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First Example of a Discrete Copper(III, II) Mixed-Valence Complex: The Triangular $Cu^{III}Cu^{II}_2O$ Core Circumscribed by Oxime Ligands

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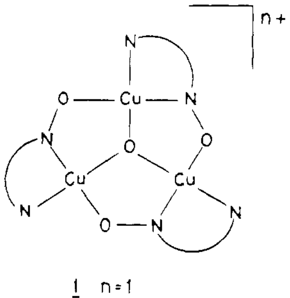
The yellow-green mixed-valence $Cu^{III}Cu^{II}_2$ complex $[Cu_3O(n\text{-PrL}')_3](ClO_4)_2 \cdot H_2O$ (**5**) is isolated by electrolytic oxidation of the corresponding Cu^{II}_3 complex $[Cu_3O(n\text{-PrL}')_3]ClO_4$ (**4**) in acetonitrile (n-PrL′ = n-PrNC(Ph)C(Ph)NO⁻). The complex **5** is diamagnetic and displays (i) a ^1H NMR spectrum in consonance with equivalence of all three n-PrL′ ligands, (ii) relatively narrow and intense solvent-sensitive intervalence bands near 840 and 720 nm, (iii) an IR spectrum that is nearly superposable on that of **4**, and (iv) a nearly reversible one-electron reduction with $E°_{298}$ of 0.44 V vs. SCE in acetonitrile. From the available data it is concluded that the gross structure of the cation in **5** is very similar to that of the cation of **4**. Thus the mixed-valence cation is concluded to have a nearly planar triangular $Cu^{III}Cu^{II}_2O$ core held in the matrix of peripheral oximato bridges. The qualitative electronic structures of **4** and **5** are discussed. Observed magnetic and spectral properties of **4** and **5** as well as the different electrochemical response patterns of species having Cu_3O and Cu_3OH cores are rationalized.

Introduction

In previous reports we have described the synthesis, magnetism, and electrochemical redox properties of groups of dinuclear[1] and trinuclear[2-4] copper(II) complexes of oxime ligands. In particular it was shown[3,4] that the novel redox couple (1) ($E°_{298}$ = 0.3–0.4 V vs. SCE) is a characteristic

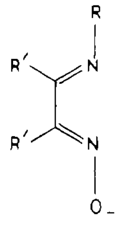
$$\mathbf{2} + e^- \rightleftharpoons \mathbf{1} \qquad (1)$$

feature of the solution chemistry of two groups of trinuclear complexes (**1**) having the Cu^{II}_3O core embedded in the matrix of peripheral oxime ligands such as isonitrosoketimines[2-4] (**3**) and pyridine-2-carbaldoxime.[5a] The proposed[3,4] mixed-valence (average metal oxidation state +2.33) cation **2** is novel in copper chemistry. In fact, discrete mixed $Cu^{III}Cu^{II}$ species of any sort are virtually unknown. Therefore the isolation and characterization of salts of **2** in the pure state are of much interest. Herein we report a case of such isolation. Evidence that supports the proposed gross structure (**2**) for the mixed-valence cation is presented. The magnetism and spectra of the cation are rationalized on the basis of the structure.



1 n = 1

2 n = 2



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Results and Discussion

Choice of System. Two groups of ligands of type **3** were tried: isonitrosoethyl methyl n-alkylketimine (**3**, R′ = Me) and α-nitrosobenzyl phenyl n-alkylketimine (**3**, R′ = Ph). The two groups are respectively abbreviated as RL and RL′. The cations $Cu_3O(RL)_3^+$ and $Cu_3O(RL')_3^+$ are isolated as perchlorate salts with use of reported methods[2-4] for EtL, n-PrL, n-BuL, n-PrL′, and n-BuL′.

Table I. Stability of $Cu_3O(RL \text{ or } RL')_3^{2+}$ in MeCN at 298 K

RL or RL′	$100Q_2/Q_1$[a]	RL or RL′	$100Q_2/Q_1$[a]	RL or RL′	$100Q_2/Q_1$[a]
EtL	44	n-BuL	36	n-BuL′	80
n-PrL	47	n-PrL′	95		

[a] Meanings of symbols used are the same as in the text.

