the present ligand having different steric constraints.

Registry No. Cu(BBDH)$Cl_2 \cdot 2C_2H_5OH$, 79682-06-7; Cu(BBDH)Cl_2, 76683-99-3; Cu(BBDH)Br_2, 79682-07-8; Cu(BBDH)$(ClO_4)_2 \cdot H_2O$, 76684-01-0; Cu(BBDH)$(BF_4)_2 \cdot H_2O$, 76831-39-5; Cu(BBDH)ClO_4, 76761-70-1; Cu(BBDH)BF_4, 79682-08-9; Cu(BBDH)NO_3, 79682-09-0; Ag(BBDH)NO_3, 79682-11-4; Zn(BBDH)Cl_2, 79682-12-5; BBDH, 57698-70-1; BBDH·2HCl, 79664-66-7; 3,6-dithiaoctanedioic acid, 7244-02-2; 1,2-diaminobenzene, 95-54-5.

Supplementary Material Available: A listing of observed and calculated structure factors and a table with calculated positions for hydrogen atoms (7 pages). Ordering information is given on any current masthead page.

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Electron Transfer in Authentic Triangular Copper(II) Trimers with a Cu_3X (X = O or OH) Core. The $Cu^{II}_2Cu^{III}$–Cu^{II}_3 and Cu^{II}_3–$Cu^{I}Cu^{II}_2$ Couples

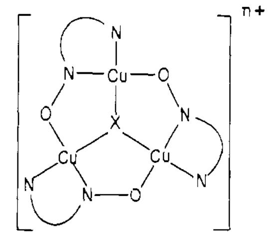
D. DATTA and A. CHAKRAVORTY*

Received February 11, 1981

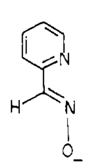
Trinuclear triangular copper(II) complexes of pyridine-2-carbaldoxime (HPL) and isonitrosoketimine ligands of type RNC(R′)C(R′)NOH (R = Et, *n*-Pr, *n*-Bu, Ph; R′ = Me, Ph) have been examined electrochemically. These strongly antiferromagnetic complexes are of types $[Cu_3O(\text{ligand})_3]^+$ and $[Cu_3OH(\text{ligand})_3]^{2+}$, having Cu_3O and Cu_3OH cores, respectively. The known structure of $[Cu_3OH(PL)_3]^{2+}$ provides an authentic reference point for data analyses. Cyclic voltammetry and constant-potential electrolysis (platinum working electrode) show that complexes with a Cu_3O core uniformly display a one-electron-transfer process characterized by the oxidation-state description $Cu^{III}Cu^{II}_2 + e^- \rightleftharpoons Cu^{II}_3$ with $E°_{298}$ in the range 0.3–0.6 V vs. SCE in acetonitrile and dimethylformamide. The species with a Cu_3OH core do not have this electrochemical response. On the other hand, such species show a novel one-electron-transfer process of the type $Cu^{II}_3 + e^- \rightleftharpoons Cu^{II}_2Cu^{I}$ with $E°_{298}$ in the range −0.3 to −0.45 V vs. SCE at a hanging-mercury-drop electrode in acetonitrile. The Cu_3O core does not display this process. In effect the electrochemical behaviors of the two cores are complementary: the Cu_3O core undergoes oxidation while the Cu_3OH core undergoes reduction. Thus the core proton acts in a valvelike fashion in controlling the direction of electron transfer. Addition of an acid ($HClO_4$) converts the Cu_3O species to the Cu_3OH species. Conversely, addition of a base (NEt_3) converts Cu_3OH to Cu_3O. The electrochemical responses change accordingly with addition of acid or base. The interconversion reactions are also useful at preparative levels.

Introduction

The triangular Cu_3X (X = OH, O) core is now known to be present in three[1-3] related groups of copper(II) complexes. The structural feature common to all the groups is the presence of three oximato functions spanning peripheral bridging positions and of three nitrogen atoms binding terminally (**1**). The three groups differ in having different types of terminal nitrogen. The ligands and their abbreviations are shown in **2**–**4**. The presence of **1** in the complexes of PL and AL is conclusively demonstrated by X-ray diffraction works. In the case of RL(RL′) complexes, the proof is based on analogy. All complexes are strongly antiferromagnetic, and only the $S = {}^1/_2$ state is populated.[1-3]

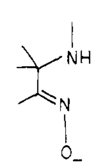


1



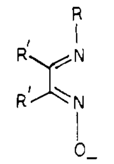
PL

2



AL

3



R′=Me, RL
R′=Ph, RL′

4

$[Cu_3X(RL \text{ or } RL')_3]^{n+}$

5a X = O, n = 1
5b X = O, n = 2
6a X = OH, n = 2
6b X = OH, n = 1

$[Cu_3X(PL)_3]^{n+}$

7a X = O, n = 1
7b X = O, n = 2
8a X = OH, n = 2
8b X = OH, n = 1

Recently we reported[4] certain aspects of the electrochemistry of the trinuclear complexes of RL and RL′ (isonitrosoketimines). The redox process (eq 1) was thoroughly charac-

$$\mathbf{5b} + e^- \rightleftharpoons \mathbf{5a} \qquad (1)$$

terized. The existence of the couple (eq 2) was also briefly

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(1) 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.

(2) 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**, *30B*, 1120.

(3) 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.

(4) (a) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 1673. (What is *p* in this reference becomes *q* in the present paper; this change is made to avoid confusion with *p* of E_{pc}, etc.) (b) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chim. Acta* **1978**, *27*, L95.

