dichloromethane containing Me$_2$SO in very low concentrations (<0.001%); the absorbance due to Mo^{IV}O(TPP) decreased with increasing absorption due to complex **1** without the appearance of spectrum of complex **2**.

The complex Mo^{IV}O(TPP) is obtained through reaction paths d and f by warming the solutions of complexes **1** and **2** to room temperature, respectively. Mo^{IV}O(TPP) in solution at room temperature does not react with either O_2^- or O_2 but is converted into complex **1** as the O_2^- solution and O_2 gas are simultaneously introduced into the reaction system. This observation suggests the presence of the reaction path i → b via the complex Mo^{V}O(TPP)(O_2^-), which was not detected experimentally.

Complex **1**, [Mo^{V}O(TPP)(O_2^{2-})]$^-$, is of the same type as the complexes [Fe^{III}(P)(O_2^{2-})]$^-$ (P = TPP or OEP) formed in the reaction of Fe^{III}(P)Cl with O_2^- in a molar ratio of 1:2.[22,23] Recently the reactions of sulfur with iron and titanium porphyrin peroxo complexes to give sulfate complexes or sulfate were reported.[45] These peroxo dioxygen complexes are of great interest as mediators in oxygenation reactions and as models of intermediates in oxygen activation cycles of the reactions in vivo.

Acknowledgment. The authors thank Professors Y. Matsunaga and I. Yamazaki (Hokkaido University) for helpful discussions. We also acknowledge Dr. S. Ito (Government Industrial Development Laboratory, Hokkaido, Japan) for the analysis of molybdenum content using ICPQ, A. Yamazaki (Hokkaido University) for mass spectrometric measurements to detect oxygen gas evolved in the reaction, and T. Goto for help with the synthesis of complex **1**.

Registry No. **1**, 102149-45-1; **2**, 94782-05-5; Mo^{V}O(TPP)Br, 73515-72-7; Mo^{V}O(TPP)Cl, 68070-21-3; Mo^{V}O(TPP)NCS, 73515-84-1; Mo^{IV}O(TPP), 33519-60-7; KO$_2$, 12030-88-5.

---

(45) Mikisztal, A. R.; Valentine, J. S. *Inorg. Chem.* **1984**, *23*, 3548.

Contribution from the Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa,
and Laboratory of Chemistry, College of General Education, Kyushu University 01, Ropponmatsu, Chuo-Ku, Fukuoka, Japan

Secondary Anion Binding to the Dicopper(II) Complex of *N*,*N′*,*N″*,*N‴*-Tetrakis(2-aminoethyl)cyclam

Ann Evers,[†] Robert D. Hancock,*[†] and Ichiro Murase*[‡]

Received September 25, 1985

The complexing of Cu^{2+} by the ligand TAEC (*N*,*N′*,*N″*,*N‴*-tetrakis(2-aminoethyl)cyclam) is investigated by potentiometric titration and by UV–visible spectroscopy in 0.5 M NaNO$_3$ at 25 °C. Equilibrium constants for the formation of the species [Cu$_2$(TAEC)]$^{4+}$ and [Cu(TAEC)H$_2$]$^{4+}$ were found to be 32.1 and 18.97 (the latter corresponding to the equilibium $Cu^{2+} + LH_2^{2+} \rightleftharpoons [CuLH_2]^{4+}$). The complex [Cu$_2$(TAEC)]$^{4+}$ binds secondary anionic ligands, presumably held between the two copper atoms in the complex in a bridging fashion, with log *K* values for the formation of these secondary complexes being 4.1 for OH$^-$, 3.26 for Br$^-$, 3.57 for Cl$^-$, 4.02 for N$_3^-$, and 2.63 for SCN$^-$. The strength of binding of these secondary ligands is contrasted to that found in other binuclear complexes containing two copper(II) ions and also with mononuclear complexes of copper(II). It is concluded that the bimetallic site increases the strength of binding of secondary ligands by some 2 or 3 orders of magnitude as compared with mononuclear complexes and that the strength of binding in the bimetallic complex may be strongly affected by the coordination geometry around the copper(II) ion.

