of O_2 molecules to dimer molecules is 1:1 in the adduct. Thus, all of the results suggest that one O_2 molecule is axially interacting with one side of the dimer.

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

Stepwise Incorporation of Copper(II) into a Double-Ring Octaaza Macrocycle and Consecutive Oxidation to the Trivalent State

LUIGI FABBRIZZI,* FABRIZIO FORLINI, ANGELO PEROTTI, and BARBARA SEGHI

The novel double-ring octaaza macrocycle **2** (*bisdioxocyclam*) has been prepared by the single-step aminolytic condensation of the appropriate tetraester and linear tetraamine in 1:2 molar ratio. The complexation of Cu^{II} by **2** in aqueous solution has been investigated by potentiometric means. Monometallic and dimetallic complex species form according to the ligand:metal ratio. In general, incorporation of the Cu^{II} ion into each tetraaza subunit promotes a simultaneous deprotonation of the two amido groups. log *k* values of complexation equilibria have been compared with those for the reference single-ring tetraaza macrocycle **1** (*dioxocyclam*). The [Cu$^{II}_2$(bisdioxocyclamato(4–))] complex undergoes a reversible oxidation to the dicopper(III) complex through two consecutive one-electron steps, whose electrode potentials are separated by 110 mV.

Introduction

Whereas binuclear metal complexes have for several years been a classical topic of coordination chemistry, the number of investigations has increased dramatically more recently, due to the introduction of appropriate ligands, of the *macrocyclic* type, able to encapsulate two metal ions.[1] In fact, the closed nature of the ligand imparts both kinetic and thermodynamic stability to the dimetallic system, permitting the study of its solution behavior, an opportunity which has been rarely found with noncyclic ligand dinuclear complexes. In most of the reported systems the two metal ions, e.g. Cu^{II}, are accommodated in a large single-ring macrocycle[2] or in a three-dimensional molecular framework, formally derived from cryptands,[3] and face together. This constrictive situation may affect deeply electronic and magnetic properties and also mutually influence the redox activity of each metal center.

In contrast, we were interested in generating a situation in which the two proximate metal centers act as independently as possible. We thought that this goal could be achieved by preparing a ligand in which two small-ring macrocycles, able to accommodate a single metal ion, were linked together. A molecule of this type, in which two cyclam subunits are linked through a covalent bond, has been fortuitously obtained, in very small yield, as a side product in the template synthesis of cyclam.[4]

We have chosen as a subunit the tetraaza diamino–diamide macrocycle **1** (dioxocyclam) for the following reasons: (i) the

1   **2**
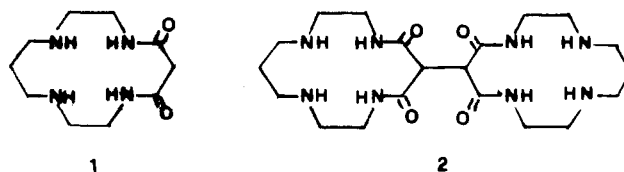
possibility exists to synthesize the dinucleating derivative **2** as a free molecule, according to an innovative single-step nontemplate reaction, with a satisfactory yield; (ii) the dioxocyclam unit can incorporate a Cu^{II} ion, with simultaneous deprotonation of the two amido groups, according to a fast reversible equilibrium, which can therefore be investigated by conventional pH methods;[5] (iii) the Cu^{II} ion, when incorporated in the dioxocyclamato(2–) unit, can be reversibly oxidized, at a moderately positive electrode potential, to give an authentic trivalent copper species that is stable in aqueous solution.[6]

We report here the synthesis of the novel double-ring macrocycle **2** (bisdioxocyclam), the study of the formation of mono- and dicopper(II) complexes of **2**, which involve several simultaneous pH-dependent equilibria, and the electrochemical investigation of the oxidation behavior of the above metal complexes. A preliminary report on the magnetic and redox properties of the dicopper(II) complex of bisdioxocyclam has appeared.[7]

Experimental Section

Synthesis of the Tetraaza Macrocycle (2). 1. 1,1,2,2-Ethanetetracarboxylate Tetraethyl Ester (3). Preparation of **3** is based on the procedure reported by Bischoff and Rach.[8] A 0.2-mol amount of sodium is dissolved in 0.5 L of absolute ethanol in a three-neck

(1) See for example: Fenton, D. E.; Casellato, V.; Vigato, P. A.; Vidali, M. *Inorg. Chim. Acta* **1982**, *62*, 57.
(2) Drew, M. G. B.; Nelson, J.; Esho, F.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1837 and references therein.
(3) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441.
(4) Barefield, E. K.; Chueng, D.; Van Derveer, D. C.; Wagner, F. *J. Chem. Soc., Chem. Commun.* **1981**, 302.

(5) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1979**, 325.
(6) Fabbrizzi, L.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1980**, 646.
(7) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166.
(8) Bischoff, C. A.; Rach, C. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2781.

round flask, equipped with a mechanical stirrer, under nitrogen atmosphere. A 0.2-mol quantity of diethyl malonate (Erba, freshly distilled under vacuum) was added dropwise in $^1/_2$ h. A solution of 0.1 M of doubly sublimated iodine (Erba) in 0.15 L of diethyl ether is then added dropwise, with vigorous stirring, in 1 h. When the addition is complete, the brown solution is transferred into a 1-L beaker and reduced on a steam bath to 0.15 L. To the cooled solution 0.1 L of diethyl ether and 0.1 L of water are added, to form two layers. The ether layer is washed with 0.1 L of a 0.1 M $Na_2S_2O_3$ solution and dried overnight over anhydrous Na_2SO_4. Ether is then distilled off on a steam bath to leave white needles, which are washed twice with cold ethanol and dried under vacuum on silica gel: yield 70%; mp 76–77 °C (lit.[8,9] mp 76 °C).

2. 1,4,8,11-Tetraazaundecane (2,3,2-tet) (4). The tetraamine was prepared from 1,2-diaminoethane (Erba) and 1,3-dibromopropane according to a procedure analogous to that reported by Barefield[10] for the synthesis of 3,2,3-tet (bp 140–142 °C (0.75 torr)).

