboxylate with 2 equiv of triethylenetetramine in refluxing ethanol (2.5×10^{-2} M scale, 3 days). Concentration of the ethanolic solution to one-third of its original volume caused formation of a white precipitate of **1**, yield 29%. Anal. Calcd for $C_{18}H_{34}N_8O_4$: C, 50.70; H, 8.03; N, 26.27. Found: C, 50.37; H, 8.26; N, 26.11. The single-ring analogue **3** was obtained in a similar way through condensation of diethyl malonate and triethylenetetramine (1:1 molar ratio).

Physical Measurements. Emf measurements of the potentiometric titrations, calculations of the equilibrium constant values, electrochemistry, ESR, and visible spectroscopy experiments were performed as previously described.[5]

Results and Discussion

Ring-to-Ring Effects in the Protonation Equilibria Involving Amino Groups. In Table I are reported the log *K* values for the protonation equilibria of [13-13]bisdioxocyclam (**1**) and of the single-ring reference molecule [13]dioxocyclam (**3**). For comparison, values are reported also for the 14-membered analogues [14-14]bisdioxocyclam (**2**) and [14]dioxocyclam (**4**). Each ring can bind two protons through amine nitrogen atoms. Comparison of single-ring systems shows that the larger ring macrocycle behaves as a stronger base for both the first and the second step. This trend reflects that found for diamine fragments, 1,3-propanediamine (log K_1 = 10.55, log K_2 = 8.88) and 1,2-ethanediamine (log K_1 = 9.98, log K_2 = 7.28).[13,14] The proton affinity is much smaller for the diamine fragment inserted in the macrocycle, especially for the addition of the second hydrogen ion. This may be due to the fact that repulsive electrostatic effects are minimized for aliphatic diamines that can assume the most favorable configuration, whereas in the cyclic system amino/ammonium groups are forced to suffer stronger mutual repulsion due to ring constrictive effects. On comparison of [13-13]bisdioxocyclam and [13]dioxocyclam behavior, it is seen that the double-ring base presents a slightly greater log K_1 value, which may result from the statistical term (0.3 log unit). log K_2, which refers to the protonation of the other ring, is smaller than log K_1 of a quantity very close to the statistical factor (0.6 log unit). Protonation of the third amine nitrogen atom feels also the influence of the adjacent protonated ring, the log K_3 value of [13-13]bisdioxocyclam being considerably smaller (0.4 log unit) than the log K_2 value of the reference system [13]dioxocyclam. Ring-to-ring electrostatic repulsive effects are obviously greater for the protonation of the fourth amine group, which suffers the influence of the double-positive charge of the close ring. A progressive decrease of log K_3 and log K_4 values has been found also with the [14-14]bisdioxocyclam molecule in comparison with the single-ring system [14]dioxocyclam.[5] The strictly analogous behavior indicates that in this case ring-to-ring effects are independent of the size of the macrocyclic subunit: this is expected in view of the fact that electrostatic repulsion effects between the two rings are controlled only by the distance between amino groups of each ring and this distance is not modified by the variation of the length of the aliphatic chain joining the two amino groups of each subunit.

Incorporation of a Cu^{II} Ion by Single-Ring Macrocycles. Coordinating tendencies of [13]dioxocyclam toward aqueous Cu^{II} ions have been investigated by means of pH titration with standard base of a solution containing the macrocycle and $Cu(ClO_4)_2$ in equivalent amounts plus excess acid. The titration curves have been simulated with the computer program MINIQUAD;[15] complex species present at the equilibrium are chosen, and their equilibrium constants are refined to the best curve fitting. In the following text, every complex species will be denoted by (*p*,*q*,*r*), where *p* is the stoichiometric coefficient of the ligand in the complex, *q* that of the metal, and *r* that of the hydrogen ions. For instance, in a hypothetical species denoted as (1,1,1) the metal ion is coordinated by a monoprotonated ligand: $M^{II}(HL)^{3+}$. A negative value of *r* indicates that the complex has released a proton (for instance from an amido group of the ligand). In the case of the Cu^{II}/[13]dioxocyclam system, the best curve fitting is obtained considering the species (1,1,0) and (1,1,–2); the corresponding equilibrium constants are reported in Table II. The species of stoichiometry (1,1,0) corresponds to a complex in which Cu^{II} ion is chelated by the neutral macrocycle. If one considers that β_{110} is even smaller than that for the $[Cu^{II}(1,2\text{-ethanediamine})]^{2+}$ complex (10.58 log units),[14] it should be concluded