There is currently considerable interest in ligands that bind two or more metal ions, which arises in part from the possibility that they might act as models for biological systems.[1] There have been several recent reports of thermodynamic studies of macrocyclic ligands that coordinate two metal ions, which are able to coordinate further, secondary, ligands,[2-4] in what has been termed "cascade" binding.[5] Martell et al.[2] thus found that the two copper(II) ions held in the BISTREN molecules (Figure 1) were able to bind a chloride ion with a log K_1 (formation constant) value of 3.55, which is very high in comparison to that reported[6] for a single free Cu^{2+} ion, namely 0.5 log units. At the same time, the binding of hydroxide ion to the two copper(II) ions in BISTREN was extraordinarily high, log *K* having a value of 11.56, in contrast to the value of 6.7 found for the Cu^{2+} ion itself.[6] Such marked changes in coordinating ability are clearly of interest.

In recent papers[7,8] it was reported that the ligand TAEC (Figure 1) formed complexes in which two copper(II) ions were bound and that[7] binding of bromide ion to these two copper(II) ions appeared to be quite strong. The dicopper(II) complex of TAEC is of interest since structural studies show[7,8] that the copper(II) ions each have four nitrogen donors bound in a planar fashion, so that the secondary ligand, e.g. the bromide ion, must bind to the axial sites on the copper(II) ions, forming a bridge between them. The structure of the monobromo dicopper(II) complex of TAEC has Cu–Br lengths of 2.73 Å to the bridging bromide ion, which can be compared with the shorter Cu–Br lengths of 2.55[9] and 2.52 Å[10] for nonbridging bromides occupying the axial site on copper(II) complexes with square-pyramidal coordination geometry. In contrast, planar coordination of the nitrogen donors to the copper(II) ions in BISTREN is not possible, so that the bridging secondary ligand must occupy the axial sites on what

Table I. Protonation Constants of the Ligand TAEC[a]

pK_{a1}[b]	10.10 (3)[c]	pK_{a5}	6.08 (7)
pK_{a2}	10.05 (2)	pK_{a6}	4.84 (7)
pK_{a3}	9.41 (4)	pK_{a7}	1.8 (1)
pK_{a4}	9.00 (3)		

[a] Determined by glass-electrode potentiometry, in 0.5 M NaNO$_3$ at 25 °C. TAEC is the ligand *N*,*N′*,*N″*,*N‴*-tetrakis(2-aminoethyl)cyclam, shown in Figure 1. [b] These are the stepwise constants such that pK_{a1} is the constant for the equilibrium $L + H^+ \rightleftharpoons LH^+$, p$K_{a2}$ for $LH^+ + H^+ \rightleftharpoons LH_2^{2+}$, and so on. [c] The numbers indicated in parentheses are the estimated errors in the last significant figure shown, which are 3 times the standard deviation indicated by the program.

[†] University of the Witwatersrand.
[‡] Kyushu University.

(1) Fenton, D. E. *Adv. Inorg. Bioinorg. Mech.* **1984**, *2*, 187–257.
(2) Motekaitis, R. J.; Martell, A. E.; Dietrich, B.; Lehn, J.-M. *Inorg. Chem.* **1984**, *23*, 1588.
(3) Motekaitis, R. J.; Martell, A. E.; Lecomte, J.-P.; Lehn, J.-M. *Inorg. Chem.* **1983**, *22*, 609.
(4) Bianchi, A.; Mangani, S.; Micheloni, M.; Nanini, V.; Orioli, P.; Paoletti, P.; Seghi, B. *Inorg. Chem.* **1985**, *24*, 1182.
(5) Lehn, J.-M. *Pure Appl. Chem.* **1980**, *52*, 2441.
(6) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1974, 1975, 1976, 1977, 1980; Vol. 1–5.
(7) Murase, I.; Mikuriya, M.; Sonoda, H.; Kida, S. *J. Chem. Soc., Chem. Commun.* **1984**, 692.
(8) Murase, I.; Mikuriya, M.; Sonoda, H.; Fukuda, Y.; Kida, S., submitted for publication.
(9) Ladd, M. F. C.; Perrins, D. H. G. *Z. Kristallogr.* **1981**, *154*, 155.
(10) Thöm, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3198.