3. Bisdioxocyclam (2). A 0.05-mol amount of **3** is dissolved in 1 L of absolute ethanol, under a nitrogen atmosphere, and 0.1 mol of **4** is added dropwise. The solution is then allowed to reflux. After a few hours a white precipitate of **2** begins to form. Reflux is continued for 3 days. The microcrystalline precipitate is separated by filtration on a Buchner funnel. Further precipitate is obtained after evaporation of the filtered solution to 0.5 L. The second crop may contain some unreacted tetraethyl ester, which is extracted with hot tetrahydrofuran: yield 30%. Anal. Calcd for $C_{20}H_{38}N_8O_4$: C, 52.86; H, 8.37; N, 24.67. Found: C, 52.85; H, 8.55; N, 24.26.

4. Dioxocyclam (1). Dioxocyclam has been prepared according to Tabushi,[11] by reflux of diethyl malonate and **4** in absolute ethanol for 5 days. In this work a much more diluted scale was empolyed (5×10^{-2} M). In these conditions, the formation of side products is avoided and dioxocyclam is simply obtained by slow crystallization (2–3 days) from the colorless ethanolic solution reduced to 0.1 L by rotoevaporation. The white crystals are washed with cold ethanol and diethyl ether: yield 24%.

EMF Measurements and Computation of the Equilibrium Constants. The potentiometric equilibrium measurements of dioxocyclam (**1**) and bisdioxocyclam (**2**) in the absence and in the presence of the metal ion were carried out with a Radiometer PHM84 research pH meter using a Beckman Futura glass electrode and an Ingold saturated sodium chloride–calomel electrode, fitted in an Ingold cell system. The temperature was maintained at 25.0 ± 0.1 °C in a thermostated Methrom cell: each titration was performed in a solution of 50 mL adjusted to 0.1 ionic strength with $NaClO_4$. Typical concentrations of experimental solutions were 5×10^{-4} M in ligand with molar concentrations of metal ion equivalent to that of the ligand or twice that of the ligand. The free ligand was first titrated by addition of 0.2 M $HClO_4$ and then back-titrated with 0.2 M NaOH. Both $HClO_4$ and NaOH standard solutions were delivered with a Radiometer ABU80 autoburet equipped with a 2.5/0.25 mL B280 buret assembly. In the presence of metal ions, titrations with NaOH were performed by starting from solutions containing a 4-fold excess (when the ligand was bisdioxocyclam) and 2-fold excess (when the ligand was dioxocyclam) of acid with respect to the ligand. Carbon dioxide was excluded from the reaction vessel by maintaining a slight positive pressure of purified and humidified (by bubbling through a 0.1 M $NaClO_4$ solution) nitrogen in the reaction cell. NaOH standard solution was prepared according to a reported procedure[12] and standardized against potassium hydrogen phthalate and proved to be carbonate free by the experimental Gran titration plots. $HClO_4$ standard solution was prepared by opportune dilution of Erba RS perchloric acid and successive standardization against the above NaOH standard solution. Sodium perchlorate solutions were obtained by dissolving in water sodium perchlorate (Erba) purified by alkaline precipitation of hydrated oxides and ultrafiltration. Stock solutions of copper perchlorate were prepared from Fluka crystals: metal and mineral acid contents were determined by atomic absorption and volumetric means against alkali (Gran titration), respectively. H_2O used for all the above solutions was first deionized and then twice distilled in quartzware equipment. The data were processed on Digital

computer systems (PDP/44 and/or VAX 11/780) using the MINIQUAD 82 program[13] and/or MINISHORT—a properly reduced version[14] of it. The graphical display of the results was obtained with the DISPLO program,[15] which gives the distribution curves of the species, and the POINTS, DRAW, and GRAPH programs,[14] which allow a direct comparison of the experimental data with those obtained from the refinements through MINIQUAD or MINISHORT. For each system at least two titrations have been performed, each of them containing not less than 50 experimental points.

Electrochemistry. Differential pulse voltammetry experiments were performed with the use of a Metrohm Polarecord E 506 apparatus. CV measurements were carried out with an Amel Model 448 electrochemical apparatus connected to a Hewlett-Packard 7040 X-Y recorder. The working electrode was carbon-paste electrode. A platinum coil was used as counterelectrode. The reference electrode (SCE) was interfaced to a solution by a bridge containing a saturated sodium chloride solution, to avoid precipitation of $KClO_4$. Solutions for electrochemistry were prepared immediately before experiments from weighed amounts of ligands **1** and **2** and of standard solutions of Cu^{II} and adjusted to the desired pH values by standard NaOH and to the ionic strength of 0.1 M $NaClO_4$. The concentration of the species in solution was evaluated by the above-mentioned computer program DISPLO.[15] Measurements were performed in a thermostated cell at 25.0 ± 0.1 °C and under a flow of nitrogen previously humidified by bubbling in a 0.1 M $NaClO_4$ solution.

Results and Discussion

A Novel Approach to the Synthesis of Double-Ring Macrocycles. We define as a "double-ring" macrocycle a molecule in which two cyclic, potentially coordinating, subunits (tetraaza in this case) are linked together by a chain or by a covalent bond. Molecules of this type have been obtained by Lehn's group[16] as intermediates in the synthesis of the so-called cyclindrical macrocycles. More recently, Dale prepared double-ring molecules in which subunits containing an O_3N donor set are linked together by an aliphatic chain.[17] This approach involves (i) preparation of the cyclic subunit and (ii) linkage of two nitrogen atoms of each subunit by an appropriate segment. A similar synthetic route for tetraaza subunits would involve also (iii) selective protection of all the nitrogen atoms except that one to be linked[18] and (iv) deprotection after the two rings have been linked.

The present approach is much more simple and overcomes the tedious steps i–iv, involving simultaneous formation and linking of two tetraaza units. It is derived from Tabushi's aminolytic condensation of an aliphatic tetraamine with diethyl malonate.[11] In this case, we use the tetraethyl ester **3**, in which
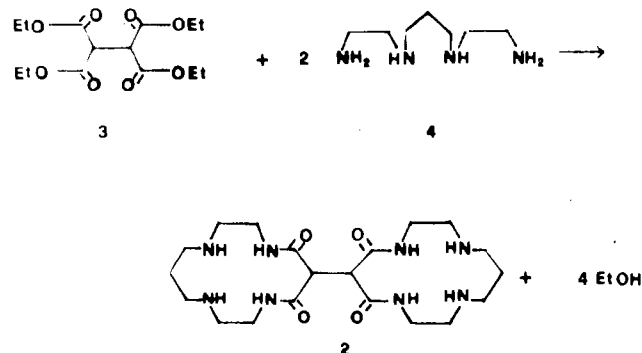
two malonate units are covalently bonded. Reaction of **3** with

(9) Bailey, W. J.; Sorenson, W. R. *J. Am. Chem. Soc.* **1956**, *78*, 2287.
(10) Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220.
(11) Tabushi, I.; Taniguchi, Y.; Kato, H. *Tetrahedron Lett.* **1977**, 1049.
(12) Micheloni, M.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1977**, *25*, 41.

