is also no simple correlation between ΔV^{*} and DN.

In the present system, since isoquinoline has no formal charge, and if there is any, its dipole may be little, $\Delta V_{os}°$ would not exceed the uncertainty in the observed ΔV^{*}. Consequently the observed activation volume ΔV_f^{*} should almost equal the ΔV_f^{**}. On the other hand, ΔV_{ex}^{*} measured by a high-pressure NMR technique involves no contribution of $\Delta V_{os}°$. The positive ΔV_{ex}^{*} values considerably smaller than those of molar volumes of solvents strongly point to a dissociative interchange (I_d) mechanism.[16] Since ΔV_f^{*} is close to ΔV_{ex}^{*}, as apparent from values in Table I, the mechanism for the complex formation should be similar to that for the solvent exchange on nickel(II) ion in different solvents.

Interestingly, values of ΔV_d^{*} are all positive and comparable to those of ΔV_f^{*} and ΔV_{ex}^{*}. Assuming the same reaction process for dissociation as for formation

$$\mathrm{Ni(isoq)^{2+}} + \mathrm{S} \xrightleftharpoons{K_{os,d}} \mathrm{Ni(isoq)^{2+}\cdots S} \xrightarrow{k_d} \left[\mathrm{Ni}\begin{matrix}\diagup \mathrm{S} \\ \diagdown \mathrm{isoq}\end{matrix}\right]^{2+\,\ddagger} \longrightarrow \mathrm{Ni(S)^{2+}} + \mathrm{isoq}$$

we have $k_d = K_{os,d}k_d^{*}[S]/(1 + K_{os,d}[S])$. In the case of dissociation, the entering ligand is a solvent molecule (S) and the leaving ligand is isoquinoline. Since $1 < K_{os,d}[S]$, we have $k_d \simeq k_d^{*}$. Thus, the observed dissociation reaction corresponds to the reaction from an outer-sphere complex $(\mathrm{Ni(isoq)^{2+}\cdots S})$ to the (solvento)nickel(II) ion. The transition state is the same as for the formation. The mechanism is a dissociative interchange also for the dissociation.

All available values of activation volume for the complexation of Ni(II) ion are compiled in Table II. The activation volume is similar for different entering ligands despite their different size. This would imply that the volume increase caused by the lengthening of the metal ion bond with a leaving solvent molecule is compensated to a similar extent for different entering ligands by the volume decrease due to penetration of a donor atom into the inner sphere.

We conclude that all the formation and dissociation of the 1:1 nickel(II) complex and the solvent exchange on nickel(II) ion in various solvents can be accommodated within the framework of a similar I_d mechanism.

Registry No. Ni, 7440-02-0; CH_3CN, 75-05-8; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; DMF, 68-12-2; isoq, 119-65-3.

Supplementary Material Available: Table SI listing numerical data of rate constants for complexation of Ni(II) ion with isoquinoline in DMF, CH_3CN, CH_3OH, C_2H_5OH, and H_2O under high pressure up to 2000 kg cm^{-2} and at 25 °C (4 pages). Ordering information is given on any current masthead page.

(18) Jost, A. *Ber. Bunsenges. Phys. Chem.* **1975**, *79*, 850.
(19) Yu, A. D.; Waissbluth, M. D.; Grieger, R. A. *Rev. Sci. Instrum.* **1973**, *44*, 1390.
(20) Inoue, T.; Kojima, K.; Shimozawa, R. *Chem. Lett.* **1981**, 259.