Table II.[a] Cyclic Voltammetric Data for the Mixed-Valence Complex $[Cu_3O(n\text{-PrL}')_3](ClO_4)_2 \cdot H_2O$ in Acetonitrile at 298 K

v, V s^{-1}	E_{pa}, V	E_{pc}, V	ΔE_p, V	$E°_{298}$, V	Q, C
0.050	0.472	0.402	0.067	0.437	0.940[b] (0.965)[c]
0.100	0.475	0.402	0.073	0.438	
0.200	0.482	0.395	0.087	0.438	
0.500	0.495	0.390	0.105	0.437	
1.000	0.500	0.385	0.115	0.437	

[a] Abbreviations: ν, scan rate; E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; ΔE_p, peak-to-peak separation. $E°_{298}$ is calculated as the average of E_{pa} and E_{pc}; all potentials are referenced to SCE. [b] Coulomb count (average of three independent determinations) for the reduction of 10^{-2} mmol of the complex at 0.100 V vs. SCE on a platinum wire gauge electrode. [c] Calculated count.

For each complex examined the couple (1) is cyclic voltammetrically reversible.[3,4] Thus the peak-to-peak separation is ~60 mV and anodic and cathodic peak heights are equal. Clearly **2** is stable on the cyclic voltammetric time scale. But this does not ensure that it is stable enough for practical isolation. To choose the systems that give reasonably stable oxidized complexes of type **2**, coulometric recycling experiments (described below) were performed on the complexes.

A 10^{-3} M solution of **1** was subjected to constant-potential electrolytic oxidation at 0.7 V vs. SCE in acetonitrile (298 K). In each case the coulomb count (Q_1) corresponded to the 1e transfer process **1** → **2**. The oxidized solution was then left to stand for 15 min. This was followed by constant-potential reduction of the solution at 0.1 V vs. SCE in order to cause the reconversion **2** → **1** (count Q_2). Usually $Q_1 > Q_2$, presumably due to decomposition of **2** while the oxidized solution was allowed to stand. The parameter $100Q_2/Q_1$ can thus be taken as a measure of the stability of **2** in solution. As can be seen from Table I, the RL′ species have good stability. The trinuclear n-PrL (α-isonitrosobenzyl phenyl n-propylketimine) complex was chosen for the practical synthesis of the corre-

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(1) Baral, S.; Chakravorty, A. *Proc.—Indian Acad. Sci., Sect. A* **1977**, *86A*, 45. Datta, D.; Chakravorty, A. *Proc.—Indian Acad. Sci.*, [*Ser.*]: *Chem. Sci.* **1981**, *90*, 1.

(2) Baral, S.; Chakravorty, A. *Inorg. Chim. Acta* **1980**, *39*, 1. Baral, S.; Singh, R. P.; Mohanty, J. G.; Chakravorty, A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 655.

(3) (a) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 1673. (b) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chim. Acta* **1978**, *27*, L95. (c) Datta, D.; Chakravorty, A. *Indian J. Chem., Sect. A* **1981**, *20A*, 289.

(4) Datta, D.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 363.

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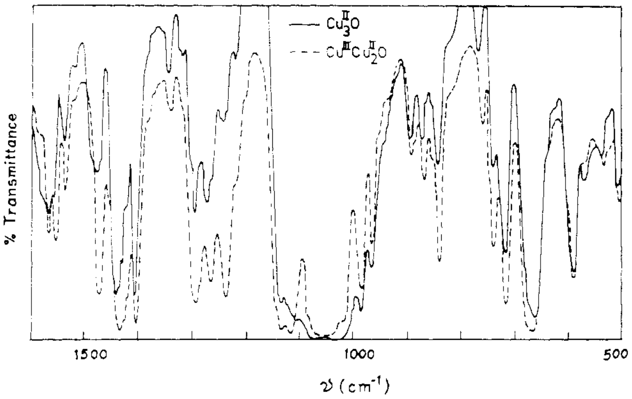

Figure 1. IR spectra of **4** (—) and **5** (---) in KBr disks.

sponding mixed-valence species.