(13) Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1974**, *21*, 53. Vacca, A.; Sabatini, A. "Modern Inorganic Chemistry"; Fackler, J. P., Ed.; Plenum Press: New York, in press.
(14) Bossi, F.; Fumagalli, G.; Perotti, A., unpublished work (programs available on request).
(15) Vacca, A.; Sabatini, A., unpublished program, kindly made available by the authors.
(16) Alberts, A. H.; Annunziata, R.; Lehn, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 8502.
(17) Calverley, M. J.; Dale, J. *J. Chem. Soc., Chem. Commun.* **1981**, 684.
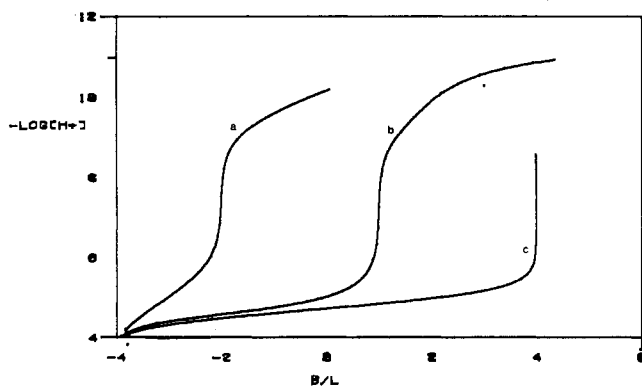(18) Hediger, M.; Kaden, T. A. *J. Chem. Soc., Chem. Commun.* **1978**, 14.

Figure 1. Titration curves of bisdioxocyclam: (a) bisdioxocyclam + 4 equiv of acid; (b) bisdioxocyclam + 4 equiv of acid + 1 equiv of copper(II); (c) bisdioxocyclam + 4 equiv of acid + 2 equiv of copper(II). B:L is the ratio of the moles of standard base added, B, to the moles of bisdioxocyclam, L. Negative values indicate excess of acid (e.g. −1 = 1 equiv of standard acid).

2 equiv of the tetraamine **4** gives the double-ring macrocycle **2** in a yield that can be defined satisfactory, if one considers the inexpensive nature of the starting materials and the simplicity of the experiment (refluxing ethanol, 3 days). Another advantage of this approach is that it involves a C–C rather than a N–N linking. In fact, it has been generally observed that the presence of alkyl substituents on nitrogen atoms reduces their coordinative tendencies toward metal ions.

In this connection we have also obtained double-ring octaaza macrocycles of different kinds through the reaction between the ester of EDTA, **5**, and an aliphatic triamine (1:2 molar
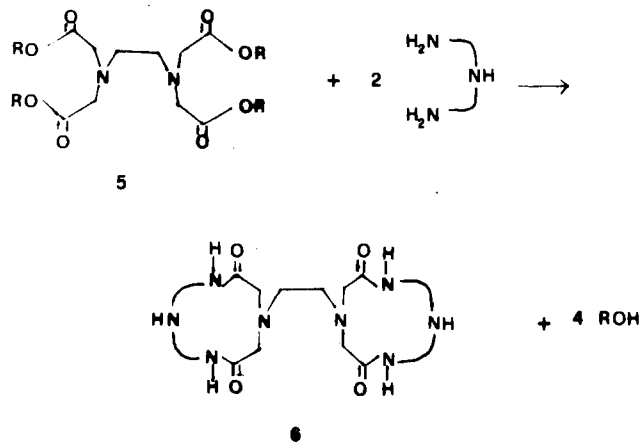
ratio).[19] This condensation is analogous to that described before, in that it involves simultaneous formation and linking of two tetraaza subunits. Its satisfactory yield reinforces the validity of the synthetic strategy toward double-ring polyaza molecules, based on the templating role of a central tetraester segment. However, preliminary equilibrium investigations[19] have shown that ligands of the type **6** show lower affinity toward Cu[II] ions compared to the C–C-linked analogue **2** and to the reference monocyclic molecules. It seems that it can be ascribed to the reduced coordinating ability of the linking nitrogen atoms.

Reactions with the Hydrogen Ions. The acid–base behavior of *bisdioxocyclam* (H_4L^2, **2**) in aqueous 0.1 M $NaClO_4$ has been investigated through pH titration. In a typical experiment, a solution containing the double-ring macrocycle and excess acid has been titrated by standard base (see Figure 1). In the pH range investigated (ca. 3–10), bisdioxocyclam binds

(19) Fabbrizzi, L.; Perotti, A.; Seghi, B.; Ciampolini, M.; Nardi, M.; Vizza, A., to be submitted for publication.

Table I. Equilibrium Constants for the Stepwise Protonation of Dioxocyclam (**1**, H_2L^1) and Bisdioxocyclam (**2**, H_4L^2) in Aqueous 0.1 M $NaClO_4$ at 25 °C

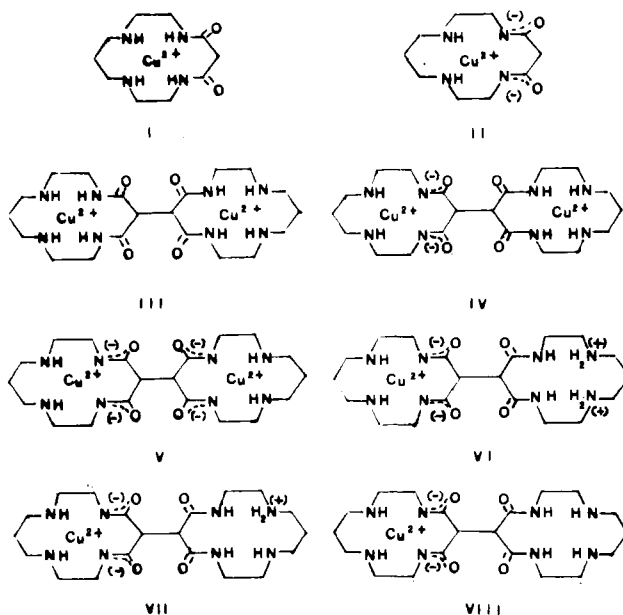| eq no.	eq	log k
1	$H_2L^1 + H^+ \rightleftharpoons [H_3L^1]^+$	9.51 ± 0.01
2	$[H_3L^1]^+ + H^+ \rightleftharpoons [H_4L^1]^{2+}$	5.80 ± 0.02
3	$H_4L^2 + H^+ \rightleftharpoons [H_5L^2]^+$	9.96 ± 0.01
4	$[H_5L^2]^+ + H^+ \rightleftharpoons [H_6L^2]^{2+}$	9.45 ± 0.01
5	$[H_6L^2]^{2+} + H^+ \rightleftharpoons [H_7L^2]^{3+}$	5.40 ± 0.03
6	$[H_7L^2]^{3+} + H^+ \rightleftharpoons [H_8L^2]^{4+}$	4.62 ± 0.04