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$$\mathbf{6a} + e^- \rightleftharpoons \mathbf{6b} \qquad (2)$$

indicated. Further details are given in this paper. The reported study[4] is complicated by the fact that the complexes as prepared were generally a mixture of **5a** and **6a**. The conclusions could be strengthened if pure **5a** and **6a** could be made. This is accomplished in the present work. An inherent weakness of the earlier study is that the structures **5a** and **6a** are based entirely on analogy. This becomes serious since redox processes such as (1) and (2) are entirely novel, and no precedences exist. The results could be put on firmer foundation if it can be shown that a trinuclear complex of proven structure displays cognate electrochemical response. This constitutes the major objective of the present work. The electrochemistry of the PL complexes were therefore investigated, and the results are reported here.

Results and Discussion

(A) The Complexes. (a) PL Ligand. In crystals of $[Cu_3OH(PL)_3]SO_4 \cdot 16.3H_2O$, the presence of the gross pattern **1** has been proved by X-ray work.[3] The corresponding perchlorate is $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$. The magnetic properties ($S = {}^1/_2$) of the sulfate and perchlorate species are entirely analogous,[5] and it is very reasonable to assume that the perchlorate, like the sulfate, contains **1**. Since our electrochemical work is done in the presence of large concentrations (0.1 M) of tetraethylammonium perchlorate, it is immaterial whether the starting complex is the sulfate or perchlorate. We have used the perchlorate salt.

A complex of formula $Cu_3(PL)_3(OH)_2ClO_4 \cdot 2H_2O$ was also reported;[5] we find that this complex is[6] actually $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$. We have observed that the interconversion (eq 3) occurs neatly and quantitatively in suitable solvents. Some characteristic features of the two complexes (**7a** and **8a**) are reported in Table I.

$$\mathbf{8a} \underset{HClO_4}{\overset{NEt_3}{\rightleftharpoons}} \mathbf{7a} \qquad (3)$$

(b) RL and RL′ Ligand. The trinuclear species in these cases were isolated earlier[4] with the composition $[Cu_3O_q(OH)_{1-q}(RL \text{ or } RL')_3](ClO_4)_{2-q}$. These are essentially mixtures of **5a** ($q = 1$) and 6a ($q = 0$). It is now shown that pure **5a** and **6a** can be isolated by treating the mixture with triethylamine and perchloric acid under appropriate conditions. This is essentially an extension of the interconversion reaction (3) to the RL,RL′ systems. Among RL ligands, the pure Cu_3OH species could be obtained only for PhL.

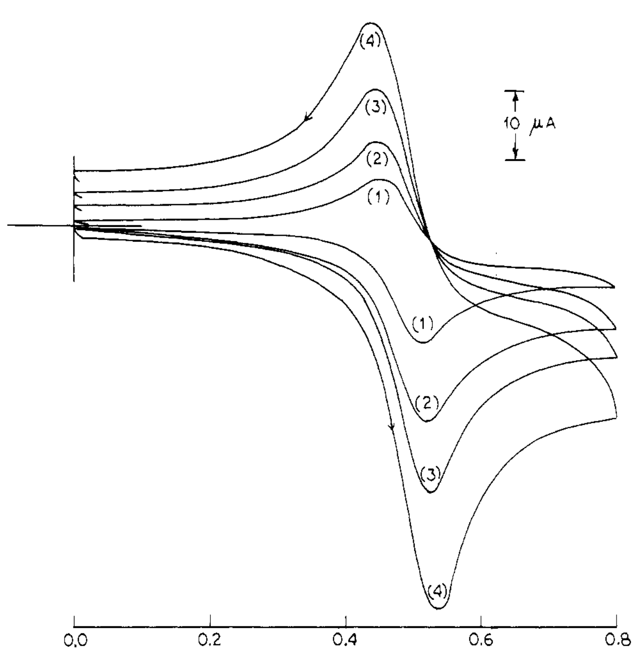

Figure 1. Cyclic voltammograms of $[Cu_3O(PL)_3]^+$ (**7a**) in DMF at various scan rates (V s^{-1}): (1) 0.020, (2) 0.050, (3) 0.100, and (4) 0.200. Solute concentration is 0.86×10^{-3} M.

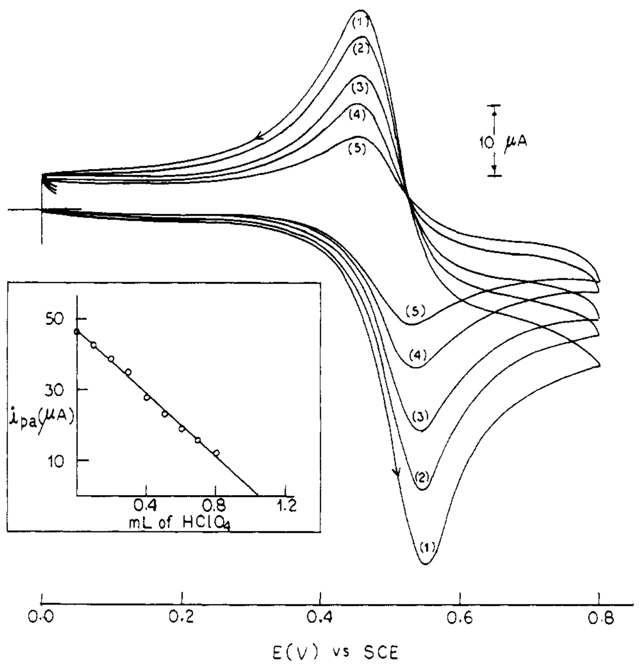

Figure 2. Effect of the addition of 0.011 M perchloric acid to 10 mL of 1.218 M solution of $[Cu_3O(PL)_3]^+$ (**7a**) in DMF. Volume (mL) of acid added: (1) 0.00, (2) 0.20, (3) 0.40, (4) 0.60, and (5) 0.8; scan rate is 0.100 V s^{-1}. The inset shows anodic peak current as a function of the volume of perchloric acid added; line drawn is least-square fitted.

