Chart I. Formation and Redox Reactions of Molybdenum–3,5-di-*tert*-butylcatechol Complexes in Acetonitrile

$$2\ \mathrm{Mo^{VI}(O)_2(acac)_2} + 4\ \mathrm{H_2Cat} \longrightarrow \underset{\underline{1}\ \text{(purple)}}{[\mathrm{Mo^{VI}(O)(Cat)_2}]_2} + 2\ \mathrm{Hacac} + 2\mathrm{H_2O}$$

$$\underline{1} + 2\ \mathrm{OH^-} \rightleftharpoons [\mathrm{Mo^{VI}(O)(OH)(Cat)_2^-}]_2^{2-} \qquad \text{(red-orange)}$$

$$\Big\uparrow\Big\downarrow \mathrm{H_2O}$$

$$\underset{\underline{2}\ \text{(orange)}}{[\mathrm{Mo_2^{VI}O_5(Cat)_2}]^{2-}} + 2\mathrm{H_2Cat}$$

$$\underline{1} \longrightarrow [\mathrm{Mo^{VI}(O)(Cat)(SQ\cdot)}]_2^{2+} + 2e^- \qquad E_{p,a},\ +0.6\ \text{V vs SCE}$$

$$\Big\downarrow$$

$$[\mathrm{Mo^{VI}(O)(Cat)}]_2\mathrm{Cat^{2+}} + \mathrm{Q}$$

$$\underline{1} \underset{}{\overset{\text{sol}}{\rightleftharpoons}} \underset{\text{(green)}}{2\ \mathrm{Mo^{VI}(O)(Cat)_2\ (sol)}}, \qquad \text{sol} = \text{DMSO, DMF, DMA, py}$$

$$\underline{1} + 2e^- \longrightarrow 2\ \mathrm{Mo^V(O)(Cat)_2^-} \qquad E_{p,c},\ -0.4\ \text{V vs SCE}$$

$$\mathrm{Mo^V(O)(Cat)_2^-} + e^- \rightleftharpoons \mathrm{Mo^{IV}(O)(Cat)_2^{2-}} \qquad E^{\circ\prime},\ -1.2\ \text{V vs SCE}$$

$$\underline{2} \rightleftharpoons \underset{\underline{3}}{[\mathrm{Mo_2^{VI}O_5(Cat)(SQ\cdot)}]^-} + e^- \qquad E^{\circ\prime},\ +0.25\ \text{V vs SCE}$$

$$\underline{3} \xrightarrow{\mathrm{H_2O}} \mathrm{Mo_2^{VI}O_5(Cat)} + \tfrac{1}{2}\mathrm{HCat^-} + \tfrac{1}{2}\mathrm{Q}$$

$$\underline{2} + 2\ \mathrm{OH^-} \longrightarrow \mathrm{Mo_2^{VI}O_7^{2-}} + \mathrm{H_2Cat} + \mathrm{Q} + 2e^- \qquad E_{p,a},\ -0.05\ \text{V vs SCE}$$

cyclic voltammetry). The product solution is ESR silent. The peak at +1.0 V is characteristic of the oxidation of catechol to quinone. An initial negative scan of **1** yields a series of peaks at −0.4, −0.8, and −1.1 V vs. SCE. The peaks at −0.8 and −1.1 V represent one-electron/molybdenum reductions of the monomer of **1** and of the reduction product of **1**, respectively. The reversible couple at −1.6 V vs. SCE appears to represent a reduction of the ligands. A peak at −0.3 V also is observed which probably is due to a quinone impurity. Controlled potential coulometry of **1** at −0.5 V yields a solution whose spectrum is characteristic of a bis(catechol) complex of molybdenum(V). The presence of an EPR peak at a *g* value of 1.95 indicates that this species is at least partially in a mononuclear form. The product solution from controlled potential coulometry of **1** at −1.2 V is characteristic of a bis(catechol) complex of Mo(IV). Again, it exhibits neither an ESR spectrum nor a magnetic moment.