Figure 2. Proposed coordinative arrangments of the copper(II) complexes of dioxocyclam and bisdioxocyclam.

four protons, presumably by the amine groups. The constants of the stepwise protonation equilibria have been determined through computer elaboration of the titration data and are reported in Table I. For comparison, log k values are also reported for the stepwise protonation equilibria, under the same conditions, for the reference single-ring macrocycle *dioxocyclam* (H_2L^1, **1**), which binds two protons. It should be noted that dioxocyclam is a much weaker base than the fully saturated analogue *cyclam*, as far as the first two steps are concerned (log k_1 = 11.58; log k_2 = 10.62).[20] log k_1 is remarkably lower than expected on statistical bases (cyclam has two more basic sites available). In the case of cyclam, formation of stable intramolecular hydrogen bonds between ammonium and amine groups, trans to each other, has been hypothesized,[21] an opportunity which is forbidden to the diamide macrocycle. The second protonation step of dioxocyclam (Table I, eq 2) involves a decrease of log k (3.7 log units) greater than for cyclam (1.0 log units): this may be due to the fact that in diprotonated dioxocyclam—$(H_4L^1)^{2+}$—the two ammonium ions are adjacent, whereas in the case of cyclam they should be trans to each other, which makes electrostatic repulsion less intense. Bisdioxocyclam in the first step is a stronger base than dioxocyclam, and the difference of log k_1 values is only slightly larger than the statistical factor (0.3). The log k_2 of bisdioxocyclam is nearly equal to log k_1 for dioxocyclam, indicating that the second protonation involves the second macrocyclic subunit. A dramatic decrease of log k is observed with the third protonation step: log k_3 of bisdioxocyclam is much lower than log k_2 for dioxocyclam. This may be due to the accu-

(20) Micheloni, M.; Sabatini, A.; Paoletti, P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 828.

(21) Micheloni, M.; Paoletti, P.; Vacca, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 945.

Table II. Equilibrium Constants for the Stepwise Complexation of Copper(II) by Dioxocyclam (**1**, H_2L^1) and by Bisdioxocyclam (**2**, H_4L^2) in Aqueous 0.1 M $NaClO_4$ at 25 °C

eq no.	eq	log k
7	$Cu^{2+} + H_2L^1 \rightleftharpoons [Cu(H_2L^1)]^{2+}$ (I)	8.75 ± 0.01
8	$Cu^{2+} + H_2L^1 \rightleftharpoons [Cu(L^1)]$ (II) $+ 2H^+$	0.44 ± 0.01
9^a	$[Cu(H_2L^1)]^{2+}$ (I) $\rightleftharpoons [Cu(L^1)]$ (II) $+ 2H^+$	-8.31 ± 0.02
10	$2Cu^{2+} + H_4L^2 \rightleftharpoons [Cu_2(H_4L^2)]^{4+}$ (III)	17.79 ± 0.01
11	$2Cu^{2+} + H_4L^2 \rightleftharpoons [Cu_2(H_2L^2)]^{2+}$ (IV) $+ 2H^+$	8.59 ± 0.01
12	$2Cu^{2+} + H_4L^2 \rightleftharpoons [Cu_2(L^2)]$ (V) $+ 4H^+$	-1.34 ± 0.01
13^b	$[Cu_2(H_4L^2)]^{4+}$ (III) $\rightleftharpoons [Cu_2(H_2L^2)]^{2+}$ (IV) $+ 2H^+$	-9.20 ± 0.02
14^c	$[Cu_2(H_2L^2)]^{2+}$ (IV) $\rightleftharpoons [Cu_2(L^2)]$ (V) $+ 2H^+$	-9.93 ± 0.02
15	$Cu^{2+} + H_4L^2 \rightleftharpoons [Cu(H_4L^2)]^{2+}$ (VI)	14.54 ± 0.01
16	$Cu^{2+} + H_4L^2 \rightleftharpoons [Cu(H_3L^2)]^+$ (VII) $+ H^+$	9.58 ± 0.01
17	$Cu^{2+} + H_4L^2 \rightleftharpoons [Cu(H_2L^2)]$ (VIII) $+ 2H^+$	0.25 ± 0.01

^{a} Obtained from combination of eq 7 and 8. ^{b} Obtained from combination of eq 10 and 11. ^{c} Obtained from combination of eq 11 and 12.
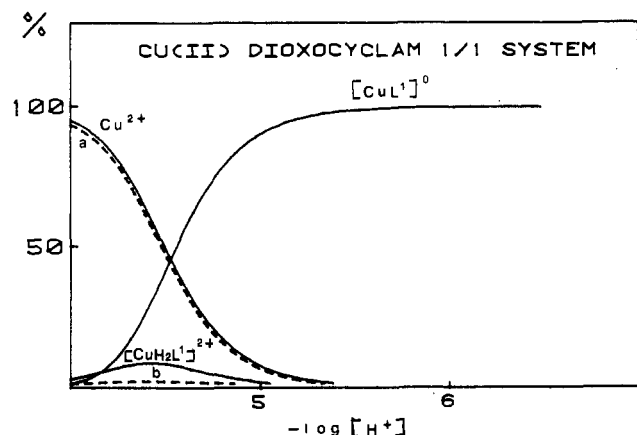

Figure 3. Distribution diagram for the system Cu^{II}–dioxocyclam (molar ratio 1:1). Proposed coordinative arrangements (see Figure 2) are I for $[Cu(H_2L^1)]^{2+}$ and II for $[Cu(L^1)]$. Dashed lines refer to the uncomplexed protonated ligands $(H_4L^1)^{2+}$ (a) and $(H_3L^1)^+$ (b).

mulation of positive charges in the double-ring macrocycle. This effect is also greater for the addition of the fourth proton (eq 6 in Table I).