---

(7) Fabbrizzi, L.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1980**, 646–647.
(8) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1981**, 694–700.
(9) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *J. Chem. Soc., Dalton Trans.* **1978**, 577–583.
(10) Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chem.* **1978**, *17*, 1042–1046. Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1980**, *19*, 535–538.
(11) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968–2981.
(12) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029–4039.
(13) Vacca, A.; Arenare, D. *J. Phys. Chem.* **1967**, *71*, 1495–1500.
(14) Barbucci, R.; Paoletti, P.; Vacca, A. *J. Chem. Soc. A* **1970**, 2202–2206. Barbucci, R.; Fabbrizzi, L.; Paoletti, P.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1972**, 740–745.
(15) Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1974**, *21*, 53–77. Vacca, A.; Sabatini, A. In "Modern Inorganic Chemistry"; Fackler, J. P., Ed.; Plenum Press: New York, 1983.

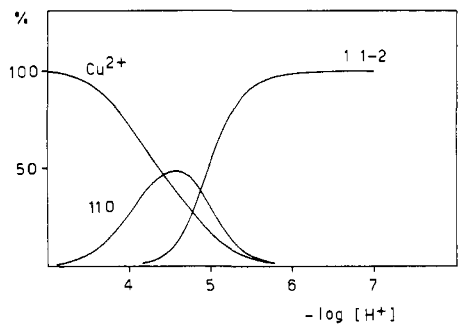


Figure 1. Distribution curves of the species present at the equilibrium in the system Cu^{2+}/[13]dioxocyclam in a 1:1 molar ratio.

that only the diamine fragment of the macrocycle is really involved in coordination. When the pH is increased, the two amido groups deprotonate to give the (1,1,–2) species in which the Cu^{II} ion is fully coordinated by the tetraaza cavity. In figure 1 the distribution curve of the two complex species is reported: the (1,1,0) species is significantly represented, reaching 50% of the total copper concentration at pH 4.6. In the case of the larger size ligand, [14]dioxocyclam, the same complex species (1,1,0) and (1,1,–2) have been found; however, in this latter case the (1,1,0) complex showed a maximum concentration lower than 15%, in spite of the fact that log β_{110} is greater for the 14-membered ligand than for the 13-membered one. The fact is that the competing species (1,1,–2) is much more stable for [14]dioxocyclam than for [13]dioxocyclam. Therefore, the (1,1,0) complex of [13]dioxocyclam is strongly represented in weakly acidic solution, not for its high intrinsic stability but due to the relatively low stability of the competing doubly deprotonated species (1,1,–2).

It has been already anticipated that in the case of (1,1,–2) complexes, in which the Cu^{II} ion is fully coordinated by a tetraaza donor set and lies in the equatorial plane, [14]dioxocyclam gives a remarkably more stable complex than [13]dioxocyclam. This behavior is consistent with arguments concerning the radius of the encircled cation and the size of the macrocyclic cavity. It has been calculated that for a fully saturated tetraaza macrocycle, the 14-membered ligand (cyclam) in its "relaxed" configuration is prepared to form M–N bonds with the encircled cation of 2.07 Å.[16] On the other hand, Cu^{II} ion usually shows in polyamine complexes bond distances ranging from 2.05 to 2.10 Å. Therefore, Cu^{II} ion has the appropriate size to fit the 14-membered cavity both of cyclam and of [14]dioxocyclam (even if, due to the presence of two sp^2 carbon atoms in the backbone, the latter ligand should have a slightly smaller ring than the fully saturated analogue). The 13-membered cavity, which prefers a M–N bond distance of 1.92 Å,[16] is too small to encircle Cu^{II} ion according to a strain-free arrangement. Coplanar coordination of Cu^{II} by [13]dioxocyclam probably induces distorsions in the ligand framework and deviations of the nitrogen atoms from the coordination sites preferred by the encircled cations (the corners of a square), which causes an increase of the strain energy and the formation of less strong coordinative bond. In this sense, it is reassuring that the energy of the d–d absorption band, which gives an empirical measure of the in-plane Cu^{II}–N interactions,[17] in the case of the [13]dioxocyclam complex is considerably lower than that for the [14]dioxocyclam species (19 230 and 21 550 cm^{-1}, respectively). Therefore, the lower stability of the 13-membered ligand complex seems to derive from the formation of the less strong M–N bonds due to the unfavorable structural features of the ligand. It is apparently surprising that, in the case of fully saturated analogoues, the reverse order of stability has been found,[18,19] i.e. the log K value is greater for $[Cu([13]cyclam)]^{2+}$ than for $[Cu([14]cyclam)]^{2+}$: however, this discrepancy may derive from the objective difficulty in performing equilibrium studies with inert systems such as metal complexes with cyclic polyamines and from the fact that the two systems have been investigated by using different techniques (polarography for $[Cu([13]cyclam)]^{2+}$; potentiometry, with copper amalgam electrode, for $[Cu([14]cyclam)]^{2+}$).