Cyclic voltammetry of **2** indicates that an initial positive scan yields a reversible couple at +0.25 V, whose height is consistent with a one-electron oxidation. (Addition of 1 equiv of base/molybdenum in **1** results in a species with similar electrochemistry to that of **2**.) However, controlled-potential coulometry of **2** at +0.3 V indicates an overall oxidation of one electron/binuclear complex. Reduction of this product solution at −0.6 V also is a one-electron process which yields a solution of **2**. Addition of 1 equiv of base to **2** yields a species with the electrochemistry of Figure 2d and causes the controlled-potential coulometry at 0.0 V to increase to an overall one-electron/Mo oxidation. The product solution exhibits an ESR resonance at a *g* value of 2.00 which is 10 G wide and characteristic of the semiquinone radical. Both oxidations appear to yield quinone as a major electroactive product.

Consideration of the analytical, spectroscopic, and electrochemical results permits the formation and oxidation-reduction reactions for **1** and **2** to be formulated in Chart I. Additional studies are in progress on the interaction of various dioxygen species (O_2, $O_2^-\cdot$, H_2O_2, and HO_2^-) with **1** and **2**.

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(15) Species 1 was isolated from benzene solution and recrystallized from hot toluene solution as a dark purple microcrystalline product. An amorphous dark purple-brown material was obtained from methanol. Microanalysis of these materials yielded results that are consistent with the formula bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI). Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The molybdenum content was determined thermogravemetrically. Anal. Calcd for $MoC_{28}H_{40}O_5$: C, 60.86; H, 7.30; Mo, 17.36. Found: C, 61.09; H, 7.50; Mo, 17.17. The molecular weight of 1 in toluene solution was determined by vapor-pressure osmometry (Mechrolab, Inc., Model 301A) to be 1130 g mol^{-1}, which is consistent with a binuclear complex, $[Mo(O)(Cat)_2]_2$, for 1 (calcd mol wt, 1128).

(16) Species **2** was prepared and isolated by either adding 1 equiv of TBAOH/molybdenum to a CH_2Cl_2 solution of species 1 or by combining in CH_2Cl_2 bis(acetylacetonato)dioxomolybdenum(VI) with 2 equiv of 3,5-di-*tert*-butylcatechol and 1 equiv of TBAOH (in methanol) under an argon atmosphere. The latter combination resulted in a red solution, and upon addition of benzene yielded a yellow microcrystalline material which was filtered, washed with cold benzene, and air dried. The product was recrystallized from hot benzene–chloroform (95:5). Microanalysis gave results that are consistent with the formula bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI). However, preliminary X-ray data for the crystal structure of **2** by C. G. Pierpont and R. M. Buchanan (Department of Chemistry, University of Colorado, Boulder) establish that the correct formula is bis(tetra-*n*-butylammonium)-*μ*-oxo-bis[(3,5-di-*tert*-butylcatecholato)dioxomolybdenum(VI)]. Anal. Calcd for $Mo_2N_2C_{60}H_{112}O_9$: C, 59.60; H, 9.34; Mo, 15.87. Found: C, 60.61; H, 9.94; Mo, 17.35.

(17) By use of the molar absorptivities for 3,5-di-*tert*-butylcatechol (λ 279 nm (ϵ 2130)), its semiquinone anion (λ 338 nm (ϵ 1240), 377 (1010)), and, where applicable, its quinone (λ 400 nm (ϵ 1550)) in CH_3CN, the concentrations of each of these groups in a solution of the complex have been estimated.

(18) The mean values of the ^1H NMR resonances (vs. Me_4Si) for the 3,5-di-*tert*-butyl groups of the free catechol, its anion, and the related *o*-quinone are 1.33 and 1.21, 1.29 and 1.17, and 1.18 and 1.16 ppm, respectively. The mean resonance values (two doublets) for the two ring protons of free catechol, its anion, and its related quinone are 6.69 (6.72 and 6.66), 6.19 (6.31 and 6.08), and 6.28 ppm (6.49 and 6.07), respectively.