Reactions with the Copper(II) Ions. a. Complexation of Dioxocyclam (H_2L^1, 1). The incorporation of Cu^{II} by dioxocyclam in aqueous solution was first considered by Kodama and Kimura,[5] who considered a very narrow pH interval for the evaluation of the complexation constant. The Cu^{II}–dioxocyclam system has now been reinvestigated in 0.1 $NaClO_4$. In the titration experiment, standard base has been added to a solution containing dioxocyclam (H_2L^1) and copper(II) perchlorate in 1:1 molar ratio. Computer analysis showed that the best curve fitting is obtained by assuming that the following species are formed: $[Cu(H_2L^1)]^{2+}$ and $[Cu(L^1)]$ (formulas I and II, respectively, in Figure 2). log k values are reported in Table II: $[Cu(H_2L^1)]^{2+}$ is only a minor species (it reaches its maximum concentration, 9.0%, at $-\log [H^+] = 4.4$—see the distribution diagram in Figure 3); in this complex the Cu^{II} ion may be potentially coordinated by the two amine nitrogen atoms and the two amido groups. The log k value for $[Cu(H_2L^1)]^{2+}$ (I) is even smaller than that found for (tri-methylenediamine)copper(2+) (log $k = 10.2$),[22] in which the two amine groups are separated by a trimethylene chain, as in the complex I (see Figure 2). We are not in the position to say whether the Cu^{II} ion lies over the N_4 plane, being eventually coordinated only by the amino groups, or is coplanarly chelated by four nitrogen atoms of the macrocycle.
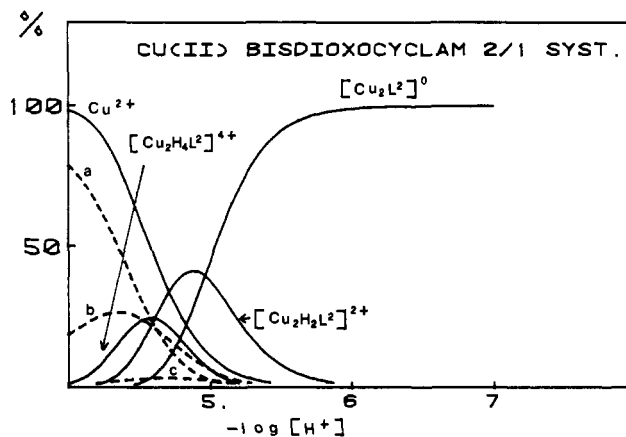
(22) Holmes, F.; Williams, D. R. *J. Chem. Soc. A* **1967**, 1702.

Figure 4. Distribution diagram for the system Cu^{II}–bisdioxocyclam (molar ratio 2:1). Proposed coordinative arrangements (see Figure 2) are III for $[Cu_2(H_4L^2)]^{4+}$, IV for $[Cu_2(H_2L^2)]^{2+}$, and V for $[Cu_2(L^2)]$. Dashed lines refer to the uncomplexed protonated ligands $(H_8L^2)^{4+}$ (a), $(H_7L^2)^{3+}$ (b), and $(H_6L^2)^{2+}$ (c).

However, in the latter hypothesis, the value of log k indicates that the contribution due to the amido groups should be very small. The major species $[Cu(L^1)]$ (II) is obtained through deprotonation of the two amido groups; its formation begins at $-\log [H^+] = 4.0$ and is complete at $-\log [H^+] = 5.9$ (see Figure 3). In this species, the Cu^{II} ion is believed to lie in the plane of the four nitrogen atoms and profits from particularly strong coordinative interactions.[6]

b. Complexation of Bisdioxocyclam (H_4L^2, 2): Incorporation of Two Cu^{II} Ions. In Figure 1 is reported the titration curve obtained on adding standard base to a solution containing bisdioxocyclam and copper(II) perchlorate in 1:2 molar ratio and an excess of acid. It is seen that pH increases abruptly at a standard base:ligand ratio ($B:L$) of 4. This behavior is consistent with the incorporation of two Cu^{II} ions by the double-ring macrocycle with simultaneous deprotonation of the four amido groups. This indicates that the major species has a stoichiometry as $[Cu(L^2)]$. Best fitting of the titration curve involves formation of the following species: $[Cu_2(H_4L)]^{4+}$, $[Cu_2(H_2L^2)]^{2+}$, and $[Cu_2(L^2)]$. The distribution curve of the above complexes is reported in Figure 4. Equilibrium constants are in Table II. It should be noticed that log k for the formation of $[Cu_2(H_4L^2)]^{4+}$ (formula III in Figure 2) is approximately twice the value found for $[Cu(H_2L^1)]^{2+}$ (I), suggesting that also in this case only the amino groups contribute significantly to the coordination. As a further step, with an increase of pH, the $[Cu_2(H_4L^2)]^{4+}$ complex releases two protons to form the species of stoichiometry $[Cu_2(H_2L^2)]^{2+}$. Whereas in principle it is impossible to assess whether the two protons are coming from the same ring or coming one from each unit, it seem reasonable to admit that one of the already coordinated Cu^{II} ions penetrates one of the macrocyclic subunits, promoting deprotonation of the two adjacent amido groups to give the coordinative arrangement depicted in formula IV in Figure 2. A further point of interest arises from the consideration of the equilibrium (13) in Table II, in which the $[Cu_2(H_4L^2)]^{4+}$ species (III) release two H^+ from two amido groups presumably of the same ring to give the $[Cu_2(H_2L^2)]^{2+}$ complex (IV). In fact, the corresponding value of k (-9.2 log units) is remarkably lower than that for the analogous equilibrium of dioxocyclam (eq 9 in Table II; -8.3 log units) in which the full incorporation of Cu^{II} by the ring causes the deprotonation of the two amido groups. This difference is also to be increased by 0.3 log unit, if one takes into account the statistical factor, which favors bisdioxocyclam. Finally, the last complexation step gives the neutral complex $[Cu_2(L^2)]$, in which the two tetraaza subunits have all the
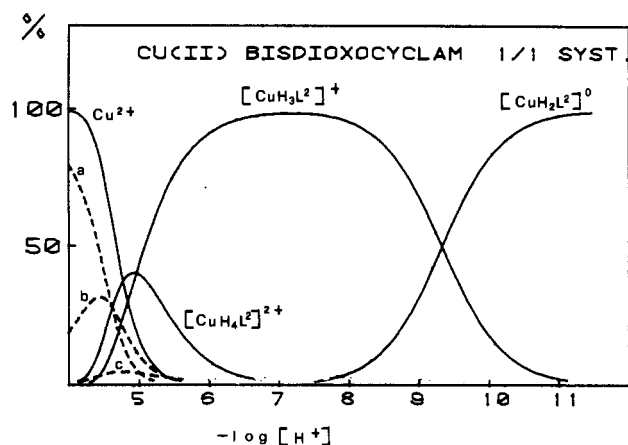
Figure 5. Distribution diagram for the system Cu^{II}–bisdioxocyclam (molar ratio 1:1). Proposed coordinative arrangements (see Figure 2) are VI for $[Cu(H_4L^2)]^{2+}$, VII for $[Cu(H_3L^2)]^+$, and VIII for $[Cu(H_2L^2)]$. Dashed lines refer to the uncomplexed protonated ligands $(H_8L^2)^{4+}$ (a), $(H_7^2)^{3+}$ (b), and $(H_6L^2)^{2+}$ (c).