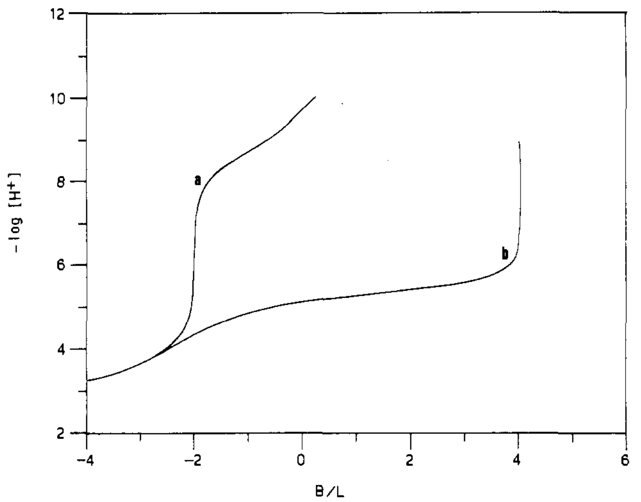


Figure 2. Titration curves of [13-13]bisdioxocyclam: (a) bimacrocycle + 4 equiv of acid; (b) bimacrocycle + 4 equiv of acid + 2 equiv of Cu^{2+}. B/L is the ratio of the moles of the standard base added, B, over the moles of bimacrocycle, L. Negative values indicate the excess of acid (e.g., –2: 2 equiv of standard acid).

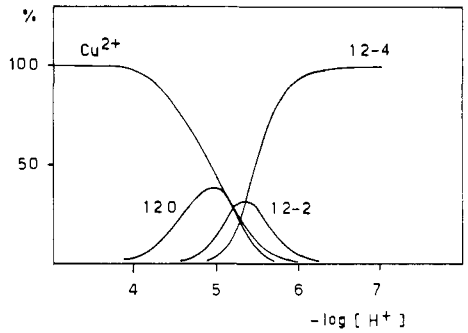


Figure 3. Distribution curves of the species present at the equilibrium in the system Cu^{2+}/[13-13]bisdioxocyclam in a 2:1 molar ratio.

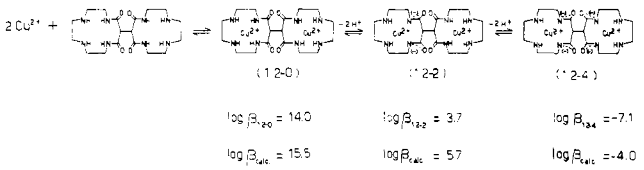


Figure 4. Hypothesized coordinative arrangements deriving from the incorporation of two Cu^{2+} by [13-13]bisdioxocyclam and successive stepwise extrusion of protons by the bimacrocycle. log β_{calcd} values have been obtained by combining values for the single-ring macrocycle [13]dioxocyclam (see text).

Formation of Dicopper(II) Complexes with Double-Ring Macrocycles. The incorporation of Cu^{II} ions by the double-ring ligand [13-13]bisdioxocyclam has been monitored by pH titration with standard base of a solution containing the bi-

---

[16] Martin, L. Y.; De Hayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4046–4048.

[17] Fabbrizzi, L.; Paoletti, P.; Lever, A. B. P. *Inorg. Chem.* **1976**, *15*, 1502–1506.

[18] Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1976**, 1720–1724.

[19] Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2341–2345.