0020-1669/86/1325-2160$01.50/0

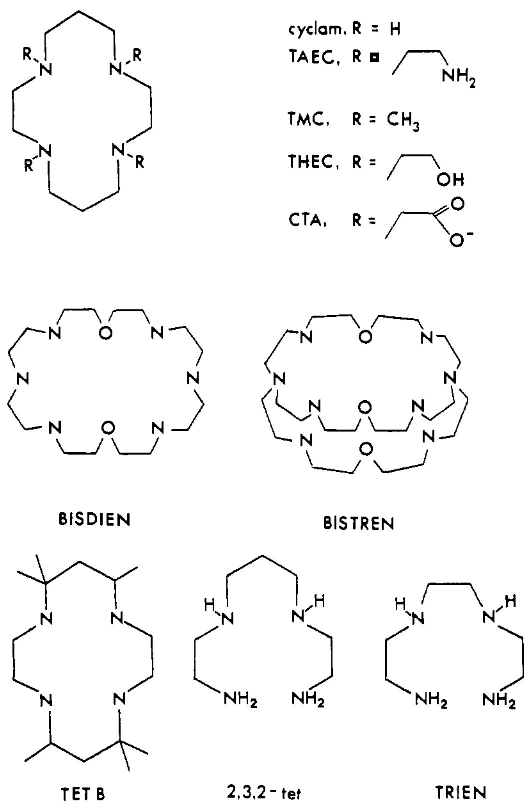


Figure 1. Ligands discussed in this work.

models suggest must be a pair of trigonal-bipyramidally coordinated copper(II) ions. A study of the dicopper(II) complexes of TAEC and the secondary anion binding of Cl^-, Br^-, N_3^-, SCN^-, and OH^-, by this complex, is reported here.

Experimental Section

The ligand TAEC was synthesized as its octahydrobromide salt as described previously.[7] Elemental analysis showed this to be pure. A stock solution of TAEC·8HBr was prepared and the calculated quantity of silver nitrate added to precipitate out the bromide. After filtration, the stock solution of the ligand was standardized by titration with base, and tests showed no significant concentration of Ag^+ or Br^- ions left in solution. This stock solution was used to make up an approximately 2×10^{-3} M stock solution of what was effectively the octanitrate salt of the protonated ligand in 0.5 M $NaNO_3$. These solutions were then titrated with base by using previously reported[11] techniques to determine the seven protonation constants reported in Table I. The glass electrode used was a Radiometer G202B electrode. The electrode was calibrated while a basic solution was titrated with acid, and the 20 or so calculated hydrogen ion concentrations were fitted to the Nernst equation. All constants in this work thus refer to concentrations and not activities. The three separate titrations of the ligand with base so as to determine the pK_a values are shown in Figure 2, where $\bar{n}$, the average number of protons bound to the ligand, has been plotted as a function of pH. The pK_a values shown in Table I were calculated from this data with the programs MINIQUAD[12] and EQUILIBRIA,[13] which gave results in excellent agreement. The pK_a determinations were repeated in the presence of bromide ion, with essentially the same results being obtained, so that it did not appear as if the protonated forms of the ligand bound bromide very strongly. Three titrations were carried out with Cu^{2+} and TAEC present at metal-to-ligand ratios varying from 0.5:1 to 2:1, and four further titrations with both Cu^{2+} and Br^- present were carried out. These seven titrations, varying widely in Cu^{2+}:TAEC and Cu^{2+}:Br^- ratios, were analyzed by the MINIQUAD program.[12] The only species found to be present in the absence of bromide were the MLH_2^{4+} and M_2L^{4+} complexes (M = Cu, L = TAEC), with an ML_2OH species occurring at higher pH. The titration points where the latter complex occurred were removed from the refinement of the formation constants, as a precipitate was apparent in these solutions. The equilibrium involving hydrolysis of the complex $[Cu_2TAEC]^{4+}$ to give $[Cu_2TAEC(OH)]^{3+}$ was thus studied spectroscopically at a lower complex concentration than was used in the potentiometric titrations, and this succeeded because no precipitation occurred. In the presence of bromide ion, the MINIQUAD program indicated the presence of the additional species M_2LBr^{3+}. The determination of the constants of the additional secondary anions Cl^-, OH^-, N_3^-, and SCN^- binding to the complex was carried out in a straightforward manner by following the electronic spectrum of the Cu_2L^{4+} complex as a function of the concentration of the secondary ligand. The spectroscopic studies were carried out in 0.5 M $NaNO_3$ in cells thermostated to 25 °C, with the spectra being recorded on a Cary 2300 UV–visible spectrophotometer. Reasonably good isosbestic points were obtained, with the good fit of the model involving only the Cu_2L^{4+} and Cu_2LX^{3+} complexes (X = Cl^-, OH^-, N_3^-, or SCN^-) in the formation constant calculations, indicating the presence of no other complexes in the system. The constants referring to the binding of these secondary ligands, together with those for the formation of the copper(II) complexes of TAEC, are seen in Table II, while the spectra obtained for $[Cu_2(TAEC)]^{4+}$ as a function of bromide ion concentration are seen in Figure 3.