amido groups deprotonated (formula V in Figure 2). Also in this case, the constant of the equilibrium of deprotonation of the two amido groups of the second ring (eq 14 in Table II) (−9.9 log units, to be reduced to −9.6 for the statistical terms) is more negative than the corresponding equilibrium for dioxocycylam (eq 9). In order to explain this behavior, one should take into account that, in the deprotonated amido groups coordinated to copper(II), the negative charge should not be considered to lie on the nitrogen atom but to delocalize through a π mechanism into the entire NCO bond, so that the C–O bond has an order lower than 2 and the oxygen atom retains a partial negative charge. Therefore, the more difficult deprotonation of the first and second rings of bisdioxocyclam, expressed by the more negative value of log k for eq 13 and 14, should be ascribed to the electrostatic repulsive effect between the partially negative oxygen atoms and the proximate carbonyl groups of the other ring (eq 13) and between partially negative oxygen atoms of the two rings (eq 14).

c. Incorporation by Bisdioxocyclam (H_4L^2) of a Single Cu^{II} Ion. In Figure 1 is reported the curve of the titration with standard base of a solution containing bisdioxocyclam and copper(II) perchlorate in 1:1 molar ratio, plus an excess of perchloric acid. Only one ring must be involved in the complexation, and a profile similar to that found for dioxocylam is expected. However, in this case (see Figure 1) the buffer zone is extended to a value of standard base:ligand ratio ($B:L$) of 1. This is indicative of the formation of a major species of stoichiometry $[Cu(H_3L^2)]^+$. The best curve fitting in the −log [H$^+$] range 4.0–10.5 is obtained by assuming the formation of complex species having the following stoichiometry: $[Cu(H_4L^2)]^{2+}$, $[Cu(H_3L^2)]^+$, and $[Cu(H_2L^2)]$. Their distribution curve is reported in Figure 5. The log k values for the complexation equilibria are reported in Table II.

The equilibrium constant for the formation of the species at lowest pH values, $[Cu(H_4L^2)]^{2+}$ (eq 15 in Table II) is incredibly large when compared to the formation of the corresponding species with the macrocyclic reference molecule dioxocyclam, $[Cu(H_2L^1)]^{2+}$ (eq 7 in Table II). We think that the two complexes have a completely different nature, and in particular the complex with the formally neutral double-ring macrocycle should be described as depicted in formula VI in Figure 2. In particular, the Cu^{II} cation penetrates one ring, causing simultaneous deprotonation of its amido groups, and the released protons migrate to protonate the two amino groups of the second ring. It is this additional favorable process that makes easier the deprotonation of the amido groups of the first ring and anticipation of the pH at which the incorporate of

Cu^{II} occurs. Therefore, the unexpectedly large value of log k for eq 15 results from the combination of these two favorable contributions. If, in a sort of "Gedanken experiment" one sums equilibria 1, 2, and 8, to reproduce (using data of the reference monocyclic ligand dioxocyclam) equilibrium 15, a value of 15.8 log units is obtained, i.e. a value larger than the experimental value of 14.5. The difference can be ascribed to the repulsive effects between the two ammonium ions in one ring and the Cu^{II} ion in the other one, whose charge is only partially shielded through coordination by the deprotonated amido groups. The most important species, present almost at 100% in the −log [H$^+$] range 6–8 (see Figure 5), is that of stoichiometry $[Cu(H_3L^2)]^+$. The nature of this species could be reasonably described by the formula VII in Figure 2 and should be considered as originating from the deprotonation of one ammonium group of the species VI, $[Cu(H_4L^2)]^{2+}$. The log k value for the overall formation of this species (eq 16 in Table II) is still smaller, but to a much lesser extent, than that calculated by combining eq 1 and 8 of dioxocyclam (9.95 log units). The lower difference of the log k values reflects the reduced electrostatic repulsion that now occurs between the Cu^{II} ion and only one ammonium group. Deprotonation of this ammonium group finally gives rise to the neutral species $[Cu(H_2L^2)]$. Due to the great stability of the complex $[Cu(H_3L^2)]^+$, the neutral complex is formed at a relatively high pH, when compared to that for dioxocyclam analogue (see Figures 3 and 5). Its overall formation constant (eq 17) is distinctly lower than that for $[Cu(L^1)]$ (eq 8). This difference, which becomes greater if the experimental value is corrected for the statistical factor (−log 2), should be ascribed once again to the electrostatic repulsion between the partially negative oxygen atoms of the deprotonated amido bond in the coordinating ring and the lone pairs of the carbonyl groups of the other ring. Present investigation on the coordinating properties in solution of diamine–diamido macrocycles, of single- or double-ring type, shows that in general the Cu^{II} ion is complexed in the more acidic region essentially by two amine groups. The increase of pH promotes the full and coplanar chelation of Cu^{II} by the four nitrogens of each ring, which occurs with simultaneous deprotonation of the two amido groups. A stepwise (one by one) deprotonation of amido groups of each ring seems to be excluded and in any case is not consistent with the data of the present investigation. In particular, species of "odd" stoichiometry, $[Cu_2(H_3L^2)]^{3+}$ and $[Cu_2(HL^2)]^+$, have been rejected in the process of curve fitting of bisdioxocyclam:Cu^{II} in 1:2 molar ratio (giving negative constants).