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Binuclear Metal Complexes. 1. Synthesis, Characterization, and Electrochemical Studies of Dicopper(II) Complexes with 4-Methyl-2,6-di(acyl/benzoyl)phenol

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Synthesis and characterization of the mono- and binuclear copper(II) complexes, $Cu(R,R')L_2\cdot H_2O$ and $Cu_2(R,R')L_2(ClO_4)_2\cdot 2H_2O$, have been made with the ligands 4-methyl-2,6-di(acyl/benzoyl)phenol, designated as (R,R′)HL, where R and R′ stand for the substituents in the di(acyl/benzoyl) moiety. The following substituents have been used: R = R′ = H, Me, Pr, Ph; R = Ph, R′ = Me. Electrochemical studies of these compounds have been made in DMF with use of a HMDE. All of the five Cu^{II}–Cu^{II} complexes undergo two-electron reduction to Cu^{I}–Cu^{I} species at a single potential as evidenced from cyclic voltammetric and coulometric measurements. Among these, the electron-transfer processes in $Cu_2(Ph,Ph)L_2(ClO_4)_2\cdot 2H_2O$ and $Cu_2(Ph,Me)L_2(ClO_4)_2\cdot 2H_2O$ occur reversibly; others show quasi-reversible behavior. The $E_{1/2}$ values are about −0.05 V vs. SCE. The electrochemically reduced Cu^{I}–Cu^{I} species show an absorption band at 470 nm. The mononuclear copper(II) complexes undergo quasi-reversible reduction with $E_{1/2} \simeq -0.43$ V.

Introduction

The structure–function relationship in copper proteins is a subject of considerable importance. Hemocyanin, tyrosinase, lacasse, ceruloplasmin, and ascorbic acid oxidase are copper proteins that contain a strongly coupled binuclear copper active site but perform different biological functions.[1-9] The dicopper units, referred to as type 3 coppers, are characterized inter alia by large antiferromagnetic coupling constants and relatively high positive two-electron redox potentials.

In the last few years, model studies with reference to the type 3 coppers have addressed ligand environment, redox behavior, magnetic exchange interactions, and reactivity of the metal centers.[10-20] In the context of redox behavior of

(1) Malmstrom, B. G. In "New Trends in Bio-inorganic Chemistry"; Williams, R. J. P., Da Silva, J. R. R. F., Eds.; Academic Press: London, 1980; p 58.
(2) Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1.
(3) Beinert, H. *Coord. Chem. Rev.* **1980**, *33*, 55.
(4) Mason, H. S. *Adv. Exp. Med. Biol.* **1976**, *74*, 464.
(5) (a) Himmelwright, R. S.; Eickman, N. C.; Lubien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378. (b) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Lerch, K.; Solomon, E. I. *Ibid.* **1980**, *102*, 7339.
(6) Farver, O.; Goldberg, M.; Lancet, D.; Pecht, I. *Biochem. Biophys. Res. Commun.* **1976**, *73*, 494.
(7) Reinhammer, B. R. M.; Vanngard, T. I. *Biochim. Biophys. Acta* **1972**, *275*, 245.
(8) Makino, N.; McMahill, P.; Mason, H. S.; Moss, T. H. *J. Biol. Chem.* **1974**, *249*, 6062.
(9) Stroth Kamp, K. G.; Dawson, C. R. *Biochemistry* **1974**, *13*, 434.
(10) Addison, A. W. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 899.
(11) Patterson, G. H.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.
(12) Gagne, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367.
(13) Gagne, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917.
(14) Grzybowski, J. J.; Merrell, P. H.; Urbach, F. L. *Inorg. Chem.* **1978**, *17*, 3078. Grzybowski, J. J.; Urbach, F. L. *Ibid.* **1980**, *19*, 2604.
(15) Fenton, D. E.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6367.
(16) Lintvedt, R. L.; Tomlonovic, B.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *No. 150*, 407.
(17) Hasty, E. F.; Wilson, L. J.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 1834.
(18) Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683.
(19) Spiro, C. L.; Lambert, S. L.; Smith, T. J.; Duesler, E. N.; Gagne, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1229.