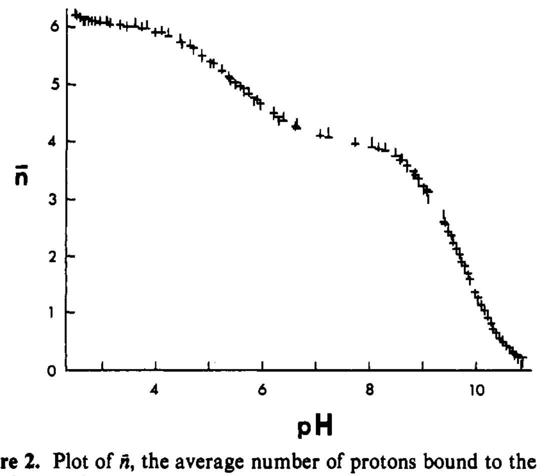


Figure 2. Plot of $\bar{n}$, the average number of protons bound to the ligand TAEC, as a function of pH. The plot was generated by the program EQUILIBRIA.[13] Vertical bars are the experimental values of $\bar{n}$ calculated from the 103 titration points obtained in three separate titrations of TAEC. The horizontal bars are the theoretical values of $\bar{n}$ as a function of pH calculated from the seven pK_a values for TAEC given in Table I. One sees that the $\bar{n}$ values in the titrations do not go much above 6.0 and so we find in Table I a rather higher uncertainty attached to pK_{a7}.

Table II. Formation Constants for Copper(II) with the Ligand TAEC and Secondary Ligands[a]

equilibrium	log K[b]
$Cu^{2+} + LH_2^{2+} \rightleftharpoons [CuLH_2]^{4+}$	18.97 ± 0.07
$2Cu^{2+} + L \rightleftharpoons Cu_2L$	32.1 ± 0.1
$[Cu_2L]^{4+} + OH^- \rightleftharpoons [Cu_2LOH]^{3+}$	4.1 ± 0.1
$[Cu_2L]^{4+} + Br^- \rightleftharpoons [Cu_2LBr]^{3+}$	3.26 ± 0.06
$[Cu_2L]^{4+} + Cl^- \rightleftharpoons [Cu_2LCl]^{3+}$	3.57 ± 0.03
$[Cu_2L]^{4+} + N_3^- \rightleftharpoons [Cu_2LN_3]^{3+}$	4.02 ± 0.07
$[Cu_2L]^{4+} + SCN^- \rightleftharpoons [Cu_2LSCN]^{3+}$	2.63 ± 0.05

[a] In 0.5 M $NaNO_3$ at 25 °C. The ligand TAEC is *N,N′,N″,N‴*-tetrakis(2-aminoethyl)cyclam, shown in Figure 1. [b] The formation constants for the first two equilibria were determined potentiometrically, while the remainder were determined spectrophotometrically.