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Bimetallic Copper(I) and -(II) Macrocyclic Complexes as Mimics for Type 3 Copper Pairs in Copper Enzymes

Sir:

The complexing of two metal ions by the same *macrocyclic ligand* is subject to much current interest.[1,6] In principle, such systems allow the study of (i) metal-metal interactions and (ii) insertion of substrates and their possible transformations. Moreover, such structures are often found in biological sys-

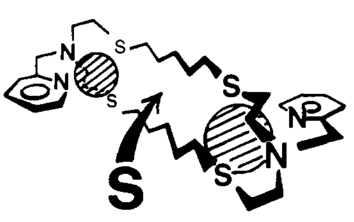
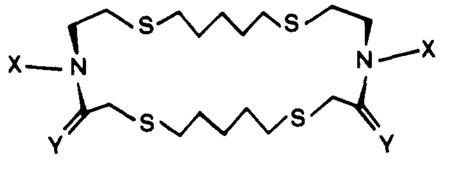


Figure 1. Schematic representation of $|Cu_2\subset(L)|^{n+}$.

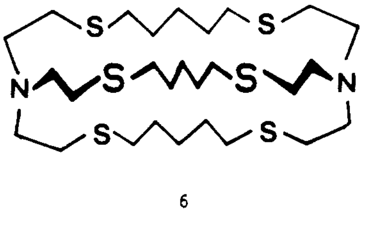
tems; metalloproteins often use *binuclear metal centers* to perform catalytic functions.[2] We report here our studies of macrocyclic bimetallic copper complexes which mimic some properties of the multicopper proteins containing pairs of copper atoms which in the cupric state are strongly antiferromagnetically coupled. The copper atoms bound in this manner in the proteins are commonly referred to as type 3 coppers.[3]

The synthesis[4] of the macromonocyclic ligand **1a** was carried out by *high dilution condensation*[5] of the required diamine with the diacid chloride to the corresponding cyclic bisamide 7 (mp 115 °C, yield 50%) which was then reduced with diborane in THF (95% yield) followed by hydrolysis with 6 N HCl at reflux and treatment with aqueous tetraethylammonium hydroxide. The other ligands, **2–6**, were synthesized in the same way, or by later attachment of side chains on the ring nitrogens.

All of these ligands form complexes of 1:2 ligand–metal stoichiometry with copper(I) and -(II) salts. The structures of all of these complexes may be schematically represented by $|2Cu^{n+}\subset L|^{2n+}$, where L symbolizes the macrocyclic ligand (Figure 1). The separation of the two metal atoms can range from 4 to 8 Å according to the conformation of the macrocyclic ligand. *Insertion* of a substrate molecule S *between the two metal cations is possible* (Figure 1); with copper(I) salts, the properties of these ligands in presence of substrates such as CO, NO, and O_2 are similar to those reported recently for the "ear muff" ligand, 1,4-bis(1-oxa-4,10-dithia-7-azacyclododecan-7-ylmethyl)benzene.[6-8] With copper(II) salts, CuX_2 ($X = NO_3^-$, BF_4^-, and ClO_4^-), subsequent reactions with substrate anions and molecules also take place.[9]



1a, X = H, Y = H_2
2, X = $CH_2CH_2NH_2$, Y = H_2
3, X = $CH_2CH_2N(CH_3)_2$, Y = H_2
4, X = CH_2CH_2SH, Y = H_2
5, X = $CH_2C_6H_4N$(ortho), Y = H_2
7, X = H, Y = O



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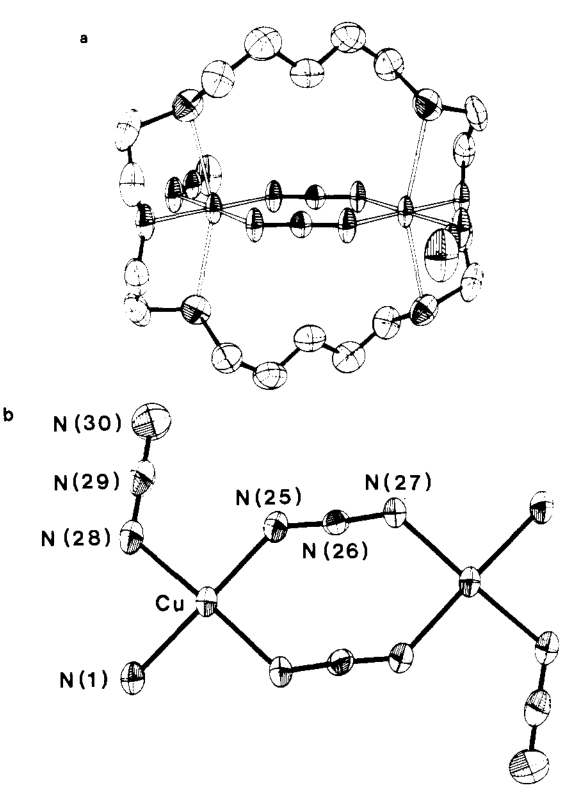