The extent of formation of the complex species in which the ligand keeps its amido groups undeprotonated depends on the ratio between the constants of formation of complexes with deprotonated and undeprotonated ligands. In the case of dioxocyclam, $[Cu(H_2L^1)]^{2+}$ is present in very small concentration, due to the relatively large stability of the $[Cu(L^1)]$ complex. In contrast, the existence of repulsive effects in the $[Cu_2(L^2)]$ species makes its stability lower and allows the formation of a considerable amount of the species in which the double-ring ligand is not or is only partially deprotonated. The Cu^{II}–bisdioxocyclam system in the 1:1 molar ratio represents an unique situation, in which the availability of the two basic sites (the amino groups) in the adjacent ring makes deprotonation of the complexing ring especially easy, so that it occurs at comparatively low pH values.

Oxidation to the Trivalent State. The knowledge of the formation constants of copper(II) complexes with bisdioxocyclam allowed us to prepare solutions in which, according to the values of pH and of the metal to ligand ratio, a desired species could be adequately represented, possibly as 100%, and investigated as far as its oxidation behavior is concerned. This

Table III. Half-Wave Potential Values for the Cu^{II}/Cu^{III} Redox Change in Complexes with Dioxocyclam and Bisdioxocyclam[a]

	$E_{1/2}$, V (vs. SCE)
$[Cu^{II}_2(L^2)]$ (VIII) $\rightleftharpoons [Cu^{II}Cu^{III}(L^2)]^+ + e^-$	0.58
$[Cu^{II}Cu^{III}(L^2)]^+ \rightleftharpoons [Cu^{III}_2(L^2)]^{2+} + e^-$	0.69
$[Cu^{II}(L^1)]$ (II) $\rightleftharpoons [Cu^{III}(L^1)]^+ + e^-$	0.65

[a] Conditions: aqueous 0.1 M NaClO$_4$, 25 °C.

goal has been easily achieved in the case of the neutral dinuclear species $[Cu_2(L^2)]$, which, for a Cu^{II}:ligand molar ratio of 2, is the only species present at pH above 6.5. The oxidation behavior of such a solution was studied by differential pulse voltammetry using a carbon-paste electrode. The DPV profile, obtained at a pulse amplitude of 10 mV, showed two distinct peaks of equal intensity at potentials of 0.578 and 0.681 V vs. SCE. For such a separation of potential, according to Richardson and Taube,[23] the peak potential values are nearly coincident with the $E_{1/2}$ values, which are reported in Table III. Significantly, the height of each peak is very close to that found for a solution of the corresponding dioxocyclam complex $[Cu(L^1)]$ under the same experimental conditions (with the same concentration of complex). Therefore, the two-peak DPV profile can be ascribed to the consecutive one-electron oxidations of each metal center, through a reversible Cu^{II}/Cu^{III} redox change, in analogy with the behavior ascertained for the mononuclear reference complex $[Cu^{II}(L^1)]$.[6] It should be noted that the cyclic voltammetry experiment performed on the dinuclear complex solution gave a composite profile that could be deconvoluted to give two peaks in the oxidation scan and two peaks in the reduction scan. The separation of the two consecutive peaks both in oxidation and in reduction was approximately 100 mV, and the evaluated $E_{1/2}$ values were approximately the same as those found by DPV investigation.

The present evidence emphasizes the superiority of the DPV technique with respect to the CV experiment for consecutive one-electron processes, when the $E_{1/2}$ values of two related electron-transfer processes are close. On purely statistical bases, the consecutive release of one electron by two equivalent and independent centers involves a potential separation $\Delta E_{1/2}$ of 36 mV $(=(RT/F) \ln 4))$. The greater value of $\Delta E_{1/2}$ found here (110 mV) reveals the existence of an interaction between the two charged metal centers. The triplet ESR spectrum of a frozen aqueous solution of $[Cu^{II}_2(L^2)]$ complex (VIII) has been previously reported[7] and interpreted on the basis of a magnetic dipolar interaction of two copper(II) ions at a distance of about 8 Å (corresponding to a stereochemical arrangement in which the two rings are kept as far as possible, as shown in the sketch below, but lie on different parallel planes):
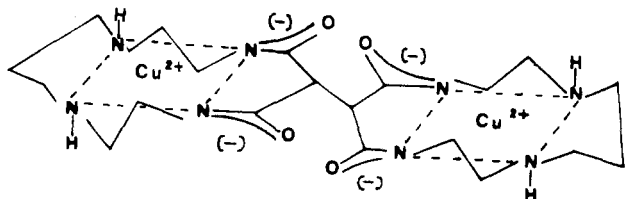
It is possible that repulsive electrostatic effects between copper cations (even if they are merged in negatively charged rings) are still operative at such distances and distinctly influence the increase of the proximate cation charge.

Compared to the situation for the mononuclear reference species $[Cu^{II}(L^1)]$, the first one-electron release of the
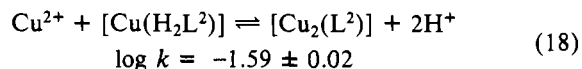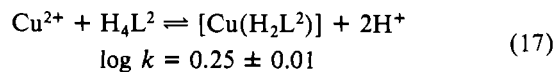
$[Cu^{II}(L^2)]$ complex, which offers two reaction sites, should be favored ($E_{1/2}$ value less positive) by 18 mV. As a matter of fact, the $E_{1/2}(1)$ value of the dicopper complex is lower than $E_{1/2}$ of the mononuclear species (see Table II), but by a more substantial quantity, i.e. 70 mV. It has been shown in the previous section that repulsive interactions between the partially negative oxygen atoms of the deprotonated amido groups of the two rings (due to a π delocalization effect) destabilize the dinuclear neutral complex, as indicated by the comparatively small value of log k. It is possible that the increase of 2+ to 3+ of the charge of the encircled metal ion provokes a return of electron charge from the deprotonated amido group to the metal, reducing the negative charge on the facing oxygen atoms. Therefore, the decrease of the $E_{1/2}$ value should reflect the stabilizing effect derived from the reduction of the intensity of O–O repulsive interactions.