(B) One-Electron Oxidation of $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$. All electrochemical measurements reported in this paper were made at 298 K, and all potentials are referenced to the saturated calomel electrode (SCE). The region 0.0–1.0 V was scanned voltammetrically with a platinum working electrode. The complex shows a well-defined cyclic response in this region (Figure 1; Table II). This response in dimethylformamide (DMF) solution is characteristic of a reversible one-electron process: $i_{pa}/i_{pc} = 1$ and $\Delta E_p = E_{pa} - E_{pc} = 60$ mV (at scan rate <50 mV s^{-1}), where i and E represent current and potential, respectively, while the subscript p, a, and c stand for peak, anodic, and cathodic, respectively. In stirred solutions, electrolysis occurred smoothly when the working potential was set above E_{pa}; below E_{pc} little electrolysis occurred. Clearly the complex is oxidizable and not reducible. The electrode reaction can be written as (4). In acetonitrile solvent the

$$\mathbf{7b} + e^- \rightleftharpoons \mathbf{7a} \qquad (4)$$

process is much less reversible ($\Delta E_p = 145$ mV) than in DMF. Constant-potential coulometry performed at 0.75 V fully confirms the one-electron involvement (Table II). The formal potential $E°_{298}$ of the couple of (4) taken as the average of E_{pa} and E_{pc} is 0.485 V (Table II).

(C) Inhibition of Oxidation by Proton. In the 0.0–1.0-V region, $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ is *not* electroactive. Since addition of $HClO_4$ converts **7a** to **8a** (reaction 3), one would

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(5) Hoskins, B. F.; Vince, D. G. *Aust. J. Chem.* **1972**, *25*, 2039.

(6) The reported[5] analytical results actually correspond to $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$. The calculated values as reported[5] for the $Cu_3(PL)_3(OH)_2ClO_4 \cdot 2H_2O$ formulation are (C, 30.6; N, 11.9; H, 3.0; Cu, 27.0; Cl, 5.0) in error, and this has led to the confusion. The correct calculated values for this formulation are as follows: C, 29.87; N, 11.61; H, 2.63; Cu, 26.36; Cl, 4.91. The reported experimental values[5] (C, 30.7; N, 11.6; H, 3.0; Cu, 27.5; Cl, 5.4) which tally well with our results (see Experimental Section) positively exclude the formulation $Cu_3(PL)_3(OH)_2ClO_4 \cdot 2H_2O$.

Table I. Some Physical Properties of PL Complexes

complex	Λ_m[a,b]	IR frequencies[c]	μ_{eff}[d]	λ_{max} (ϵ)[e]
$[CO_3OH(PL)_3](ClO_4)_2·H_2O$	136	3440[f] b, 1545[g] s, 1220[h] s, 1130[i] b, 1090[i] b, 625[i] m, 1605[j] s, sp, 1475[j] s, sp, 1440[j] w	1.05	624 (135), 336 (6400)
$[Cu_3O(PL)_3]ClO_4·H_2O$	68	3440[f] b, 1540[g] s, 1220[h] s, sp, 1100[i] b, 630[i] m, 1610[j] s, sp, 1580[j] w, 1475[j] s, sp, 1445[j] m	1.01	648 (215), 584 (200), 340 (9700)

[a] Given in Ω^{-1} cm^2 mol^{-1}. [b] Conditions: solvent, DMF; concentration ~10^{-3} M. [c] Given in cm^{-1}; KBr disk. Key: b, broad; s, strong; sp, sharp; m, medium; w, weak. [d] Given in μ_B per copper at 298 K. [e] Band maximum in nm in DMF; ϵ is given in L mol^{-1} cm^{-1} (per mole of copper). [f] ν_{OH}. [g] $\nu_{C\cdots C} + \nu_{C\cdots C}$. [h] ν_{N-O}. [i] ClO_4^- vibrations. [j] Pyridine ring vibrations (Holmes, F; Lees, G; Underhill, A. E. *J. Chem. Soc. A* **1971**, 999. Krause, R. A.; Colthup, N. B.; Busch, D. H. *J. Phys. Chem.* **1961**, *65*, 2216).

Table II. Electrochemical Data[a–c] for the Couple of (1) for the $[Cu_3O(ligand)_3]ClO_4$ System

ligand/ system	solvent	E_{pa}, V	E_{pc}, V	ΔE_p, mV	$E°_{298}$, V	Q[d]	10^2A[e]
PL[f]	DMF[g]	0.515	0.455	60	0.485		0.95
PL[f,h]	CH_3CN[i]	0.660	0.515	145	0.587	0.97	
n-PrL	CH_3CN	0.405	0.335	70	0.370	0.92	0.96
PhL	CH_3CN	0.375	0.315	60	0.345	0.93	0.92
n-PrL′	CH_3CN	0.438	0.380	58	0.404	0.96	0.94

[a] Meanings of symbols are the same as in the text or are as indicated below. [b] Conditions: electrode, platinum; concentration of complexes, ~1 × 10^{-3} M unless otherwise specified; electrolyte, 0.1 M TEAP. [c] Scan rate = 50 mV s^{-1} unless otherwise stated. [d] Coulomb counts (at 0.75 V) for 10^{-2} mmol of complexes. Calculated count is 0.965 in all cases; each data point is an average of three independent determinations. [e] A in mmol is the amount of $HClO_4$ needed to convert 10^{-2} mmol of 7a to 8a or **5a** to **6a**. [f] Contains one molecule of water of crystallization. [g] Scan rate = 20 mV s^{-1}. [h] $[Cu_3O(PL)_3]^{2+}$ produced coulometrically in CH_3CN is unstable but fresh solutions give rise to a voltammogram (E_{pa} = 0.685 V; E_{pc} = 0.560 V; ΔE_p = 115 mV; $E°_{298}$ = 0.622) that is closely analogous to that of $[Cu_3O(PL)_3]^+$ in CH_3CN. [i] For solubility reasons, a saturated solution of unknown concentration was used for cyclic voltammetry.