Electrosynthesis and Characterization. Coulometric oxidation of $[Cu_3O(n\text{-}PrL')_3]ClO_4$ (**4**) in MeCN under suitable conditions followed by addition of water yields yellow-green flaky crystals having an elemental composition corresponding to $[Cu_3O(n\text{-}PrL')_3](ClO_4)_2 \cdot H_2O$ (**5**) in 85% yield. Details are given in the Experimental Section. Complex **5** is soluble in polar organic solvents like Me_2CO, MeCN, and MeOH but is insoluble in water.

In MeCN **5** is a 1:2 electrolyte (Λ_M = 257 Ω^{-1} cm^2 M^{-1}) and displays a nearly reversible cyclic voltammogram (Table II) as in the case[3] of **4**. The couple

$$\mathbf{5} + e^- \rightleftharpoons \mathbf{4} \qquad (2)$$

is a particular example of couple 1. The coulometric reduction **5** → **4** conveniently occurs at 0.1 V vs. SCE and the reoxidation **4** → **5** at 0.7 V vs. SCE. *The cycle can be repeated at least three times without substantial loss in coulomb counts.*

Structure. Our original proposal of structure **1** for $Cu_3O(RL)_3^+$ and $Cu_3O(RL')_3^+$ was based on magnetic[2] and electrochemical data [3,4] and on analogy with oximates of known structures.[5] The recent X-ray work[6] on the perchlorate of $Cu_3O(MeL')_3^+$ has now confirmed this beyond all doubt. This cation is nearly coplanar, but the central oxygen atom is slightly raised above the plane to form a weak intertrimer bond. The gross structure of the cation in **4** must then be of type **1**.

The near electrochemical reversibility[3,4] (Table II) of the couple (2) and the facile and nondestructive coulometric interconversions between **4** and **5** strongly suggest that gross solution structures of the cations in **4** and **5** are very similar. The infrared spectra (400–3000 cm^{-1}) of **4** and **5** are also virtually superposable except for small differences in intensities and band positions (Figure 1), showing that the ligand frames in **4** and **5** are very similar. Complex **5** is diamagnetic (see below), and its ^{1}H NMR spectrum[7,8] (in $CDCl_3$) is shown in Figure 2. The broadness of the bands probably arises from the contamination by traces of the paramagnetic Cu^{II}_3 parent. This spectrum is significant on two counts: (i) the presence of the intact *n*-PrL′ ligand (Ph and *n*-Pr signals) in **5** is confirmed; (ii) since only one signal for each kind of proton (note particularly the Me triplet) is seen, the three *n*-PrL′ ligands are grossly equivalent as implied in structure **2**. Taking all the evidences collectively, it is most logical to conclude that the structure of the cation of **5** is indeed **2**.

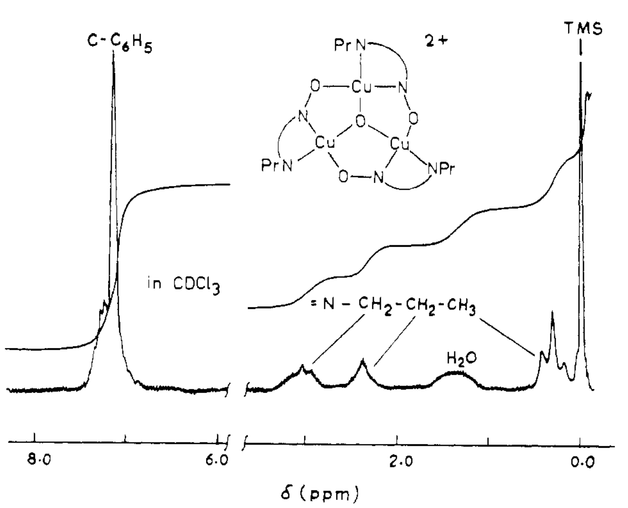

Figure 2. ^{1}H NMR spectrum of **5** in $CDCl_3$.