The electrochemical investigation of a solution containing Cu^{II} and bisdioxocyclam in 1:1 molar ratio is complicated by the possible simultaneous coexistence of several species, potentially electroactive (see the distribution diagram in Figure 5). In a solution adjusted at pH 7, the $[Cu^{II}(H_3L^2)]^+$ species is predominant (98%). If the coordinative situation in this complex is that depicted in formula VII (Figure 2), this species should be electroactive, permitting an easy attainment of the Cu(III) state. As a matter of fact, oxidation profiles have been obtained on both CV and DPV studies, with an $E_{1/2}$ value of 0.605 V. Furthermore, progressive addition of strong acid cause (i) a shift of $E_{1/2}$ toward more positive values and (ii) a progressive decrease of i_p. The effect (i) is consistent with the decrease of the concentration of the $[Cu^{II}(H_3L^2)]^+$ species and the simultaneous increase of the $[Cu^{II}(H_4L^2)]^{2+}$ complex, which, according to the formula VI (Figure 2), must be still electroactive. This latter species should be oxidized to the trivalent state at a potential more positive than that for VII, due to the increased electrostatic repulsive effects exerted by the double protonated ring. Limiting voltammetric profile for $[Cu^{II}(H_4L^2)]^{2+}$ could not be obtained, since this species does not exist at any pH value as 100%. The maximum concentration of $[Cu^{II}(H_4L^2)]^{2+}$, ca. 40%, is achieved at pH 5, where $[Cu^{II}(H_3L^2)]$ exists as ca. 35%. For this solution a value of $E_{1/2}$ of 0.63 V was measured. Progressive decrease of pH causes decomplexation of copper, which explains the effect (ii).

The $[Cu^{II}(H_2L^2)]$ species (VIII) can be obtained in large amounts at a pH greater than 10.5. CV investigation on a solution adjusted at that pH value produced a poorly reversible oxidation profile, probably due to the decomposition of the Cu^{II} complex, a phenomenon already observed for trivalent copper complexes in basic solutions.[25]

Conclusions

Bisdioxocyclam (**2**) has been thought of and designed as a molecule able to accommodate two cations in separate and noninterfering chambers, so that metal centers could display independent reactivity, even if at a limited distance each from the other. However, equilibrium studies reported here have shown that the incorporation and coordination of a cation (e.g. Cu^{II}) by each macrocyclic subunit are mutually heavily influenced. This is definitively shown by the two stepwise equilibria

$$Cu^{2+} + H_4L^2 \rightleftharpoons [Cu(H_2L^2)] + 2H^+$$
$$\log k = 0.25 \pm 0.01 \tag{17}$$

$$Cu^{2+} + [Cu(H_2L^2)] \rightleftharpoons [Cu_2(L^2)] + 2H^+$$
$$\log k = -1.59 \pm 0.02 \tag{18}$$

in which two Cu^{II} ions consecutively penetrate the bisdioxo-

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cyclam ring, simultaneously promoting deprotonation of the amido groups.[26] It is seen that the incorporation of the second Cu[II] ion is more disfavored than is expected on statistical bases ($\Delta \log k_{stat}$ = log 4 = 0.6), showing mutual influence between rings. However, this seems to be due to the repulsion between the facing negatively charged oxygen atoms bound to each ring, rather than to interactions between the encircled metal centers. Mutual effects between the two rings settled in their definitive coordinative arrangements are expected to be small. The difference of the electrode potentials for the stepwise Cu[II]/Cu[III] oxidation processes involving the dimetallic bis-dioxocyclamato complex [Cu₂(L²)] (0.07 V, when corrected for the statistical term) must be considered small, if one takes

into account that repulsive effects between metal centers are now involving tripositive cations.

In conclusion, double-ring macrocyclic complexes of the type described here present two proximate metal center that are able to release (or receive, provided that some coordinative features of the chambers and/or the cations are appropriately changed) a pair of electrons nearly at the same potential (*in a single step*). We believe that this situation may present some advantages in the assistance of many important two-electron redox processes, compared to the case for mononuclear analogues. This advantage should become larger and larger if the concentration of the metal complex is progressively reduced (e.g. to a *catalytic* level).

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(26) Equation 18 is the difference of eq 12 and 17, reported in Table II.

Contribution from the Departments of Chemistry, Western Washington University, Bellingham, Washington 98225, and Drexel University, Philadelphia, Pennsylvania 19104

# Adduct Formation and Electrochemistry of a Unipositive Nickel(II) Macrocycle, [Ni(cyclops)]⁺

A. W. ADDISON,*[1a] B. WATTS,[1b] and M. WICHOLAS*[1b]

A series of diamagnetic five-coordinate square-pyramidal adducts of Ni(cyclops)⁺ have been synthesized and characterized with the axial ligands NCS⁻, I⁻, pyridine, and *N*-benzylimidazole. Two binuclear ligand-bridged complexes of formula [Ni₂(cyclops)₂X]ClO₄ have also been isolated, where X = I⁻, N₃⁻. Formation constants for mononuclear 1:1 adduct formation have been measured both spectrophotometrically and electrochemically. The redox chemistry of the parent Ni(cyclops)ClO₄ has been reinvestigated. The cyclic voltammogram in CH₃CN exhibits two reversible one-electron reductions for which the potentials are concentration dependent. This is explained by the existence of a rapid dimerization equilibrium for the first reduced species, 2Ni(cyclops) ⇌ Ni₂(cyclops)₂, for which K_d = 5900 ± 200.

Introduction

Recent work with copper(II) complexes of the anionic macrocycle 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenate, hereafter abbreviated as cyclops (**1**), has shown that

1
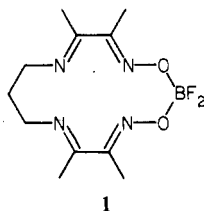
this macrocycle possesses unusual coordination properties related in part to its ring flexibility and uninegative charge.[2–5] The most extensively investigated system containing cyclops has been its complexes with copper. A series of interesting square-pyramidal Cu(cyclops)⁺ adducts have been reported.[6] These display very strong axial ligand coordination wherein

the copper(II) is pulled out of the tetraaza plane by as much as 0.58 Å—an unprecedented out-of-plane displacement for copper(II).[7] The redox chemistry of Cu(cyclops)⁺ has proven even more unusual. Stable square-pyramidal copper(I) adducts have been isolated, and the carbon monoxide adduct exhibits strong Cu–CO bonding with the metal displaced 0.96 Å from the tetraaza plane.[8]

Since our initial work, others have synthesized related copper(II) macrocyclic systems capable of forming square-pyramidal adducts.[9,10] These reports also have focused upon the interesting metal–axial ligand interactions and the structural and spectroscopic consequences.

Little has been reported for the analogous nickel(II) system. Uhlig and Friedrich[11] first synthesized the precursor Ni(II) macrocycle in which H is substituted for BF₂. Also reported were the diamagnetic square-pyramidal adducts with I⁻, Br⁻, and SCN⁻. Subsequently both Rose[12] and Gagné[5] prepared Ni(cyclops)⁺ complexes with the latter focusing upon the redox properties of Ni(cyclops)⁺ and the CO adducts of Ni(cyclops).

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