Table II. log *K* Values for the Complexation Equilibria between the Cu^{II} Ion and Single- and Double-Ring Macrocycles (25 °C, in 0.1 M NaClO$_4$)[a]

	single-ring ligands	
	[13]-dioxocyclam	[14]-dioxocyclam[b]
$Cu^{2+} + H_2L \rightleftharpoons [Cu(H_2L)]^{2+}$ (1,1,0)[c]	7.73 (2)	8.75
$Cu^{2+} + H_2L \rightleftharpoons [Cu(L)]^0 + 2H^+$ (1,1,−2)[c]	−2.02 (3)	0.44
	double-ring ligands	
	[13-13]-bisdioxocyclam	[14-14]-bisdioxocyclam
$2Cu^{2+} + H_4L \rightleftharpoons [Cu_2(H_4L)]^{4+}$ (1,2,0)[d]	14.00 (4)	17.79
$2Cu^{2+} + H_4L \rightleftharpoons [Cu_2(H_2L)]^{2+} + 2H^+$ (1,2,−2)[d]	3.66 (2)	8.59
$2Cu^{2+} + H_4L \rightleftharpoons [Cu_2(L)]^0 + 4H^+$ (1,2,−4)[d]	−7.09 (3)	−1.34

[a] Uncertainties in the last figure are given in parentheses. [b] Values taken from ref 5. [c] The (*p,q,r*) symbology denotes a species of stoichiometry $[Cu_q(H_{2-r}L_p)]^{(2-r)+}$. [d] The (*p,q,r*) symbology denotes a species of stoichiometry $[Cu_q(H_{4-r}L_p)]^{(4-r)+}$.

macrocycle and $Cu(ClO_4)_2$ in a 1:2 molar ratio plus excess acid (see Figure 2). Best fitting of experimental data has been obtained by assuming the presence of the following species whose formation constants are reported in Table II: (1,2,0), (1,2,−2), (1,2,−4). Noticeably, species showing an odd number of released protons, i.e., (1,2,−1) and (1,2,−3), have been rejected in the computation, giving negative values of the equilibrium constants. The same complex species have been found also with [14-14]bisdioxocyclam.[5] The distribution curves of the species present at the equilibrium are illustrated in Figure 3. The hypothesized coordinative arrangements of the three complexes are depicted in Figure 4. In the (1,2,0) complex each Cu^{II} cation is bound to the neutral undeprotonated subunit. We can obtain a calculated value of β_{120} for the (1,2,0) complex multiplying by two the log β value of the (1,1,0) complex of the single-ring reference ligand [13]dioxocyclam. The calculated value (15.5), which expresses the metal–ligand interaction in absence of ring-to-ring effect, is larger by 1.5 log units than the observed value. The corresponding energy difference (2.0 kcal mol^{-1}) should essentially give the repulsion electrostatic energy between the two proximate metal centers. The (1,2,−2) species is obtained on extrusion of two protons by two amido groups: we are inclined to believe that the two protons come from the same ring, to allow the full incorporation of a Cu^{II} ion in a subunit, rather than one from each ring, considering that the possibility of release of an odd number of protons has been rejected in the case of monocyclic reference systems. The calculated log *K* value, obtained by summing the log values for (1,1,0) and (1,1,−2) species of [13]dioxocyclam, is larger than the experimental value by 2.0 log units, thus suggesting a greater ring-to-ring repulsive effect than for the (1,2,0) complex. This behavior is surprising if one considers that with (1,2,0) species repulsive interactions involved cations bonded by neutral moieties, whereas with (1,2,−2) species one of the Cu^{2+} ions is merged in a dinegative cavity and its electrical charge should be partially quenched. However, one must consider also that metal-promoted deprotonation of the amido groups induces a charge delocalization over the N–C–O backbone through a π mechanism to make oxygen atoms partially negatively charged. This type of repulsive interaction is expected to be much more important in the (1,2,−4) species, where all the facing oxygen atoms of the two rings retain a partial negative charge. As a matter of fact, the difference between the calculated (2 log β_{11-2} of the [13]dioxocyclam complex) and the experimental values is much larger than for other dimetallic complexes: 3.1 log units. The corresponding energy term (4.2 kcal mol^{-1}) is comprehensive of the metal–metal contribution (repulsion between incorporated Cu^{II} ions) and effects due to the facing of negatively charged oxygen atoms. In the case of the (1,2,−4) complex with the 14-membered analogoue [14-14]bisdioxocyclam, the difference between the calculated and observed log $\beta_{1,2-4}$ values is less conspicuous (1.5 log units), showing considerably weaker ring-to-ring effects. Probably, incorporation of the Cu^{II} ions by the tailor-made 14-membered cavities should quench the electrical charge to a greater extent, making inter-ring repulsion less intense. Therefore, in the [13-13]bisdioxocyclam (1,2,−4) complex, greater ring-to-ring effects seem to exist, which are ascribed essentially to a less shielded electrostatic repulsion between the metal centers. This in turn originates from the lower coordinative ability toward Cu^{II} of the 13-membered subunit, compared to the 14-membered one.[20]