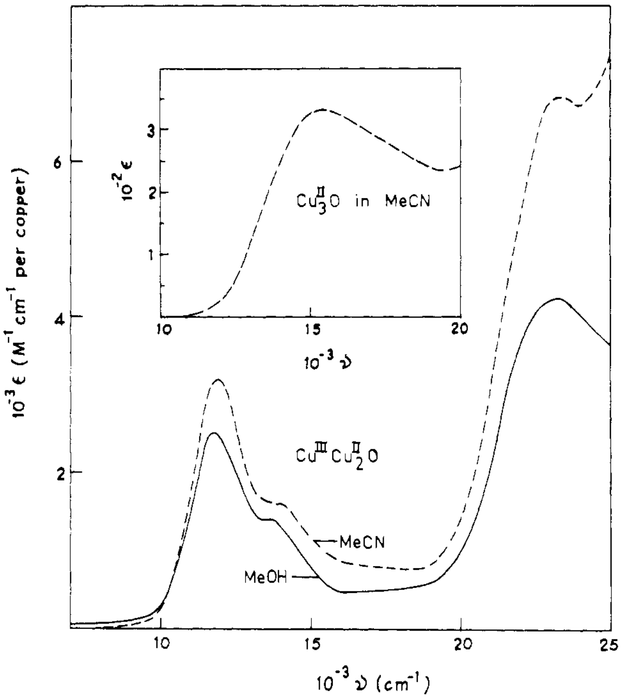

Figure 3. Electronic spectra of **5** in MeOH (—) and MeCN (---). The spectrum of **4** in MeCN is shown in the inset.

Since planar tetracoordination[9] is compatible with both copper(II) and copper(III),[10,11] the similarity in the gross structures[12] of the Cu^{II}_3 and $Cu^{III}Cu^{II}_2$ species is understandable. The possibility that in the process **1** → **2** (hence **4** → **5**) the ligand rather than the metal is oxidized was discounted earlier:[3b,4] binuclear copper(II) and nickel(II) complexes of isonitrosoketimines do *not* display any oxidation up to +1 V. Neither does [3,4] (see below) the protonated form of

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[5] (a) Beckett, R.; Colton, R.; Hoskins, B. F.; Martin, R. L.; Vince, D. G. *Aust. J. Chem.* **1969**, *22*, 2527. Beckett, R.; Hoskins, B. F. *J. Chem. Soc., Dalton Trans.* **1972**, 291. (b) Young, J. E.; Murmann, R. K. *J. Phys. Chem.* **1963**, *67*, 2647. Ross, P. F.; Murmann, R. K.; Schlemper, E. O. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1120.

[6] Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 537.

[7] The ^{1}H NMR spectrum of **4** was also examined. It shows very broad (width 0.5–1 ppm) and structureless signals centered at δ 0.70, 7.12, and 9.98 with intensity ratio 5:10:2. It is significant that **4** (**1** in general) does not show well-defined EPR signals.[8] Probably electron relaxation is fast enough in **1**, making the observation of ^{1}H NMR signals just possible but at the expense of EPR signals.

[8] Baral, S. Ph.D. Thesis, Indian Institute of Technology, Kanpur, India, 1978.

[9] Weak axial coordination of some form (solvent, ClO_4^-, dimerization) may occur. Such coordination is usually very weak compared to the tetracoordination in the perpendicular plane.

[10] Bossu, F. P.; Chellappa, K. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 2195. Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1971**, *10*, 463.

[11] Bour, J. J.; Birker, P. J. M. W. L.; Steggarda, J. J. *Inorg. Chem.* **1971**, *10*, 1202. Birker, P. J. M. W. L. *Inorg. Chem.* **1977**, *16*, 2478.

[12] Due to an increase in the level of metal oxidation it is likely that in **5** the central oxygen atom is nearer to the Cu_3 plane than it is in **4**.

1 (Cu_3OH in place of Cu_3O in **1**). The oxidation near 0.4 V specifically involves the oxo-bridged metal core of **1**.