expect a progressive decrease in the electrochemical response of **7a** on proton addition. This does happen (Figure 2). The amount of acid needed to complete the conversion **7a** → **8a** can be calculated by extrapolating experimental i_{pa} values to 0. Each mole of **7a** is found to require 1 mol of proton (Table II). The reaction thus proceeds quantitatively in DMF. By adding NEt_3 to the acidified solution process 5 can be reversed and the original voltammogram can be reestablished.

$$\mathbf{7a} + H^+ \rightarrow \mathbf{8a} \qquad (5)$$

This brings us to the possibility of making a solution of $[Cu_3OH(PL)_3](ClO_4)_2·H_2O$ electroactive by adding NEt_3 to it. This effect is indeed observed (Figure 3). So that the conversion **8a** → **7a**, could be completed i.e., the maximum value of i_{pa} reached, more than the stoichiometric amount of NEt_3 is needed. Proton removal by this base appears to be an equilibrium reaction

$$\mathbf{8a} + NEt_3 \rightleftharpoons \mathbf{7a} + NHEt_3^+ \qquad (6)$$

No attempt was made to determine the equilibrium constant.

(D) Status of the Work on $[Cu_3O(RL\ or\ RL')_3]ClO_4$. Earlier[4] we identified the couple of (1) in complexes containing both **5a** and **6a**. With the pure **5a** complexes prepared in course of the present work, this identification is fully confirmed. The formal potential data (Table II) are in complete agreement with earlier results.[4]

The couple of (1) is entirely analogous to the couple of (4). Since the structure of **7a** is known,[7] our assertion[4] that the one-electron oxidation is a characteristic property of the spin-doublet ion **1** (X = O) is vindicated. As far as reactions 5 and 6 and their effect on the electrochemical response are concerned, the qualitative parallelism with corresponding reaction[4] involving **5a** and **6a** is surprisingly close. There is a difference in quantity. The $E°_{298}$ value of the couple of (4) is significantly more positive than those of couples of the type of (1) (Table II). Thus **7b** is a stronger oxidant than **5b**. Alternatively, **7a** is oxidized with more difficulty than **5a**. This granted, the rest are much alike, as outlined in Figure 4. The **6a**–**6b** and **8a**–**8b** interconversions are considered in detail in the next section. The **6b**–**5b** and **8b**–**7b** interconversions involve two electrons and a proton and is not directly achievable.

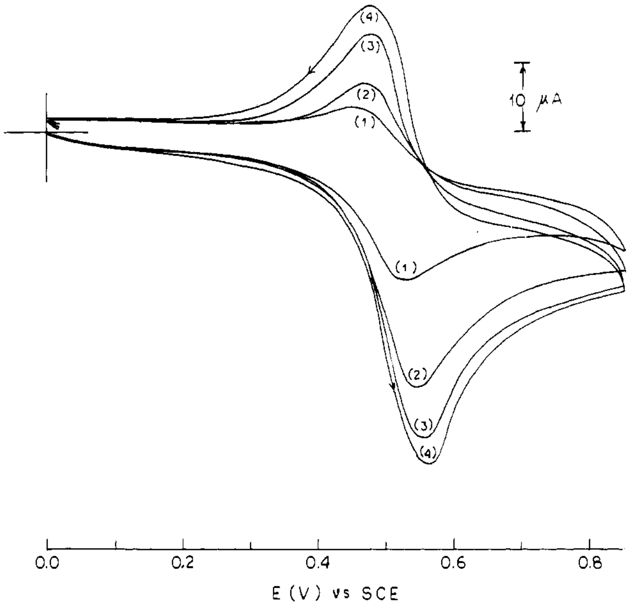

Figure 3. The effect of addition of triethylamine (28.01 × 10^{-3} M) to 10 mL of 1.205 M solution of $[Cu_3OH(PL)_3]^{2+}$ (**8a**) in DMF. Volume (mL) of base added: (1) 0.4, (2) 0.6, (3) 0.8, and (4) ≥1.1. Scan rate is 0.100 V s^{-1}.

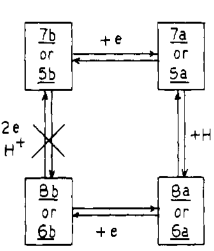

Figure 4. Electron-transfer and proton-transfer steps.

(E) One-Electron Reduction of $[Cu_3OH(PL)_3](ClO_4)_2·H_2O$. At a hanging-mercury-drop electrode (HMDE), this complex shows good cyclic response[8,9] in acetonitrile in the potential range 0.0 to –0.6 V (Figure 5). The $E°_{298}$ values are in Table III. In a stirred solution, brisk electrolysis occurred only at

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(7) Actually, the structure of **8a** is known—but it is a very good guess that the structure of **7a** is similar.

(8) It is necessary to do the experiment with fresh HMDE. With time, the electrode gets poisoned. This is evident in the appearance of a hump near –0.2 V in the cyclic voltammogram of **8a** in acetonitrile. This hump is totally absent when a fresh electrode is used.

(9) The couples of (2) and (7) were studied at a platinum working electrode also. Only an irreversible reduction peak was observed near –0.5 V. The anodic response was virtually absent.