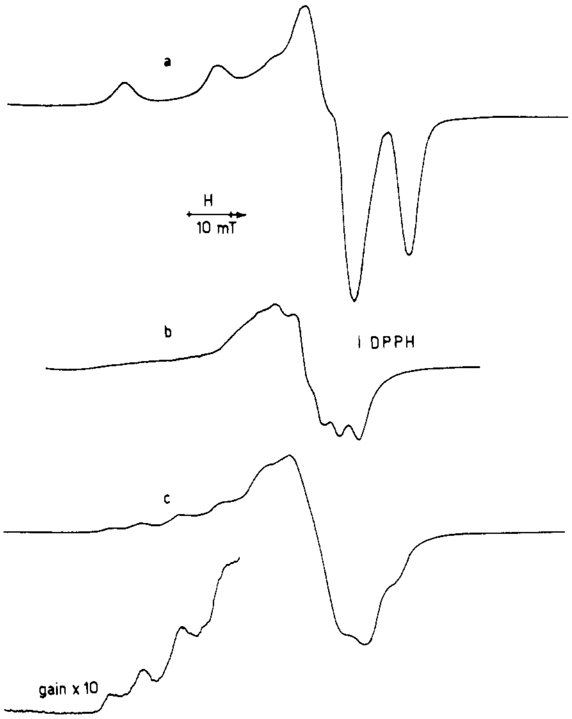


Figure 5. ESR spectra of Cu^{II} macrocyclic complexes in aqueous solution: (a) 77 K spectrum of the (1,1,−2) Cu^{II}([13]dioxocyclam) complex; (b) room-temperature spectrum of the (1,2,−4) Cu_2([13-13]dioxocyclam) complex; (c) 77 K spectrum of the (1,2,−4) Cu_2([13,13]dioxocyclam) complex.

ESR Properties of the Dicopper(II) Complexes. The ESR spectrum of the aqueous neutral dicopper(II) complex of [13-13]bisdioxocyclam, of stoichiometry (1,2,−4), has been measured both in frozen conditions at 77 K and in the liquid phase at room temperature. For comparative purposes, also the corresponding spectra of the Cu^{II} complex of [13]dioxocyclam (1,1,−2) were recorded. Solutions were prepared by dissolving appropriate amounts of Cu^{2+} and the ligand (10^{-3} M) in 0.1 M NaClO$_4$ solution at a minimum pH at which 100% of the species under investigation was presented (see distribution curves in Figures 1 and 3). The single-ring com-

---

(20) It should be noted that the Cu^{II} complexes with the single-ring macrocycles [13]dioxocyclam and [14]dioxocyclam having (1,1,−2) stoichiometry can be obtained as solids by mixing an aqueous solution of copper(II) acetate and an ethanolic solution of the diamido macrocycle. The complexes contain crystallization water that is eliminated after drying in vacuo at 50 °C. Corresponding complexes with bimacrocycles could not be isolated and characterized as solids since the same synthetic procedure gave oily blue-violet material.

Table III. Half-Wave Potential Values for the Cu^{III}/Cu^{II} Redox Change in Single- and Double-Ring Macrocyclic Complexes (25 °C, in 0.1 M $NaClO_4$)[a]

ligand	E_1-(Cu^{III}/Cu^{II})[b]	E_2-(Cu^{III}/Cu^{II})[b]
[13]dioxocyclam	0.58	
[14]dioxocyclam	0.65	
[13-13]bisdioxocyclam	0.56	0.66
[14-14]bisdioxocyclam	0.58	0.69

[a] The redox change involves metal complexes in which each macrocyclic subunit is twice negatively charged, i.e. $Cu^{III}L^+ + e^- \rightleftharpoons Cu^{II}L^0$. [b] V vs. SCE; uncertainties within ±5 mV.