Magnetic Properties and Spectra. All $Cu^{II}{}_3O$ complexes, including **4**, display[2,6] strong antiferromagnetic exchange ($|J| > 350$ cm^{-1}) mediated[2] by the central oxo bridge and the peripheral oximato bridges. In effect only the $S = {}^1/_2$ state is populated. The idea that the unpaired electron in **1** might be readily ionizable, leaving a spin-paired even-electron system with retention of the original structural frame, led us to perform the initial electrochemical experiments[3] on the isonitrosoketimines of $Cu^{II}{}_3O$ and to the discovery of couple 1. We now report that **5** is indeed diamagnetic in the solid state. The magnetic properties of **4** and **5** will be reconsidered following an examination of their electronic spectra.

Complex **4** shows a broad ligand field feature around 600 nm. In contrast **5** displays two solvent-sensitive and relatively narrow allowed transitions at ~840 and ~700 nm (Figure 3). A ligand → metal charge-transfer assignment is untenable on the following grounds: (i) such transitions should occur at relatively high energies since the acceptor oribtal has to be an antibonding metal orbital ($d_{x^2-y^2}$); (ii) in known copper(III) complexes[10,11] no transitions are observed above 580 nm even when the ligand is unsaturated; (iii) in imine oxime (a functionality also present in **5**) complexes of pseudooctahedral nickel(III) and nickel(IV) charge-transfer transitions (to a metal e orbital) occur[13] at ≤ 500 nm; (iv) the presence of low-energy ligand → metal charge-transfer transitions in complexes of imine oxime ligands is usually attended[13] with relatively low diimine vibration frequencies—no such effect is observed in **5** (Figure 1).

We assign the visible-energy bands of **5** to intervalence transitions. The transition is of type $d_{x^2-y^2}(Cu^{II}) \rightarrow d_{x^2-y^2}(Cu^{III})$ since the other d orbitals are relatively deeply buried (as judged from the energy of the ligand field transition of **4**). The relative narrowness of the observed bands suggests the presence of considerable valence delocalization.[14]

In the framework of delocalized bonding a qualitative MO description of **1** and **2** is in order. In the limit of D_{3h} symmetry, the three $d_{x^2-y^2}$ orbitals of the three copper atoms can interact[2,5a,15] with ligand (central oxygen and RL or RL′) orbitals. The highest antibonding levels a_1' and e' are primarily of metal character. A C_{3v} distortion (central oxygen out of plane on C_3 axis) does not change the qualitative picture: the metal–ligand interaction however decreases, bringing a_1 and e closer. The magnetic properties of *both* **4** and **5** fall in place if the level order is e > a_1. The e → a_1 gap is believed to widen considerably in going from **4** to **5** due to increased interaction resulting from higher metal positive charge and augmented molecular planarity.[12] The visible absorption of **5** can arise from the transition $a_1{}^2e^0 \rightarrow a_1{}^1e^1$, i.e., ${}^1A_1 \rightarrow {}^1E$. The ^1E level may be split due to static distortion of molecular geometry caused by Jahn–Teller distortion of the excited state, thus giving rise to the two observed bands.

Concluding Remarks. It is demonstrated that the mixed-valence copper(III, II) cation **2** can be isolated as a pure salt. Its gross structure is shown to be similar to that of **1**. The allowed transitions of **2** in the 900–600 nm region are of intervalence origin. The magnetic properties of **1** ($S = {}^1/_2$) and **2** ($S = 0$) can be qualitatively understood by considering the interactions of the three copper $d_{x^2-y^2}$ orbitals with the ligands. The MO level order e > a_1 (C_{3v} symmetry) provides a rationale for both spin multiplicity and spectra.