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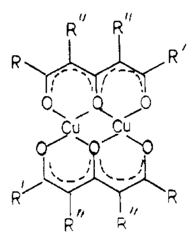
Table I. Analytical Data for Copper(II) Complexes

compd	color	% C calcd	% C found	% H calcd	% H found	% Cu calcd	% Cu found
$Cu(H,H)L_2{\cdot}H_2O$	greenish yellow	53.01	53.42	3.92	3.69	15.59	15.68
$Cu(Me,Me)L_2{\cdot}H_2O$	greenish yellow	56.95	56.56	5.17	5.14	13.70	13.95
$Cu(Pr,Pr)L_2{\cdot}H_2O$	dark brown	62.54	62.12	6.94	6.82	11.39	11.45
$Cu(Ph,Ph)L_2{\cdot}H_2O$	brown	70.83	71.18	4.49	4.65	8.92	8.84
$Cu(Ph,Me)L_2H_2O$	brown	65.36	65.02	4.77	4.59	10.81	10.75
$Cu_2(H,H)L_2(ClO_4)_2{\cdot}2H_2O$	green	31.39	31.26	2.63	2.82	18.48	18.57
$Cu_2(Me,Me)L_2(ClO_4)_2{\cdot}2H_2O$	green	36.36	36.48	3.37	3.27	17.50	17.64
$Cu_2(Pr,Pr)L_2(ClO_4)_2{\cdot}2H_2O$	emerald green	42.05	41.75	4.90	4.88	14.44	14.40
$Cu_2(Ph,Ph)L_2(ClO_4)_2{\cdot}2H_2O$	dark green	50.80	50.61	3.43	3.63	12.81	12.92
$Cu_2(Ph,Me)L_2(ClO_4)_2{\cdot}2H_2O$	light green	44.24	44.05	3.46	3.64	14.64	14.71

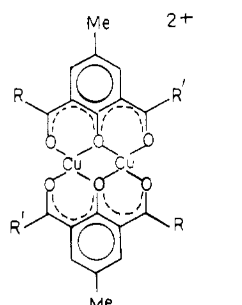
coupled binuclear copper(II) centers, the observation made by Fenton and Lintvedt[15] that bis(1,3,5-triketonato)dicopper(II) chelates, $Cu_2(TKO)_2$ (**1**), undergo reversible one-step two-electron transfer is very significant. This is in conflict with the known electron-transfer properties of other binuclear copper(II) complexes that exhibit (a) one-electron reduction to a mixed-valence Cu(II)–Cu(I) species,[10] (b) two sequential reductions at different potentials yielding a Cu(I)–Cu(I) complex,[11-13] or (c) irreversible reduction to metallic copper or to two mononuclear copper(I) products.[14]

The question whether the unusual electrochemical behavior of $Cu_2(TKO)_2$, which contains the Cu_2O_6 unit, is confined only to a particular class of compounds or has more general relevance in the realm of systems that would contain the same chromophoric group has not yet been answered. In our pursuit to generate binuclear copper(II) chelates that would mimic the intriguing redox behavior of type 3 coppers, as typified by $Cu_2(TKO)_2$, we have investigated the copper(II) complexes with 4-methyl-2,6-di(acyl/benzoyl)phenol (**2**). It may be



$Cu_2(TKO)_2$

1



$Cu_2(R,R')L_2(ClO_4)_2{\cdot}2H_2O$
R = R' = H , Me , Pr , Ph
R = Ph , R' = Me

2

pointed out that albeit literature[21,22] contains a large volume of work on binuclear complexes derived from the condensation products of 4-methyl-2,6-diformylphenol with various amine-functionalized molecules, complexes with the parent ligand remained unexplored. It also appeared to us that while $Cu_2(TKO)_2$, being neutral complexes, undergo reductions in the potential range –0.45 to –0.65 V, more facile reductions (that is, at more positive potentials) would take place in the case of **2** as they are dipositively charged species. The present study has substantiated this expectation.