plex exhibited a tetragonal pattern with $g_\parallel = 2.16$ and $A_\parallel{}^{Cu} = 21$ mT in the glass and a four-line isotropic set with $g_{iso} = 2.08$ and $a_{iso}{}^{Cu} = 9$ mT in the liquid phase (Figure 5a). On the other hand, the solution spectrum of the dimetallic double-ring complex (Figure 5b) presented a seven-line set, which is indicative of the interaction of two copper(II) nuclei ($I = {}^3/_2$) having $g_{iso} \simeq 2.08$ and $a_{iso}{}^{Cu} = 4.5$ mT. Also the frozen-solution spectrum (Figure 5c) presented a similar multiplet structure with $A_\parallel{}^{Cu} = 9.5$ mT, ca. half of the value found for the monomeric complex: this behavior is consistent with a ferromagnetical coupling of the two copper(II) ions to produce a triplet state ($S = 1$). The similarity of the ESR response to that found for the corresponding dimetallic complex of [14-14]bisdioxocyclam suggests that the intensity of the Cu^{II}–Cu^{II} magnetic interaction is independent of the ring size. This may depend upon the fact that in the two different double-ring complexes the two metal centers are separated by the same malonate fragment and their distance is unaffected by a variation of the size of the macrocyclic subunits.

Formation of Cu^{III} Species with Single-Ring Macrocycles. Cyclic voltammetry investigation on a solution containing the $[Cu^{II}([13]dioxocyclamato)^{2-}]$ species, using a platinum or a carbon-paste electrode, disclosed an oxidation peak followed by a reduction peak of equal intensity in the reverse scan. The ratio of the anodic and cathodic peak currents, i_{pa}/i_{pc}, was unity in the explored range of potential scan rates, v (20–200 mV s^{-1}). In the same range, the $i_p/v^{1/2}$ ratio was found constant. The peak separation Δp at 20 mV s^{-1} was 80 mV (i.e., larger than the value expected for a fully reversible, in an electrochemical sense, process: 57 mV) and was found to increase with increasing potential scan rate (110 mV at 200 mV s^{-1}). This behavior is indicative of a quasi-reversible Cu^{II}/Cu^{III} redox change, analogous to that disclosed by the $[Cu^{II}([14]\text{-}dioxocyclamato)^{2-}]$ complex (for which Δp varied from 65 to 90 mV in the same scan rate range). The values of $E_{1/2}$ for both [13]dioxocyclam and [14]dioxocyclam are reported in Table III. It is seen that the $E_{1/2}(Cu^{III}/Cu^{II})$ value is less positive, i.e. the attainment of the trivalent copper is easier in the case of the smaller ring ligand. This behavior can be interpreted in terms of more or less favorable fitting of the Cu^{II} and Cu^{III} ions in the macrocyclic cavity. The change from the Cu^{II} to the Cu^{III} state (d^8 low spin) involves drastic reduction of the metal ion radius. In the case of the square-planar complex of Cu^{III} with a deprotonated tripeptide, a Cu^{III}–N(deprotonated amido) distance of 1.80 Å and a Cu^{III}–N(amino) distance of 1.90 Å have been found.[21] Such distances fit quite well with the 13-membered cavity relaxed to its minimum strain-energy configuration. Therefore, oxidation of the [13]dioxocyclamato complex is favored since it involves the change from a situation of poor fitting (the too large Cu^{II} cation in a too small cavity) to a situation of excellent fitting (the small Cu^{III} cation in the appropriate ring).

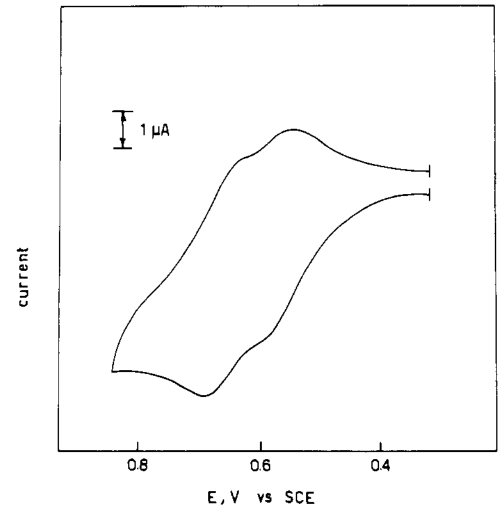


Figure 6. Cyclic voltammetry profile of a solution containing 100% of the Cu^{II}_2([13-13]bisdioxocyclam) complex (stoichiometry (1,2,–4)) (carbon-paste electrode, potential scan rate 100 mV s^{-1}).