Figure 2. (a) Structure of the $[2Cu^{II}(N_3)_4\subset$**1a**$]$ molecule. The symmetry is $2/m$. All atoms are represented by 50% probability thermal ellipsoids. (b) Structure of the molecule in the plane of symmetry. For clarity, only the N(1) and N(12) nitrogen atoms of the ligand **1a** are represented. Selected bond distances (in ångstroms) follow: Cu–N(1) (ligand), 2.072 (3); Cu–N(25) and Cu–N(27′) (azide end to end), 2.013 (3) and 1.994 (3); Cu–N(28) (azide end on), 1.987 (3); Cu–S(4), 2.919 (1); N(25)–N(26), 1.170 (5); N(26)–N(27), 1.185 (5); N(28–N(29), 1.186 (6); N(29)–N(30), 1.160 (7). The Cu•••Cu interatomic distance is 5.145 (0) Å. Selected bond angles (in degrees) follow: N(1)–Cu–N(28), 86.8 (1); N(1)–Cu–N(27′), 90.3 (1); N(25)–Cu–N(28), 91.4 (1); N(25)–Cu–N(27′), 91.6 (1); S(4)–Cu–N(1), 79.03 (7); S(4)–Cu–N(25), 100.83 (8); S(4)–Cu–N(27′), 94.12 (7); S(4)–Cu–N(28), 85.33 (8); Cu–N(25)–N(26), 136.0 (2); N(25)–N(26)–N(27), 174.3 (4); Cu–N(28)–N(29), 120.7 (3); N(28)–N(29)–N(30), 178.6 (5).

Addition of a sodium azide solution in water to a solution of **1a** and $Cu(NO_3)_2$ in methanol gave dark green crystals of $|Cu_2^{II}(N_3)_4\subset$**1a**$|$ (I). The electronic spectrum of I (solvent, acetonitrile) shows bands at 380 nm (ϵ 3000 L mol^{-1} cm^{-1}) and 640 (350). The IR spectra of I shows two $\nu_{asym}(N_3^-)$ absorptions at 2030 and 2065 cm^{-1} and one $\nu_{sym}(N_3^-)$ band at 1285 cm^{-1}. The structure[10] of I consists of discrete $|Cu_2^{II}(N_3)_4\subset$**1a**$|$ molecules (Figure 2a) which present $2/m(C_{2h})$ crystallographic symmetry. The metal ions are located *inside* the macrocyclic ligand, linked each to a NS_2 ligand donor set, to one nitrogen of an *end-on* bonded azide ion, and to two nitrogens of two di-μ(1,3)-azido *end-to-end* bridging azide ions. The coordination geometry of each copper ion is an elongated octahedron with a long Cu–S bond distance of 2.919 (1) Å. All of the nitrogen atoms are located in the *symmetry plane* and the Cu–N bond distances are almost *identical:* Cu–N(1) (ligand), 2.072 (8); Cu–N(25) and Cu–N(27′) (N_3^- *end-to-end* di-μ bridging), 2.013 (3) and 1.994 (3), respectively; Cu–N(28) (N_3^- *end on*), 1.987 (3) Å. The Cu•••Cu separation within the $Cu_2(N_3)_2$ ring is 5.145 (0) Å (Figure 2b).[11,12] Variable-temperature magnetic susceptibility measurements[13] between 4.2 and 390 K show that compound I is *completely diamagnetic*[14] (Figure 3). The small increase in χ_M at very low temperature is most likely due to a small amount of a monomeric paramagnetic impurity (~1%) (vide infra). To eliminate the effect of this impurity, the experimental χ_M values have been corrected assuming Curie law behavior. The results (Figure 3) show that the χ_M values of I are *completely independent of temperature.* The room temperature and 100 K X-band EPR powder spectra[15] of I show a signal at $g_\perp = 2.05$ and a four-line hyperfine signal at $g_\parallel = 2.24$, with spacings between successive peaks of $\simeq 153$ G. The lack of the half-field $\Delta M_S = 2$ transition is consistent with a