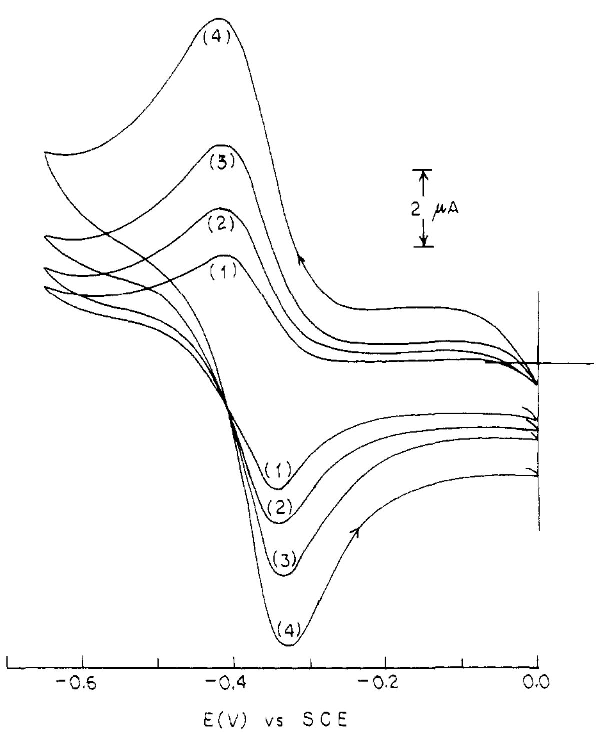

Figure 5. Cyclic voltammogram of $[Cu_3OH(PL)_3]^{2+}$ (**8a**) in MeCN at various scan rates (V s^{-1}): (1) 0.050, (2) 0.100, (3) 0.200, and (4) 0.500. Solute concentration is 0.86×10^{-3} M.

Table III. Electrochemical Data[a-c] for the Couple of (2) in Acetonitrile for $[Cu_3OH(ligand)_3](ClO_4)_2$ Complexes

ligand	E_{pa}, V	E_{pc}, V	ΔE_p, mV	$E°_{298}$, V	$10i_{pc}$, μA	Q^d
PL[e]	-0.345	-0.418	73	-0.380	32.6	*f*
PhL	-0.375	-0.305	70	-0.340	33.0	0.98
EtL′	-0.385	-0.295	90	-0.340	31.4	0.94
n-PrL′	-0.420	-0.265	155	-0.345	29.6	0.94
n-BuL′	-0.415	-0.302	113	-0.360	28.4	0.93

[a] Symbols have the same meaning as in text. [b] Conditions: electrode, HMDE; concentration of complexes, 10^{-3} M; electrolyte, 0.1 M TEAP. [c] Scan rate = 50 mV s^{-1}. [d] Coulomb count (at -0.7 V) for reduction of 10^{-2} mmol of complex. Calculated count is 0.965; each value given is the average of three independent determinations. [e] Complex has one molecule of water of crystallization. [f] Cannot be accurately measured (see ref 9).

working potentials more negative than E_{pc}, showing that the primary process is the reduction of **8a**. Coulometric counts at a mercury-pool electrode approximately[10] correspond to one-electron transfer. Cyclic voltammetric current height (Table III) at HMDE also corresponds to the transfer of one electron. The ΔE_p values (Table III) suggest quasi-reversibility for the couple of (7).

$$\mathbf{8a} + e^- \rightleftharpoons \mathbf{8b} \tag{7}$$

As shown earlier (eq 5), acids bring about the conversion **7a** → **8a**. Consequently, when acids are added to pure **7a** complexes, the couple of (7) becomes observable and the cathodic current comes to its full height when the mole ratios of H^+ and **7a** become equal (Table III).

(F) Case of $[Cu_3OH(RL\ or\ RL')_3](ClO_4)_2$. Among RL ligands, only PhL gave pure Cu_3OH species. The RL′ complexes could all be prepared in the pure Cu_3OH form. The cyclic response of all these pure complexes on the negative side of SCE at HMDE[9] is entirely similar to that of **8a** (Table III). The concerned couple is that of (2). Coulometric data are in Table III.

We now consider the RL complexes which are inherently mixtures of **5a** and **6a**: $[Cu_3O_q(OH)_{1-q}(RL)_3](ClO_4)_{2-q}$. Their cyclic voltammograms also display the couple of (2) but with a diminished i_{pc} value. The value of q is known from earlier experiments4 pertaining to the couple of (1). Since the PhL complex has $q = 0$ (100% of **6a**), it is possible to calculate the i_{pc} of each RL complex with the help of eq 8 where $(i_{pc})_0$ is

$$i_{pc} = [(i_{pc})_0](1 - q) \tag{8}$$

the peak current for the PhL complex and all measurements are made under the same conditions of concentration, electrode area, and scan rate for both RL and PhL complexes. The experimental values of i_{pc} agree very well with the calculated values (Table IV). The results are thus internally consistent.

Addition of $HClO_4$ to **5a** converts it to **6a** (vide supra) and thus brings about the reductive response due to the couple of (2). This was tested for several pure **5a** complexes. For the RL complexes which are mixtures of **5a** and **6a**, addition of $HClO_4$ augments the response near -0.4 V and the full one-electron response $[i_{pc} = (i_{pc})_0]$ for the entire amount of the complex is observed when the number of moles of $HClO_4$ added equals that of the **5a** component originally present (Table IV) in the mixture.

The $E°_{298}$ values of the couple of (2) for the entire group of PL, RL, and RL′ complexes cover the relatively narrow range of -0.34 to -0.38 V, within which the order PL < RL < RL′, PhL obtains. Since the structure of **8a** is known, it is a very good inference that **6a** has structure **1** (X = OH) and that one-electron reduction is a common and characteristic property of the cluster **1** (X = OH).

(G) Nature of Oxidized and Reduced Complexes. We consider first the case of **7b**. Since process 4 is reversible, it is very likely that it occurs with little immediate structural rearrangement. Thus **7a** and **7b** are both believed to belong to the structural type **1** (X = O). After complete coulometric oxidation of **7a** to **7b**, we attempted to reduce **7b** back to **7a**. A diminished number of coulombs were found to collect. This decrease was progressive on successive cycling of oxidation and reduction. This suggests that the oxidized species **7b** is not very stable in the solution phase. Attempts to isolate **7b** in the form of perchlorate salt has not yet succeeded.