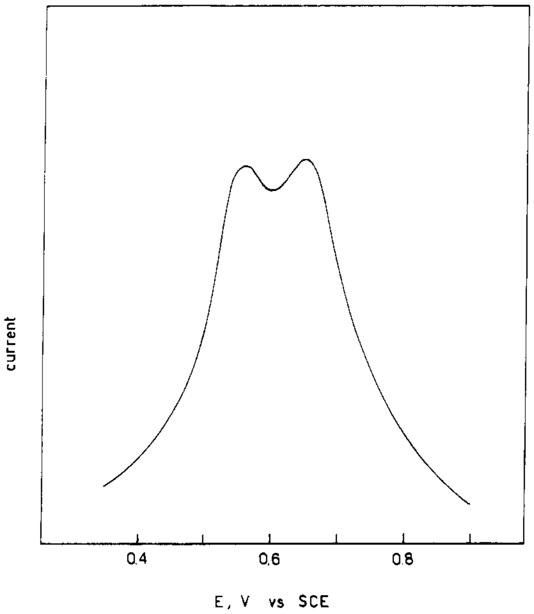


Figure 7. Differential-pulse voltammetry profile of a solution containing 100% of the Cu^{II}_2([13-13]bisdioxocyclam) complex (stoichiometry (1,2,–4)) (carbon-paste electrode, potential scan rate 2 mV s^{-1}, pulse voltage 10 mV).

An opposite trend occurs with the 14-membered system, where the Cu^{II} cation fits well into the ring and the reduction of the ion size due to the oxidation forces the macrocycle to contract the hole leaving its energetically preferred configuration.

Formation of Dimetallic Cu^{III} Species with Bimacrocycles. A solution of the neutral dicopper(II) complex of [13-13]-bisdioxocyclam (1,2,–4) obtained by mixing 2 equiv of Cu^{2+} and 1 equiv of the bimacrocycle and adjusting to pH 7 was investigated by electrochemical means using a carbon-paste electrode. The CV presented a composite profile, which was deconvoluted to disclose two one-electron oxidation peaks and two reduction peaks in the reverse scan (Figure 6). The two consecutive peaks (both in the oxidation and reduction scan) were separated by ca. 100 mV. Peak separation was definitely achieved by using the differential-pulse voltammetry technique (see Figure 7). The experimental peak potential difference ΔE was 90 mV, to which corresponds a $E_{1/2}$ value of 100 mV.[22] The $E_{1/2}$ values for the two consecutive one-electron Cu^{II}/Cu^{III}

---

(21) Diaddario, L. J.; Robinson, W. R.; Mergerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021–1025.

(22) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278–1285.

redox changes are reported in Table III. It is seen that the $E_{1/2}$ value associated to the first oxidation step of the dimetallic complex is slightly less positive than that for the single-ring reference [13]dioxocyclam complex (consider that for the statistical effects the dimetallic species should be in any case favored by 18 mV). The oxidation of the second metal center occurs at a potential 100 mV more positive than for the first one. This difference is larger than that expected on statistical bases (36 mV) and is indicative of a small but detectable mutual influence of the two redox centers of electrostatic nature. A quite similar behavior is observed with the single and double 14-membered ring systems. For the [14-14]bisdioxocyclam system a slightly large $E_{1/2}$ value has been found (110 mV), but the difference with respect to [13-13]bisdioxocyclam is too small to justify any speculation. It should be noted that, in the case of 14-membered rings, the oxidation of the first metal center of the dinuclear complex occurs at a potential considerably less positive than for the single-ring system (by 70 mV, well beyond the statistical term of 18 mV). This has been ascribed[5] to the possible decrease of the intensity of the O-O repulsions due to an increased withdrawing of electrical charge by the tripositive cation. The same does not occur with the dimetallic complex of [13-13]dioxocyclam, for which the first oxidation process is advantaged on the single-ring complex only by a quantity corresponding to the statistical effect. It has been pointed out that the Cu^{II}/Cu^{III} change causes a drastic rearrangement of the 13-membered ring complex, which can affect in some way the intensity of the O-O ring-to-ring repulsion. This further effect may contribute to the overall energy term involved in the $Cu^{II}Cu^{II}/Cu^{III}Cu^{II}$ redox change in the 13-membered bimacrocycle complex, but a full explanation seems not possible, at present.

Registry No. 1, 92284-95-2; **3**, 71248-02-7; tetraethyl 1,1,2,2-ethanetetracarboxylate, 632-56-4; triethylenetetramine, 112-24-3.