Experimental Section

Materials. All chemicals were reagent grade and were used as received. Copper(II) perchlorate was prepared from freshly precipitated basic copper carbonate, the crystals were dried in vacuo, and the compound was used as $Cu(ClO_4)_2{\cdot}6H_2O$. Tetraethylammonium perchlorate (TEAP) was made from tetraethylammonium bromide.[23] Solvents such as methanol, ethanol, acetone, etc. were dried by standard methods.[24] For electrochemical work, reagent grade *N,N*-dimethylformamide (DMF) was dried successively over $MgSO_4$, $CuSO_4$, and 4-Å molecular sieves and vacuum distilled prior to use.

Ligand. 4-Methyl-2,6-diformylphenol, (H,H)HL, was prepared by a method described in literature.[25] The syntheses of the other compounds will be described in a future publication.[26]

Complexes. Mononuclear Copper(II) Chelates, $Cu(R,R')L_2{\cdot}H_2O$. These compounds were obtained by following the same general procedure with minor variation in detail. To an ethanol solution (80 mL) of (Me,M)HL (1.54 g, 8 mmol) was added an ethanol solution (30 mL) of $Cu(OAc)_2{\cdot}H_2O$ (0.8 g, 4 mmol). The resulting solution was refluxed for 3 h, during which $Cu(Me,Me)L_2{\cdot}H_2O$ separated in crystalline form. The product was collected by filtration, washed with ethanol and petroleum ether, and finally recrystallized from chloroform. $Cu(H,H)L_2{\cdot}H_2O$ and $Cu(Ph,Ph)L_2{\cdot}H_2O$ separated out during boiling, while $Cu(Pr,Pr)L_2{\cdot}H_2O$ and $Cu(Ph,Me)L_2{\cdot}H_2O$ were obtained on cooling the solutions to room temperature. Except for the case of $Cu(H,H)L_2{\cdot}H_2O$, which was sparingly soluble, recrystallization was made from chloroform.

Binuclear Copper(II) Chelates, $Cu_2(R,R')L_2(ClO_4)_2{\cdot}2H_2O$. These compounds were obtained by following either of the two procedures described below.

Method I. To a boiling dry ethanol solution (50 mL) containing (H,H)HL (0.98 g, 6 mmol) and triethylamine (0.61 g, 6 mmol) was slowly added $Cu(ClO_4)_2{\cdot}6H_2O$ (2.4 g, 6.5 mmol) dissolved in dry ethanol (30 mL). The resulting solution was refluxed for 0.5 h, when crystals of $Cu_2(H,H)L_2(ClO_4)_2{\cdot}2H_2O$ began to separate slowly. The mixture was cooled to room temperature and filtered, and the product was washed with dry acetone and chloroform.

Method II. In 100 mL of dry acetone was suspended 1.18 g (2 mmol) of $Cu(Ph,Me)L_2{\cdot}H_2O$, and $Cu(ClO_4)_2{\cdot}6H_2O$ (1.1 g, 3 mmol) dissolved in dry acetone (25 mL) was added to the mixture. On refluxing, the mixture became clear, but almost immediately crystals of $Cu_2(Ph,Me)L_2(ClO_4)_2{\cdot}2H_2O$ began to separate. *Caution*! The mixture started bumping at this stage. After being refluxed for 0.5 h, the mixture was cooled to room temperature and filtered, and the compound was washed with dry acetone and chloroform. Analytical data[28] of the compounds are given in Table I.

Physical Measurements. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer with KBr pellets. Electronic spectra in solution were obtained with a Pye-Unicam SP8-150 spectrophotometer, and a Cary 17D spectrophotometer was used to record reflectance spectra of the compounds diluted with $CaCO_3$. Magnetic susceptibilities at room temperature were determined by the Gouy method using $HgCo(SCN)_4$ as standard. EPR spectra for the mononuclear copper(II) complexes in polycrystalline form were recorded at 77 K with a Varian E-4 X-band spectrometer. DPPH was used as the calibrant. A Philips PR9500 bridge was used for conductivity measurements.