In **7b** the copper oxidation states can be written as Cu^{II}_2-Cu^{III}. The average metal oxidation number is +2.33. We wish to stress that such mixed-valence species are unknown in literature outside our previous report.[4] Fresh solutions of **7b** (prepared coulometrically) display intense (ϵ >5000) bands at 806 and 704 nm presumably due to intervalence excitation or ligand-to-metal charge transfer. In contrast, **7a** shows only a broad ligand field band near 600 nm (Table I).

The spectral behaviors of the RL(RL′) mixed-valence species **6b** briefly reported earlier[4] closely follow those of **7b**. Here the low-energy bands appear at ~840 and ~720 nm. In general the RL complexes are relatively unstable. The RL′ species are much more stable, and we have succeeded in preparing the pure mixed-valence complex $[Cu_3O(n\text{-}PrL')_3](ClO_4)_2$ in the crystalline state. Spectral and electronic structural details of the unique mixed-valence **5b** and **7b** species will be reported separately.

We now turn to species **6b** in (2). Here the oxidation-state description is believed to be $Cu^{II}_2Cu^I$ with an average metal oxidation number of +1.67. A coulometrically produced solution of **6b** is light green and displays a relatively broad absorption band of medium intensity near 1050 nm (ϵ ~100). This band may be due to an intervalence[11] Cu(II)Cu(I) ex-

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(10) Due to the poisoning[8] of mercury, the coulometric experiment cannot be considered as highly reliable. Coulometry was performed several times at -0.65 V in acetonitrile, and the number of electrons transferred was varied from experiment to experiment, lying in the range 1-1.5 e.

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Table IV. Electrochemical Data[a-c] for the Couple of (2) in $[Cu_3O_q(OH)_{1-q}(RL)_3](ClO_4)_{2-q}$ Systems in Acetonitrile

RL	q[d]	E_{pc}, V	E_{pa}, V	ΔE_p, mV	$E°_{298}$, V	i_{pc}, μA		Q[e]	
						calcd	found	calcd	found
EtL	0.81	−0.410	−0.325	85	−0.367	6.3	6.4	0.18	0.20
n-PrL	0.44	−0.435	−0.305	130	−0.370	18.5	19.0	0.54	0.61
n-BuL	0.38	−0.430	−0.325	105	−0.378	20.5	19.2	0.60	0.55

[a] Meanings of symbols are the same as in the text. [b] Conditions: electrode, HMDE; electrolyte, 0.1 M TEAP; concentration of complexes, 10^{-3} M. [c] Scan rate = 50 mV s^{-1}. [d] From ref 4. [e] Coulomb count (at −0.7 V) for reduction of 10^{-2} mmol of complex.

citation. The reduced solution is not particularly stable as is evident from diminishing coulomb counts, on redox cycling. The species **8b** behaves similarly. Attempts to isolate the species **6b** and **8b** are under way.

Concluding Remarks

It is demonstrated that the trinuclear copper(II) complexes of pyridine-2-carbaldoxime undergo novel one-electron oxidation or one-electron reduction depending on the absence or presence of proton on the central bridging oxygen. The redox behaviors of RL and RL′ complexes are completely parallel to those of **7a** and **6a**. This confirms our earlier[1,4] proposal regarding the structures of these complexes. In this context it would be interesting to study the electrochemistry of trinuclear HAL (3) complexes, which are known[2] to have both Cu_3O and Cu_3OH moieties in the crystalline state. We have stressed earlier[4,12] the symbiotic relationship between electron transfer and proton transfer. Indeed the proton acts as an effective valve in these systems and strictly controls the direction of electron transfer.

The possibility that in **5b** (and hence **7b**) a ligand radical cation rather than copper(III) exists was considered and rejected earlier.[4b] In **6b** and **8b** it is the metal ion and not the ligand that is reduced: complexes of nickel(II) derived from iminooxime ligands closely related to RL *do not* display[13] reduction anywhere near −0.4 V.

Presently we are investigating the redox behaviors of **7a** and **8a** in aqueous medium where proton transfer may occur with electron transfer in a "concerted" manner.[12] A cyclic voltammetric study of the trinuclear complexes in acetonitrile at HMDE shows the presence of another couple at potentials much more negative than those of the couple of (7) and (2): ∼−0.75 V in the case of PL complexes and at ∼−0.9 V in the case of the RL(RL′) complexes. This is quasi-reversible and appears to involve two electrons. Addition of protons beyond the Cu_3OH stage affects this couple. Further details are being examined.

Experimental Section

Materials. Pyridine-2-carbaldehyde was obtained from Sigma Chemical Co.. Other materials and solvents used were obtained or prepared as reported earlier.[4] Before experiments with the complexes were undertaken, electrochemical inertness of the solvents up to at least +1.0 V at the platinum electrode and −1.5 V at HMDE was carefully established.

Physical Measurements. Magnetic moments were determined by the Guoy method using $HgCo(SCN)_4$ as standard. Molar electrical conductivities were measured with the help of a Philips (India) conductivity bridge. Infrared spectra were recorded on a Beckman IR 20A spectrophotometer. Either a Cary-17D or a Pye Unicam SP8-150 spectrophotometer was used to record the electronic spectra.

Electrochemical Experiments. A PAR model 370-4 electrochemistry system was used. Many of the details are given in the earlier paper.[4] The three-electrode measurements were carried out with either a Metrohm E410 hanging-mercury-drop electrode (HMDE) or a Beckman Model 39273 platinum-inlay electrode in conjunction with a platinum-wire auxiliary electrode and an SCE. In the case of HMDE, the size of the mercury drop could be reproduced by turning the vernier scale of the Metrohm device to the same extent (two divisions) every time. For coulometry at positive potentials a platinum wire gauge electrode was used, and at negative potentials a mercury pool electrode was used. All measurements were performed in solvents which were 0.1 M in TEAP at 298 K under nitrogen atmosphere. The potentials reported in this paper are uncorrected for junction potentials.