Results and Discussion

The pK_a values of TAEC are of interest because of the large number of protonation sites on the ligand. The first four pK_a values, as seen in Table I, are bunched very closely together. The calculations have indicated that the first two pK_a values are separated by only 0.05 log units, which, as pointed out by a reviewer, is less than the 0.3 log units that we would expect on purely statistical grounds. The good fit of the theoretical to the experimental $\bar{n}$ vs. pH curve in Figure 2, coupled with the fact that both the programs EQUILIBRIA[13] and MINIQUAD[12] give virtually identical sets of pK_a values, suggests that this is a real effect. Such unusual sequences of pK_a values are not without precedent for tetraaza macrocycles, since cyclam itself[14,15] shows the unusual

---

(11) Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 416.
(12) Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1974**, *21*, 53.
(13) Wade, P. W.; Hancock, R. D., to be submitted for publication. The program EQUILBRIA employs the Marquard algorithm, a more rapid means of finding the best fit for the constants.

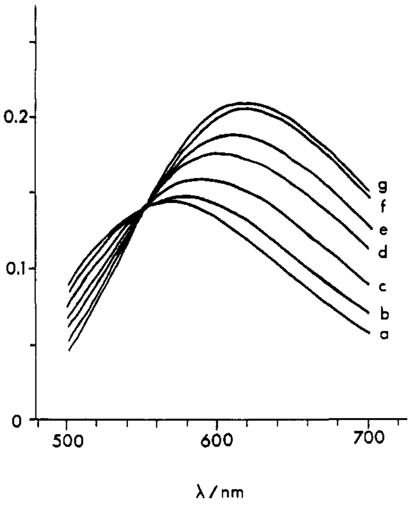


Figure 3. Electronic spectra of 4.48 × 10^{-4} M solutions of the complex $[Cu_2(TAEC)]^{4+}$ as a function of bromide ion concentration. The absorbance of the solutions, A, is shown as a function of wavelength, λ. The bromide concentration in each solution is (a) zero, (b) 1.75 × 10^{-4}, (c) 4.37 × 10^{-4}, (d) 8.75 × 10^{-4}, (e) 1.75 × 10^{-3}, and (g) 1.65 × 10^{-2} M. Spectra were recorded in 0.5 M $NaNO_3$.

Table III. Secondary Anion Binding Constants for Copper(II) Complexes[a]

secondary ligand	complex	log K^b	ref
OH^-	$[Cu_2(TAEC)]^{4+}$	4.1	this work
	$[Cu_2(BISTREN)]^{4+}$	11.6	2
	$[Cu_2(BISDIEN)]^{4+}$	7.3	3
	$[Cu(BISDIEN)]^{2+}$	3.2	3
	$[Cu(TETB)]^{2+}$	2.7	18
	$[Cu(cyclam)]^{2+}$	v small	16
	$[Cu(trien)]^{2+}$	3.0	19
Cl^-	$[Cu_2(TAEC)]^{4+}$	3.6	this work
	$[Cu_2(BISTREN)]^{4+}$	3.6	2
	$[Cu(TETB)]^{2+}$	1.2	18
Br^-	$[Cu_2(TAEC)]^{4+}$	3.3	this work
	$[Cu(TETB)]^{2+}$	1.3	18
N_3^-	$[Cu_2(TAEC)]^{4+}$	4.0	this work
	$[Cu(TETB)]^{2+}$	1.9	18
	$[Cu(cyclam)]^{2+}$	2.1	16
NCS^-	$[Cu_2(TAEC)]^{4+}$	2.6	this work
	$[Cu(TETB)]^{2+}$	2.2	18
	$[Cu(cyclam)]^{2+}$	1.8	16

[a] For key to ligand structures, see Figure 1. [b] The equilibrium constant here is for the binding of the secondary ligand indicated, L′, to the complex indicated, CuL. The equilibrium is thus $CuL + L' \rightleftarrows CuL{\cdot}L'$, where the complex contains a single Cu(II) ion, or $Cu_2L + L' \rightleftarrows Cu_2L{\cdot}L'$ where the complex contains two Cu(II) ions.