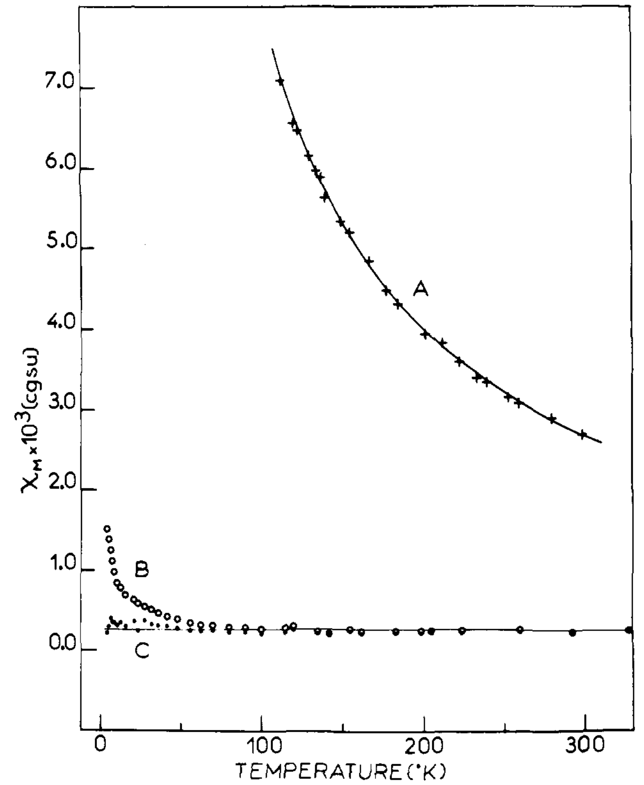

Figure 3. Magnetic susceptibility data for $[2Cu^{II}(N_3)_4 \subset \mathbf{1a}]$ (curve B) and for $[2(CuCl_2) \subset \mathbf{1a}]$ (curve A) vs. temperature. Curve C represents the variation of χ_M for $[2Cu^{II}(N_3)_4 \subset \mathbf{1a}]$ corrected for the paramagnetic monomeric impurity (1%).

monomeric copper(II) species. Moreover, the integration of the EPR signal indicates that *only* 1% *of the copper present in the sample is responsible for the signal.* Thus, EPR spectroscopy confirms the presence of a paramagnetic impurity and justifies the correction applied to the experimental χ_M values.

To study the magnetic exchange interactions between two copper atoms enclosed in ligand **1a** without other bridging groups, we have studied the structure and magnetic properties of $|2(CuCl_2) \subset \mathbf{1a}|$ (II). II has been obtained by slow evaporation at room temperature of solutions of ligand **1a** and copper(II) dichloride in methanol. The structure[16] of II consists of discrete molecules in which the two copper ions are enclosed by ligand **1a** and bonded each to one NS_2 donor set and to two chlorine atoms (Figure 4). The coordination geometry of both copper ions is a square pyramid in which the metal atom lies ~0.4 Å out of the basal NS_2Cl plane toward the axial chlorine atoms. The Cu···Cu separation is 7.228 (1) Å. The magnetic susceptibility measurements between 4.2 and 293 K show that II follows the Curie law (Figure 3) with a Curie constant of 0.798 cgs mol^{-1} and magnetic moment of 2.53 μ_B mol^{-1} or a μ_{eff} of 1.79 μ_B/Cu atom.