Preparation of Pyridine-2-carbaldoxime (HPL). This preparation followed a reported method[14] with some modifications. A 1.0-g sample of pyridine-2-carbaldehyde was dissolved in 10 mL of ethanol and was treated with 0.7 g of hydroxylamine hydrochloride. The temperature was maintained between 0 and 10 °C (ice bath). The resulting yellow solution was neutralized with NaOH (0.4 g of NaOH in 15 mL of water) under cold conditions. Needle-shaped crystals appeared toward the end of the neutralization process. The mixture was then left at room temperature overnight. The yellowish white crystalline mass so obtained was filtered and washed with cold water. The product was recrystallized from an acetone–water mixture to obtain white needles: mp 109 °C; yield 700 mg.

Preparation of Complexes. $[Cu_3OH(PL)_3](ClO_4)_2{\cdot}H_2O$. This was prepared by mixing cold ethanolic solutions of HPL and copper(II) perchlorate hexahydrate following the procedure of Svasti and Green.[15] This same complex was also obtained in aqueous medium by modifying a reported procedure.[10] To a stirred aqueous solution (100 mL) containing HPL (0.25 g) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.75 g) was added slowly a solution of NaOH (0.6 g in 100 mL) till the pH became ∼5.5. The dark green solution was allowed to stand overnight. The deposited dark needles were filtered off and dried in vacuo over P_4O_{10}; yield 300 mg.

$[Cu_3O(PL)_3]ClO_4{\cdot}H_2O$. The reported procedure[5,6] was followed. Anal. Calcd for $C_{18}N_6H_{17}Cu_3ClO_9$: C, 31.44; N, 12.22; H, 2.47; Cu, 27.74; ClO_4, 14.48; Cl, 5.17. Found: C, 31.19; N, 11.98; H, 2.3; Cu, 28.05; ClO_4, 14.61.

$[Cu_3O_q(OH)_{1-q}(RL\text{ or }RL')_3](ClO_4)_{2-q}$. These were prepared as reported earlier.[4]

$[Cu_3O(RL\text{ or }RL')_3]ClO_4$. A 0.2-mmol sample of $[Cu_3O_q(OH)_{1-q}(RL\text{ or }RL')_3](ClO_4)_{2-q}$ was dissolved in 20 mL of acetonitrile, and 5 mL of distilled triethylamine was added dropwise with constant stirring to precipitate the green crystalline compound which was filtered, washed thoroughly with water, and dried in vacuo over P_4O_{10}; yield 60–80%.

Analysis. All coplexes analyzed well. Data for two representative cases are given here. Calcd for $C_{30}N_6H_{33}Cu_3ClO_8$ (PRL): C, 43.27; N, 10.10; H, 3.97; Cu, 22.92; ClO_4, 12.01. Found: C, 43.51; N, 10.23; H, 4.06; Cu, 22.73; ClO_4, 11.84. Calcd for $C_{54}N_6H_{57}Cu_3ClO_8$ (*n*-BuL′): C, 56.59; N, 7.34; H, 4.98; Cu, 16.66; ClO_4, 8.73. Found: C, 56.34; N, 7.23; H, 4.76; Cu, 16.82; ClO_4, 8.90.

The room-temperature magnetic moments (μ_{eff} in Bohr magnetons per copper) of the complexes are as follows: EtL, 1.02; *n*-PrL, 1.01; *n*-BuL, 1.06; PhL, 1.05; EtL′, 1.07; *n*-PrL′, 1.08; *n*-BuL′, 1.08. Molar electrical conductivity (Λ_M in Ω^{-1} cm^2 mol^{-1}) data in acetonitrile solution (∼10^{-3} M) are as follows: EtL, 151; *n*-PrL, 157; *n*-BuL, 158; PhL, 142; *n*-PrL′, 130; *n*-BuL′, 125.

$[Cu_3OH(RL')_3](ClO_4)_2$. These were obtained by the following general procedure. Aqueous ∼0.1 N $HClO_4$ (3 mL) was added to 0.2 mmol of $[Cu_3O_q(OH)_{1-q}(RL')_3](ClO_4)_{2-q}$ taken in 20 mL of acetonitrile. The green solution was left in air. A gummy mass slowly deposited. Eventually this became crystalline in the presence of water. The green complex was washed thoroughly with water to remove excess perchloric acid, filtered, and dried in vacuo over P_4O_{10}; yield 80–90%.

Anal. Calcd for $C_{48}N_6H_{46}Cu_3Cl_2O_{12}$ (EtL′): C, 49.61; N, 7.24; H, 3.96; Cu, 16.43; ClO_4, 17.23. Found: C, 49.40; N, 6.98; H, 3.64; Cu, 16.21; ClO_4, 17.46. Calcd for $C_{51}N_6H_{52}Cu_3Cl_2O_{12}$ (*n*-PrL′): C, 50.87; N, 6.98; H, 4.32; Cu, 15.85; ClO_4, 16.63. Found: C, 51.62;

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N, 7.21; H, 4.60; Cu, 16.01; ClO_4, 16.22. Calcd for $C_{54}N_6H_{58}Cu_3Cl_2O_{12}$ (*n*-BuL′): C, 52.05; N, 6.75; H, 4.66; Cu, 15.32; ClO_4, 16.06. Found: C, 52.32; N, 6.33; H, 4.51; Cu, 15.09; ClO_4, 16.53. The above procedure when applied to $[Cu_3O_q(OH)_{1-q}(RL)_3](ClO_4)_{2-q}$ gave back the original product.