Table IV. Stability of Complexes of Copper(II) with Tetraaza Macrocycles Having Tertiary Nitrogen Donor Atoms

ligand[a]	equilibrium	log K	ref
TAEC	$Cu^{2+} + LH_2^{2+} \rightleftharpoons [CuLH_2]^{4+}$	18.97	this work
TMC	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	18.3	21
THEC	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	15.7	22
CTA	$Cu^{2+} + L^{4-} \rightleftharpoons [CuL]^{2-}$	18.6	23

[a] For structures of ligands, see Figure 1.

order $pK_{a4} > pK_{a3}$. Interestingly, the program EQUILIBRIA[13] reproduces this surprising result using data from the same potentiometric equipment as used here,[15] which was first found by the group of Paoletti[14] in a very careful study of the protonation of cyclam. For the ligand TAEC it is not clear why pK_{a1} should be so close to pK_{a2}. By analogy with cyclam,[15] one must suggest that addition of the first proton to TAEC causes a conformational change in the ligand, as does addition of the third proton on cyclam,[14] facilitating the addition of the next proton. What the conformation change is that TAEC might undergo on addition of the first proton is not at all clear.

In Table III are shown the binding constants of TAEC with the copper(II) ion. The analysis of the titrations by MINIQUAD[12] indicated that only the diprotonated form of the complex of TAEC containing a single copper(II) can be detected, with no simple $[Cu(TAEC)]^{2+}$ complex present. This can be understood if we consider that the copper(II) is unlikely to be more than six-coordinate in $[Cu(TAEC)]^{2+}$, which would leave two of the pendent aminoethyl groups uncoordinated. These free aminoethyl groups are likely to be of high basicity and so protonated up to a high pH. At a pH high enough to deprotonate these groups, the titrations were bedeviled by the formation of unidentified precipitates, so that the high-pH (above pH 9) regions of the titrations were not analyzed. In Table IV we see the formation constants of Cu(II) with some tetraaza macrocycles having tertiary nitrogen donors. The diprotonated form of TAEC appears to be a more effective ligand than the other cyclam ligands with tertiary nitrogen donors, such as CTA or THEC. It thus seems that the electrostatic repulsion expected between the Cu^{2+} ion and the two protons in the $CuLH_2^{4+}$ complex (L = TAEC) does not lead to significant destabilization.

The secondary anion binding constants for $Cu_2(TAEC)$ are seen in Table III, with secondary anion constants of binding to other complexes of copper(II). As found[2] for the $Cu_2(BISTREN)$ complex, the binding to anions is generally much higher in $Cu_2(TAEC)$ than for monocopper complexes. However, the binding of hydroxide ion to $Cu_2(BISTREN)$ is remarkably much higher than for $Cu_2(TAEC)$. The difference must relate to the square-planar coordination of the nitrogens to copper(II) ions found[7,8] in $Cu_2(TAEC)$, as opposed to the proposed[2] trigonal-bipyramidal coordination for copper(II) in $Cu_2(BISTREN)$. This dependency of hydroxide-binding ability on the planarity of the four nitrogen donors and the copper(II) ion can be seen in a somewhat less marked extent in simple monocopper complexes. For the cyclam complex of copper(II), where the copper lies in the plane of the nitrogen donors, binding of hydroxide to the axial coordination site does not occur even in 0.1 M NaOH.[16] On the other hand, when the copper is forced to lie out of the plane of the nitrogen donors, as it does[17] for the CuL^{2+} complex where L is 1,4,7-triazacyclononane, a log K_1 value with hydroxide of 8.25 is found.[20]