While a great many binuclear copper(II) complexes have been shown to exhibit antiferromagnetism, very few are diamagnetic at room temperature.[14] I is until now the only example known exhibiting this property and presenting two copper(II) cations *doubly bridged*[20] and *separated by a distance as long as* 5.145 Å.[17] The magnetic exchange interactions[18] appear to be very strong in I in comparison with those reported recently for several nonmacrocyclic di-μ(1,3)-azido bridged binuclear copper species, as for instance $|Cu_2(Me_5dien)_2(N_3)_2|(BPh_4)_2$[11] (III). It is known that structural features play an important role in the strength of the superexchange interactions[18] and several of these features appear to be slightly different for I and III (see Figure 2 caption and ref 11). Moreover, in the solid state, the molecules of I are

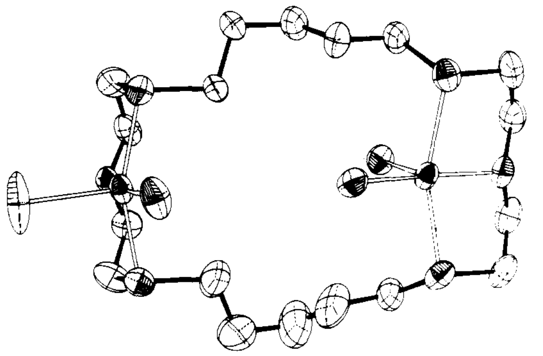

Figure 4. Structure of the $[2(CuCl_2) \subset \mathbf{1a}]$ molecule. The two copper ions, the four chlorine atoms, and the two nitrogen atoms of the ligand are located approximately in a pseudoplane of symmetry. Selected bond distances (in ångstroms) follow: Cu(1)-Cl(1), 2.260 (0); Cu(1)-Cl(2), 2.453 (0); Cu(1)-N(1), 2.033 (5); Cu(1)-S(4), 2.350 (1); Cu(1)-S(22), 2.236 (1); Cu(2)-Cl(3), 2.499 (0); Cu(2)-Cl(4), 2.240 (0); Cu(2)-N(13), 2.015 (4); Cu(2)-S(10), 2.435 (1); Cu(2)-S(16), 2.407 (1). The Cu···Cu interatomic distance is 7.228 (0) Å.

weakly associated by Cu—N(1) H···N(28)—Cu hydrogen bonds with an N(1)···N(28) distance of 3.149 (5) Å. Although magnetic superexchange interactions can take place through hydrogen-bonded ligand atoms,[19] NMR measurements in several solvents indicate that such intermolecular interactions must be very weak in I and that most probably *only intramolecular interactions* are responsible for the diamagnetism.

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(7) Addition under argon of $Cu^I(CH_3CN)_4BF_4$ in butan-2-one to a solution of 1a yielded a white crystalline product $|Cu_2{}^I \subset 1a|(BF_4)_2$. A acrylonitrile solution of this complex treated with carbon monoxide at 35 °C yielded a *carbonyl adduct* (ν_{CO} 2105 cm^{-1}; Cu:CO ratio, 2:1). The CO adduct formation was slowly reversed under vacuum. Solutions of $|Cu_2{}^I \subset \mathbf{1a}|(BF_4)_2$ treated with dioxygen at 25 °C slowly became green. In the solid state, $|Cu_2{}^I \subset \mathbf{1a}|(BF_4)_2$ reacted rapidly with dioxygen at 60 °C to give a green powder. When this powder was heated under vacuum at 120 °C, the green color was slowly reversed to white. The oxygenation–deoxygenation cycle was accompanied with some decomposition of the starting material. Solutions of $|Cu_2{}^I \subset \mathbf{1a}|(BF_4)_2$ treated with NO at 25 °C rapidly became green. A green powder was obtained by evaporation of this solution under argon. IR spectra of this powder did not show any absorption which could be attributed to coordinated NO.