Magnetic moments (μ_{eff} in Bohr magnetons per copper) of the complexes at room temperature are as follows: EtL′, 1.09; *n*-PrL′, 1.08; *n*-BuL′, 1.09. Λ_M (in Ω^{-1} cm^2 mol^{-1}) data in acetonitrile solution ($\sim 10^{-3}$ M) are as follows: EtL′, 221; *n*-PrL′, 262; *n*-BuL′, 250.

Conversion of $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ to $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$. A 800-mg sample of $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ was dissolved in 40 mL of acetonitrile. To the bright green solution was added dropwise with constant stirring 2 mL of distilled triethylamine. Immediately a grayish green compound started precipitating. After 15 min, the compound was filtered off, washed thoroughly with acetonitrile, and dried in vacuo over P_4O_{10}; yield 600 mg.

Conversion of $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$ to $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$. To 270 mg of $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$ taken in 30 mL of acetonitrile was added dropwise with constant stirring 5 mL < of 0.11 N $HClO_4$ in DMF. The mixture was filtered after stirring for 0.5 h. The filtrate was left in air. When the volume decreased to 2 mL, the green crystalline compound $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ was filtered off, washed with 5 mL of cold water, and dried in vacuo over P_4O_{10}; yield 150 mg.

Conversion of $[Cu_3OH(n\text{-}BuL')_3](ClO_4)_2$ to $[Cu_3O(n\text{-}BuL')_3]ClO_4$. A 200-mg sample of $[Cu_3OH(n\text{-}BuL')_3](ClO_4)_2$ was dissolved in 50 mL of methanol, and 2 mL of NEt_3 was added dropwise with stirring. Within 5 min, the crystalline compound started precipitating. The compound was filtered, washed with methanol, and dried in vacuo over P_4O_{10}; yield 120 mg.

Conversion of $[Cu_3O(n\text{-}BuL')_3]ClO_4$ to $[Cu_3OH(n\text{-}BuL')_3](ClO_4)_2$. Starting with $[Cu_3O(n\text{-}BuL')_3]ClO_4$, a procedure identical with that for preparing pure $[Cu_3OH(RL')_3](ClO_4)_2$ (vide supra) was followed to obtain the desired complex in 90% yield.

The interconversions of Cu_3O and Cu_3OH species derived from PhL and other RL′ ligands were achieved by similar procedures.

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Registry No. **5a**·ClO_4 (RL = PhL), 79682-14-7; **5a**·ClO_4 (RL′ = *n*-BuL′), 76986-47-5; **5a**·ClO_4 (RL′ = *n*-PrL′), 76986-49-7; **5a**·ClO_4 (RL′ = EtL′), 76986-51-1; **5a**·ClO_4 (RL = *n*-BuL), 73689-14-2; **5a**·ClO_4 (RL = *n*-PrL), 73668-62-9; **5a**·ClO_4 (RL = EtL), 53598-80-4; **6a**·2ClO_4 (RL = PhL), 73689-16-4; **6a**·2ClO_4 (RL′ = *n*-BuL′), 76998-84-0; **6a**·2ClO_4 (RL′ = *n*-PrL′), 76986-56-6; **6a**·2ClO_4 (RL′ = EtL′), 76986-58-8; **6a**·2ClO_4 (RL = *n*-BuL), 76986-60-2; **6a**·2ClO_4 (RL = *n*-PrL), 76986-62-4; **6a**·2ClO_4 (RL = EtL), 76986-64-6; **7a**·ClO_4, 79703-96-1; **8a**·2ClO_4, 79703-98-3; HPL, 873-69-8.

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Study of the Insertion Products of Manganese in the Silicon-Hydrogen Bond. Nature of the Bond and Proton Exchange in the H-Mn-Si-H System

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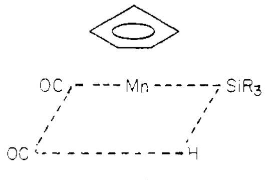
NMR studies (^{29}Si, ^{13}C, and ^1H) on silicon manganese hydrides show the possibility of a bond interaction between silicon and hydrogen. Evidence is given for a slow intramolecular equilibrium (on the NMR time scale) between the silicon manganese hydride and the deinserted complex (silicon hydride and manganese moiety). In the latter, however, both moieties are associated and a strong ligand is needed to displace the silicon hydride. Chemical reactions show that protonation of the anion $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2SiPh_3]^-$ leads only to the lateral hydride independent of its mode of generation. When the anion is alkylated, only the diagonal isomer is formed, showing that sterically crowded complexes prefer this geometry; thus the short distance observed between silicon and hydrogen does not seen to arise solely from steric hindrance.

Introduction

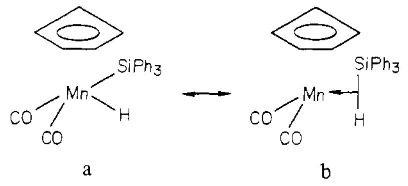
Insertion reactions of metals into the silicon-hydrogen bond are of current interest because of their implication in catalytic hydrosilylation reactions.[2]

In previous work carried out in our laboratory, we have studied the chemical and stereochemical behavior of complexes arising from the insertion of manganese into the Si-H bond.[3-5]



R = alkyl, aryl

Scheme I



Scheme II

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2(H)SiPh_3 + PPh_3 \xrightleftharpoons[\text{determining}]{\text{rate}}$$

18-electron complex

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2 + HSiPh_3 + PPh_3 \xrightleftharpoons{\text{fast}}$$

16-electron complex

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2PPh_3 + HSiPh_3$$

This type of complex was first described by Jetz and Graham[6] (R = phenyl). An X-ray diffraction study[7] showed a bonding interaction between silicon and hydrogen.

The manganese-silicon bond length (2.42 Å) and the manganese-hydrogen length (1.55 Å) show normal values,

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