If complexes containing two metal ions are fairly rigid, then the distance between the two metal ions should be relatively fixed. A possible benefit of this is that greater selectivity toward ligands that fit the gap between the metal ions might be expected. Two different forms of the dicopper(II) complexes of TAEC have been found, indicated as[7,8] the B-1 and B-2 forms. These are shown in Figure 4. The B-1 form has ethylene bridges linking the halves of the complex together, while the B-2 form has trimethylene bridges. The distance between the two copper atoms should thus be smaller in B-1 than in B-2, suggesting that the B-1 form would be better at accommodating small ligands and the B-2 form better for large ligands. However, if we examine space-filling models of these two forms, we see that they are both highly sterically crowded. These models suggest that in the B-1 form there is no space at all between the two copper atoms, this space being filled by the trimethylene groups. The form of the complex is such that it can best be regarded as two separate copper(II) complexes of

---

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

(15) Thöm, V. J.; Hosken, G. D.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 3378.

(16) Hancock, R. D.; Darling, E. A.; Hodgson, R. H.; Ganesh, K. *Inorg. Chim. Acta* **1984**, *96*, L83.

(17) Bereman, R. D.; Churchill, M. R.; Schaber, P. M.; Winkler, M. E. *Inorg. Chem.* **1979**, *18*, 3122.

(18) Wu, S. Y.; Lee, C. S.; Chung, C. S. *Inorg. Chem.* **1984**, *23*, 2584.

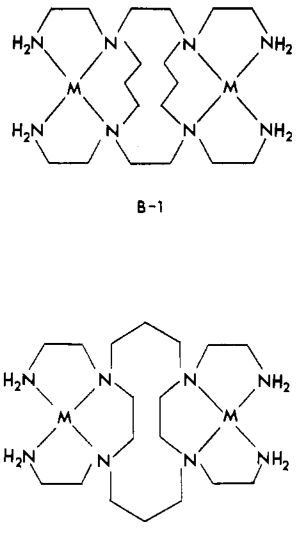
(19) Paoletti, P.; Ciampolini, M. *Ric. Sci., Parte 2: Sez. A* **1963**, *3* 399.

(20) Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531.

(21) Nakani, B. S.; Welsh, J. J. B.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 2956.

(22) Madeyski, C. M.; Michael, J. P.; Hancock, R. D. *Inorg. Chem.* **1984**, *23*, 1487.

(23) Stetter, H.; Frank, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 686.



B-1

B-2

Figure 4. The two forms of dicopper(II) complex of TAEC.[7,8] The trimethylene bridges in the B-1 form completely block the space between the two metal ions, so that it is unlikely the secondary ligands will be able to bridge the gap between the two metal ions (M). There is more space in the B-2 form, which is that actually found in the monobromide complex, $[Cu_2(TAEC)Br]^{3+}$,[7,8] although bridging ligand will still be considerably sterically hindered.

2,3,2-tet stacked on different levels and held together by ethylene bridges. The B-2 form of the complex is also highly sterically crowded and is found in the monobromo complex, as indicated by X-ray crystallographic studies.[8] The level of steric crowding indicated by models for the B-2 form of $[Cu_2(TAEC)Br]^{3+}$ is such that the two coppers are not able to approach each other very closely if they lie in the plane of the four nitrogens coordinated to each of them. One must conclude that the fact that the two copper(II) ions lie[8] some 0.43 Å out of the mean plane of the nitrogen donor atoms, coupled with the unusually long Cu–Br lengths, is mainly a result of the steric crowding that prevents closer approach of the two copper(II) ions to each other. The low affinity of the $[Cu_2(TAEC)]^{4+}$ complex for hydroxide might thus have a steric component to it, with the hydroxide ion being too small to bridge the gap between the two copper(II) ions. One might have expected the binding of long ligands such as azide or thiocyanate to be relatively much higher than it is. However, structural studies show that azide binds in an end-on fashion to $[Cu_2(TAEC)]^{4+}$, with both copper(II) ions bound to the same terminal nitrogen atom of the azide ion, so that it would seem that these anions are too long to fit into the gap between the two copper(II) ions. The strong binding of secondary anions to $[Cu_2(TAEC)]^{4+}$ in spite of the considerable amount of steric strain apparently present is remarkable. The strong binding suggests that if similar systems with lower strain energy could be synthesized, very much stronger binding of secondary anions would be observed. In contrast to the TAEC analogues, models suggest that strain in the dicopper(II) complexes of BISDIEN and BISTREN is comparatively low and that there is considerable flexibility in the connecting ethereal groups bridging between the halves of the complex.