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(10) $|Cu_2(N_3)_4\subset \mathbf{1a}|$ crystallizes in the monoclinic space group $C2/m$ with a = 10.126 (2), b = 13.246 (3), c = 11.156 (2) Å; β = 93.474 (8)°; Z = 2 formula units per cell. A total of 1084 independent nonzero reflections were measured on a Philips PW 1100 diffractometer and 954 reflections with $I > 3\sigma(I)$ were used in subsequent structure solution and least-squares refinement. Final refinements with anisotropic thermal parameters for all nonhydrogen atoms converged to $R_F = 0.038$ and $R_{wf} = 0.051$.

(11) For structurally characterized Cu(II) azide complexes having the $Cu_2(N_3)_2$ ring, see T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, **17, 444** (1978) ($|Cu_2(Me_5dien)_2(N_3)_3|(BPh_4)_2$); the data for this complex are d_{Cu-Cu} = 5.227 (7) Å and $J = -6.5$ cm^{-1}. This $M_2(N_3)_2$ ring is recognized in few complexes with M = Cu(I), Ni(II): $Cu_2^I(PPh_3)_4(N_3)_2$, R. F. Ziolo, A. P. Gaugnan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10,** 1289 (1971); $|Ni_2(tren)_2(N_3)_2|(BPh_4)_2$, C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.*, **14,** 604 (1975).

(12) For comparison with structures of azide complexes, see ref 11; R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, 11, 3044 (1972); U. Müller, *Struct. Bonding* (*Berlin*), **14,** 141 (1973).

(13) Variable-temperature susceptibility measurements were recorded on a Foex–Forrer translation balance between 390 and 100 K and on a Foner magnetometer in the range of 4–120 K. $HgCo(SCN)_4$ and platinium metal were used for calibration. Diamagnetic corrections χ_D were applied for all nonmetallic atoms using tabulated values of Pascal's constants: $\chi_D = -333\ 10^{-6}$ cgs mol^{-1}.

(14) Complete diamagnetism of nonbiological dicopper(II) compounds has been reported for three complexes. (i) Tetrakis(1,3-diphenyltriazene)dicopper(II): C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959); A. K. Majumdar and S. C. Saka, *J. Indian Chem. Soc.*, **50**, 697 (1973); M. Corbett, B. F. Hoskins, N. J. McLeod, and B. P. O'Day, *Acta Crystallogr., Sect. A*, **28**, 576 (1972). (ii) Tetrakis(arylazo oxime)dicopper(II): S. Gupta, K. C. Kalia, and A. Chatravorty, *Inorg. Chem.*, **10,** 1534 (1971). (iii) Di-μ-5,7,7-trimethyl-4,8-diazaundec-4-ene-1,11-diolato-*ONN′O′*-dicopper(II) perchlorate: J. S. De Courcy, T. N. Waters, and N. F. Curtis, *J. Chem. Soc., Chem. Commun.*, 572 (1977).

(15) EPR spectroscopic data were obtained using a Brucker spectrometer.

(16) $|2(CuCl_2)\subset \mathbf{1a}|$ crystallizes in the monoclinic space group $P2_1/c$ with a = 7.943 (2), b = 22.481 (6), c = 17.538 (5) Å; β = 100.97 (2)°; V = 3074.47 $Å^3$; ρ_m = 1.48 and ρ_c = 1.47 g cm^{-3}; Z = 4 formula units per cell. A total of 3150 independent nonzero reflections, measured on a Philips PW 1100 diffractometer, with $I > 3\sigma(I)$ were used in structure determination; $R_F = 0.048$ and $R_{wF} = 0.057$.

(17) For general reviews of doubly bridged compounds, see U. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, **23,** 31 (1977).

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(20) In a recent paper, H. B. Gray et al. suggest that a multiply bridged dioxygen–copper center is a more attractive structural possibility for oxyhemocyanin: D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **75,** 3019 (1978).

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Fluoroxysulfate: A Powerful New Oxidant and Fluorinating Agent[1]

Sir:

In 1926 Fichter[2] observed that the passage of fluorine through aqueous solutions of sulfate or bisulfate led to the production in the solutions of a "vergängliches Oxidationsmittel", or "ephemeral oxidant", that was more powerfully oxidizing than peroxymonosulfate and that decomposed over the course of several hours. Fichter's work was largely ignored for many years, and his conclusions have recently been challenged.[3] However, we have repeated a number of his experiments and have generally confirmed his results. In addition, we have isolated the "ephemeral oxidant" in the form of its rubidium and cesium salts and have identified it as the fluoroxysulfate ion, SO_4F^-.