Contribution from the Department of Chemistry, University of Newcastle, Shortland, NSW 2308, Australia,
and Institute for Physical Chemistry, University of Frankfurt, 6000 Frankfurt/Main, FRG

Aquation of Chloropentaammine and Chloropentakis(methylamine) Complexes of Cobalt(III) and Chromium(III): Comparative Activation Volumes and Mechanistic Implications

GEOFFREY A. LAWRANCE,*[1a] KAREN SCHNEIDER,[1b] and RUDI VAN ELDIK*[1b]

Received February 24, 1984

Volumes of activation for the aquation of $Co(NH_2CH_3)_5Cl^{2+}$ (-2.3 cm^3 mol^{-1}), *trans*-$Co(NH_3)_4(NH_2CH_3)Cl^{2+}$ (-4.6 cm^3 mol^{-1}), and $Cr(NH_2CH_3)_5Cl^{2+}$ ($+0.5$ cm^3 mol^{-1}) have been determined and differ markedly from those for $Co(NH_3)_5Cl^{2+}$ (-9.9 cm^3 mol^{-1}) and $Cr(NH_3)_5Cl^{2+}$ (-10.6 cm^3 mol^{-1}). The activation volumes for the cobalt(III) series become more positive with increasing experimentally determined molar volume of the cation, and the activation entropy varies in a similar way. The behavior is consistent with a dissociative-interchange mechanism operating in all cases. The behavior of the chromium(III) complexes is similar to, but not identical with, that of the cobalt(III) complexes, since variation in $\Delta V^{\ddagger}$ is greater, but in $\Delta S^{\ddagger}$ smaller. The data are not fully consistent with a persistent associative-interchange process, and variation in the importance of bond-making and bond-breaking processes from the pentaammine to the pentakis(methylamine) complex is suggested.

Introduction

Volumes of activation ($\Delta V^{\ddagger}$) have been employed successfully in the elucidation of both organic and inorganic reaction mechanisms.[2-5] It has been recognized that the experimentally determined activation volume ($\Delta V^{\ddagger}_{exptl}$) can be considered as a composite of contributions originating from the displacement of atoms at the activation site (the intrinsic component, $\Delta V^{\ddagger}_{int}$) and from changes in electrostriction in forming the activated state ($\Delta V^{\ddagger}_{el}$). The latter term is principally related to changes in solvation of the precursor and activated states. In cordination chemistry, reactions often involve displacement of charged groups; hence, $\Delta V^{\ddagger}_{exptl}$ involves a substantial contribution from $\Delta V^{\ddagger}_{el}$, which may mask the mechanistically important $\Delta V^{\ddagger}_{int}$ component. Reactions involving neutral leaving groups such as solvent-exchange reactions[6] are more readily interpreted, and mechanistic differentiation can be quite clear from $\Delta V^{\ddagger}_{exptl}$ data.

Aquation reactions of octahedral halo amine complexes of cobalt(III) and chromium(III) have been subjected to extensive and detailed investigation over recent decades.[7-9] The mechanisms for reactions of cobalt(III) are generally accepted to be dominated by bond-breaking (dissociative) processes, while those of chromium(III) are apparently characterized by bond-making (associative) processes. Comparative studies of pentaammine and pentakis(methylamine) complexes have defined the difference.[10,11] An increase in the rate of aquation when the five ammine ligand in $Co(NH_3)_5Cl^{2+}$ are replaced by bulkier alkylamine ligands is consistent with steric relief in a dissociated activated state; by contrast, the analogous chromium(III) system exhibits retardation, in accord with steric congestion of an associated state. Similar behavior is observed with $CF_3SO_3^-$ as leaving group.[12]

Despite this apparent mechanistic variation for cobalt(III) and chromium(III), it is notable that $\Delta V^{\ddagger}_{exptl}$ for aquation of $Co(NH_3)_5Cl^{2+}$ (-9.9 cm^3 mol^{-1})[13] and $Cr(NH_3)_5Cl^{2+}$ (-10.8

---

(1) (a) University of Newcastle. (b) University of Frankfurt.
(2) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.
(3) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.
(4) Lawrance, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *12*, 403. Stanks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.
(5) le Noble, W. J.; Kelm, H. *Angew. Chem.* **1980**, *92*, 887.
(6) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479.
(7) *Inorg. React. Mech.* **1971-1980**, *1-7*.
(8) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.
(9) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974.
(10) Parris, M.; Wallace, W. J. *Can. J. Chem.* **1969**, *47*, 2257.
(11) Swaddle, T. W. *Can. J. Chem.* **1977**, *55*, 3166.
(12) Curtis, N. J.; Lawrance, G. A.; Sargeson, A. M., to be submitted for publication.
(13) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739.

0020-1669/84/1323-3922$01.50/0