We note that complexes with $Cu^{II}{}_3OH$ cores are also known[2-6] but their oxidation to the mixed-valence $Cu^{III}Cu^{II}{}_2OH$ state has not been achieved.[3,4] It is now clear[5,6] that in Cu_3OH the central oxygen atom is very considerably displaced from the plane of Cu_3. Thus the a_1–e separation is less in Cu_3OH than in Cu_3O and hence the e level is more stable in Cu_3OH than in Cu_3O. Since the electron in couple 1 is transferred from the e level (as stipulated by the energy order e > a_1) the oxidation of Cu_3OH should occur at a higher potential than that of Cu_3O. This shift will be further augmented by the presence of the proton near the oxygen atom. In practice no oxidation is observed[3,4] for Cu_3OH in the accessible potential range. Supporting this logic is the fact that the converse is found to be true for reduction (electron added to the e level). Thus the $Cu^{II}{}_3OH$ core is readily converted[4] to the $Cu^{II}{}_2Cu^{I}OH$ core; the corresponding reduction of $Cu^{II}{}_3O$ is not observed. We thus have a molecular basis of the "proton valve" action.[3a]

Experimental Section

Materials. Acetonitrile and methanol were purified as before.[3a] Other solvents used were of analytical grade. Tetraethylammonium perchlorate (TEAP) was prepared as before.[3a] Preparations of pure $[Cu_3O(RL\text{ or }RL')_3]ClO_4$ complexes have already been reported.[4]

Synthesis of $[Cu_3O(n\text{-}PrL')_3](ClO_4)_2\cdot H_2O$. A solution of 0.15 g of $[Cu_3O(n\text{-}PrL')_3]ClO_4$ in 20 mL of acetonitrile (0.1 M in TEAP) was electrolyzed coulometrically with use of a PAR 377A cell system at a constant potential of 0.7 V vs. SCE with a platinum wire gauge electrode. After complete electrolysis, 100 mL of water saturated with TEAP was quickly added with constant stirring. A flaky yellow-green crystalline compound started precipitating within a few minutes The mixture was kept in the refrigerator for 0.5 h. The deposited solid was filtered off, washed thoroughly with water, and dried under vacuum over P_4O_{10}. The yield was 0.14 g (85%). Anal. Calcd for $Cu_3C_{51}N_6H_{53}O_{13}Cl_2$: Cu, 15.59; C, 50.10; N, 6.88; H, 4.45; ClO_4, 16.27. Found: Cu, 15.80; C, 50.53; N, 6.70; H, 4.30; ClO_4, 16.12.

Measurements. Electronic spectra were recorded with a Cary 17-D spectrophotometer, IR spectra (KBr disk) with a Beckman IR-20A spectrophotometer, and ^1H NMR spectra with a Varian T-60A spectrometer. The diamagnetism of **5** was checked with both a Gouy balance and a PAR vibrating-sample magnatometer (Model 155). Cyclic voltammetric and coulometric experiments were performed with a PAR 370-4 electrochemistry system as described elsewhere.[3,4]

Registry No. **4** (R = Et, R′ = Me), 53598-80-4; **4** (R = *n*-Pr, R′ = Me), 73668-62-9; **4** (R = *n*-Bu, R′ = Me), 73689-14-2; **4** (R = *n*-Pr, R′ = Ph), 76986-49-7; **4** (R = *n*-Bu, R′ = Ph), 76986-47-5; **5** (R = *n*-Pr, R′ = Ph), 85335-35-9; **5** (R = Et, R′ = Me), 85335-37-1; **5** (R = *n*-Pr, R′ = Me), 85335-39-3; **5** (R = *n*-Bu, R′ = Me), 85354-78-5; **5** (R = *n*-Bu, R′ = Ph), 85335-41-7.

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(13) Mohanty, J. G.; Singh, R. P.; Chakravorty, A. *Inorg. Chem.* **1975**, *14*, 2178. Singh, A. N.; Chakravorty, A. *Inorg. Chem.* **1980**, *19*, 1969.

(14) Piepho, S. B.; Krause, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996. Tanner, M.; Ludi, A. *Inorg. Chem.* **1981**, *20*, 2348.

(15) The local coordinate system implied in this discussion is the same as that shown elsewhere:[2] the *x* axis on each copper is along the Cu–O bond (O is the central oxygen) and the *z* axis is parallel to the C_3 axis.