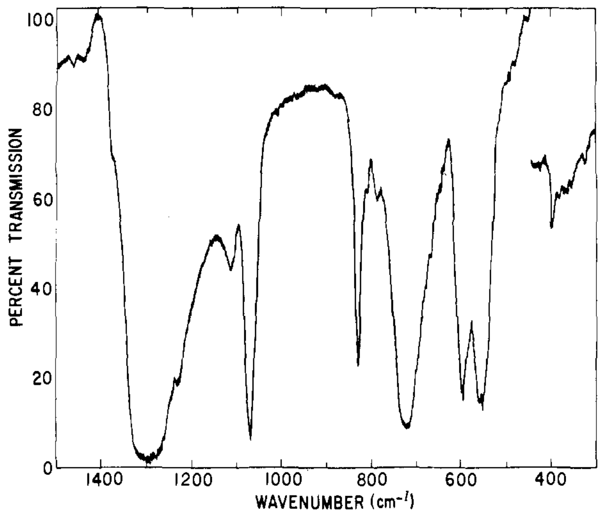

Figure 1. Infrared spectrum of $RbSO_4F$, taken with a Beckman IR 4260 spectrophotometer using a diamond anvil cell and a 4X beam condenser (ref 10). This technique was necessitated by the tendency of the fluoroxysulfates to react with KBr and AgCl infrared windows. The spectrum of $CsSO_4F$ is very similar, except that the band at 1105 cm^{-1} is considerably less prominent.

We prepared rubidium and cesium fluoroxysulfates by passing fluorine into solutions of Rb_2SO_4 and Cs_2SO_4, respectively. Approximately 20 mmol of F_2 (as a 20% mixture in nitrogen) was passed into 8 mL of 1.3 M Rb_2SO_4 or 2 M Cs_2SO_4 in a Tefzel tube over the course of an hour. An ice-salt bath was used to keep the solution temperature between 0 and −4 °C. The yellowish-white precipitates were centrifuged, washed with a little water, and dried in vacuo without heating. Yields were about 1 g of the rubidium salt and about 2 g of the cesium salt.

Samples for analysis were dissolved in water in Teflon bottles, and a slight excess of sodium carbonate was added. The solutions were then heated for 48 h at 90 °C to hydrolyze any fluorosulfate that might be present either as an impurity or as a decomposition product of the fluoroxysulfate.[4] Rubidium and cesium were determined by atomic absorption, fluoride with a fluoride-sensitive electrode, and sulfur gravimetrically as barium sulfate.[5] Anal. Calcd for $RbSO_4F$: Rb, 42.6; F, 9.5; S, 16.0. Found: Rb, 42.2; F, 8.8; S, 15.5. Calcd for $CsSO_4F$: Cs, 53.6; F, 7.7; S, 12.9. Found: Cs, 54.1; F, 7.3; S, 12.4. In addition, the oxidizing titers of the salts were determined by dissolving weighed amounts in a potassium iodide solution, acidifying, and titrating the liberated I_3^- immediately with standard thiosulfate solution. Results (mequiv/g): Calcd for $RbSO_4F$: 10.0. Found: 9.6. Calcd for $CsSO_4F$: 8.1. Found: 7.5. The salts contained an impurity that slowly oxidized iodide, thereby increasing the titer by 1–2%. The rate of this oxidation was unaffected by addition of molybdate, and we identify this impurity as peroxydisulfate.

The infrared and Raman spectra of the salts (Figures 1 and 2) agree well with those of the isoelectronic species ClO_4F[6-8] and its analogs ClO_4Cl[9] and ClO_4Br,[9] and they support the formulation of SO_4F^- as a fluoroxy ion or hypofluorite: O_3SOF^-. We assign the band at 830 cm^{-1} to the O-F stretch.

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