(20) Gagne, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 4073.
(21) Groh, S. E. *Isr. J. Chem.* **1976–1977**, *15*, 277.
(22) Casellato, U.; Vigato, P. A.; Vidali, M. *Coord. Chem. Rev.* **1977**, *23*, 31.
(23) Sawyer, D. T.; Roberts, J. L., Jr. "Experimental Electrochemistry for Chemists"; Wiley: New York, 1974; p 212.
(24) Vogel, A. I. "Practical Organic Chemistry", 3rd ed.; ELBS and Longman Group Ltd.: London, 1965; pp 163–179.
(25) Ullmann, F.; Brittner, K. *Chem. Ber.* **1909**, *42*, 2539.
(26) Mandal, S. K.; Nag, K. *J. Chem. Soc., Dalton Trans.*, in press.
(27) C and H analyses were performed by the Microanalytical Services of the Australian Mineral Development Laboratories. Copper was estimated as CuSCN by us.
(28) Piklington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225.

Table II. Electronic Spectra, Magnetic Moments, and Molar Conductivities of Copper(II) Complexes

complex	medium	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	Λ_M,[a] Ω^{-1} cm^{-1} mol^{-1}	μ, μ_B
$Cu(H,H)L_2 \cdot H_2O$	solid[b]	680		1.76
$Cu(Me,Me)L_2 \cdot H_2O$	chloroform	650 (75), 700 (60)		1.84
	DMF	350 (7500), 450 (11 200), 650 (95), 700 (85)		
	solid[b]	660		
$Cu(Pr,Pr)L_2 \cdot H_2O$	chloroform	650 (65), 710 (60)		1.95
	DMF	350 (6900), 410 (10 400), 640 (85), 710 (80)		
	solid[b]	660		
$Cu(Ph,Ph)L_2H_2O$	chloroform	660 (75), 710 (70)		1.87
	DMF	350 (7100), 415 (7400), 660 (90), 710 (85)		
	solid[b]	670		
$Cu(Ph,Me)L_2 \cdot H_2O$	chloroform	655 (70), 705 (65)		2.02
	DMF	340 (7000), 405 (8600), 660 (85), 710 (80)		
$Cu_2(H,H)L_2(ClO_4)_2 \cdot 2H_2O$	acetone	750 (145)	202	0.91
	DMF	330 (8700), 390 (7700), 760 (138)	170	
	solid[b]	760		
$Cu_2(Me,Me)L_2(ClO_4)_2 \cdot 2H_2O$	acetone	740 (144)	182	1.05
	DMF	350 (6500), 405 (10 500), 750 (132)	166	
	solid[b]	740		
$Cu_2(Pr,Pr)L_2(ClO_4)_2 \cdot 2H_2O$	acetone	750 (145)	172	1.14
	DMF	345 (7300), 405 (9400), 750 (151)		
	solid[b]	750		
$Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$	acetone	745 (140)	200	1.22
	DMF	350 (7400), 415 (9700), 750 (155)		
	solid[b]	750		
$Cu_2(Ph,Me)L_2(ClO_4)_2 \cdot 2H_2O$	acetone	750 (146)	165	1.13
	DMF	340 (7100), 405 (8300), 750 (150)		
	solid[b]	760		

[a] Concentration $\sim 10^{-3}$ M. [b] Reflectance spectra.