Table III shows that binding of ligands with a potential for bridging between the two copper(II) ions is usually larger than to comparable monocopper(II) complexes by about 2 orders of magnitude. One thus has a kind of "chelate effect" in reverse. Instead of the usual situation where two donor atoms that are part of a single ligand bind a single metal ion, one has here a situation where two metal ions that are part of a single complex bind a single ligand. This increase in ability to bind ligands such as bromide, which virtually do not bind to Cu(II) at all, is of considerable interest. The increased binding ability of complexes containing more than one metal ion suggests one way in which nature may be able to overcome the lack of ability to bind strongly such soft ligands by the metal ions that normally occur in biological systems.

Acknowledgment. We thank the Council Research Grants Committee of the University of the Witwatersrand, and the Foundation for Research Development, for generous financial support for this work.

Registry No. OH^-, 14280-30-9; Br^-, 24959-67-9; Cl^-, 16887-00-6; N_3^-, 14343-69-2; SCN^-, 302-04-5.

Contribution from Rocketdyne, A Division of Rockwell International,
Canoga Park, California 91303

Synthesis and Characterization of CrF_4O, $KrF_2 \cdot CrF_4O$, and $NO^+CrF_5O^-$

Karl O. Christe,* William W. Wilson, and Roland A. Bougon[†]

Received January 14, 1986

Chromium(VI) tetrafluoride oxide can be prepared in high yield and purity from CrO_2F_2 and KrF_2 in HF solution. The vibrational spectra of gaseous, solid, and matrix-isolated CrF_4O and its BrF_5 and HF solutions are reported, as well as the ^{19}F NMR spectra of the BrF_5 and SO_2ClF solutions. The data confirm for gaseous, matrix-isolated, and dissolved CrF_4O a monomeric, square-pyramidal structure of symmetry C_{4v} and for solid CrF_4O a fluorine-bridged polymeric structure. CrF_4O is a strong Lewis acid, and with FNO it forms a stable $NO^+CrF_5O^-$ salt, which was characterized by vibrational spectroscopy. With KrF_2 it forms an unstable 1:1 adduct that has in the solid phase an essentially covalent structure containing a Kr–F- - -Cr bridge but is completely dissociated in SO_2ClF solution. With AsF_5 it does not form a stable adduct at temperatures as low as −78 °C, indicating that CrF_4O is a weak Lewis base. It was also shown that CrF_3O is a weak Lewis base and does not form a stable adduct at −78 °C.

Introduction

Chromium tetrafluoride oxide, CrF_4O, was first described by Edwards in 1963 as a byproduct in the direct fluorination of metallic chromium, and its unit cell dimensions were reported.[1] In 1974, Edwards and co-workers published an improved synthesis from CrO_3 and F_2 at 220 °C and gave the melting point, boiling point, vapor pressure, and description of a solid–solid transition at 24 °C.[2] Reference was made in this paper to unpublished work indicating that the low-temperature phase of CrF_4O has an endless, cis-fluorine-bridged chain structure, similar to those of MoF_4O[3] and ReF_4O.[4] The only other report on CrF_4O is a recent paper by Ogden and co-workers, who studied its infrared and UV–visible

---

[†] Permanent address: Centre d'Etudes Nucléaires de Saclay, IRDI/DESICP/DPC, 91191 Gif sur Yvette, France.

(1) Edwards, A. J. *Proc. Chem. Soc., London* **1963**, 205.
(2) Edwards, A. J.; Falconer, W. E.; Sunder, W. A. *J. Chem. Soc., Dalton Trans.* **1974**, 541.
(3) Edwards, A. J.; Steventon, B. R. *J. Chem. Soc. A* **1968**, 2503.
(4) Edwards, A. J.; Jones, G. R. *J. Chem. Soc. A* **1968**, 2511.

0020-1669/86/1325-2163$01.50/0