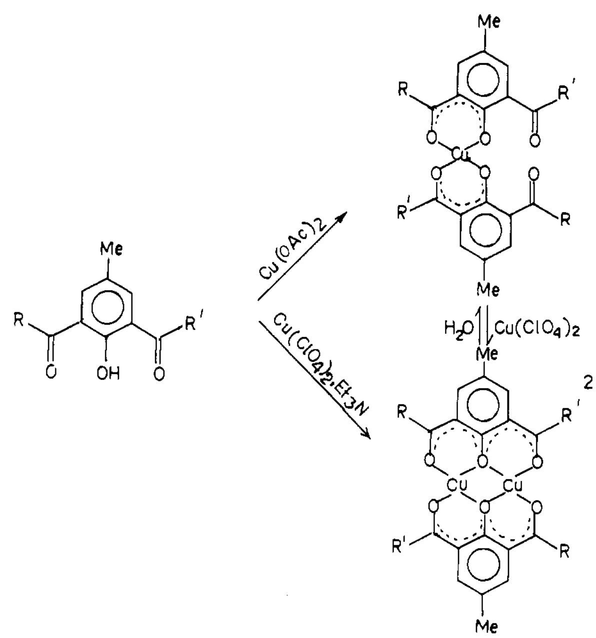
Electrochemical Experiments. All measurements were performed under nitrogen atmosphere in DMF, which was 0.1 M in TEAP. A PAR Model 370-4 electrochemistry system was used. Cyclic voltammetry was performed with the help of a PAR 174A polarographic analyzer, a PAR 175 universal programmer, and a RE0074 X-Y recorder. The three-electrode measurements were carried out with a Metrohm E410 hanging-mercury-drop electrode (HMDE) in conjunction with a Pt-wire auxiliary electrode and a saturated calomel electrode (SCE). Constant-potential electrolysis was performed in a mercury pool with the use of a PAR 173 potentiostate and a PAR 179 digital coulometer.

Results and Discussion

Synthesis and Characterization. The mononuclear copper(II) complexes, $Cu(R,R')L_2 \cdot H_2O$, are obtained in high yields (80%) by reacting copper acetate with the ligands. These, in turn, react with copper perchlorate to form the binuclear chelates, $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$. Alternatively, the binuclear complexes are obtained by reacting copper perchlorate, the ligands, and triethylamine in the molar ratio 1:1:1. In both methods the yields are 80%. The formation of binuclear complexes takes place only in dry solvents; otherwise the products get contaminated with the corresponding mononuclear species. Spectral studies have shown that the hydrolytic decomposition of $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$ can be prevented by the addition of excess of copper perchlorate. The stability of the binuclear chelates in dry solvents has been verified by following Beer's law over a 20-fold change in concentration. The reaction sequences are shown in Scheme I. The labile nature of the phenoxide bridge in these compounds is in contrast to the stability of the binuclear copper(II) complexes obtained by condensing (H,H)HL with amine derivatives.[28,29] This shows that the carbonyl groups are not as good donors for copper(II) as the azomethines are.

The molar conductivities of $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$ (Table II) are typical of those of 1:2 electrolytes. The room-temperature magnetic moments (Table II) of $Cu(R,R')L_2 \cdot H_2O$ range from 1.8 to 2.0 μ_B, which are close to the values normally observed for magnetically discrete copper(II) complexes.[30]

Scheme I



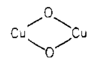
The moments of the binuclear complexes (0.9–1.2 μ_B) on the other hand show strong antiferromagnetic interaction between the copper centers. Pending a detailed magnetic study, which is under way, suffice it to say here that the observation is consistent with other related phenoxo-bridged copper(II) complexes.[14,18]

Electronic Spectra. In the ultraviolet region both the mono- and binuclear copper(II) complexes show two absorption bands at 350 and 410 nm. Only the 350-nm band is observed in the free ligands. The 410-nm absorption probably arises due to a combination of the intraligand transition and ligand to metal charge-transfer (CT) transition. Similar CT bands in the range 380–430 nm have been reported[14,31] in several oxo-

(29) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1759.

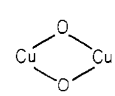
(30) Hathaway, B. J.; Billig, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

Table III. Infrared Spectral Data (cm^{-1}) of Ligands and Copper(II) Complexes

compd	ν(C=O) free	ν(C┄O) H/Cu bonded	ν(C┄O) phenolic	
(H,H)HL	1670	1658		
$Cu(H,H)L_2 \cdot H_2O$	1675	1622	1535	
$Cu_2(H,H)L_2(ClO_4)_2 \cdot 2H_2O$		1627	1540	508
(Me,Me)HL	1668	1638		
$Cu(Me,Me)L_2 \cdot H_2O$	1645	1575	1527	
$Cu_2(Me,Me)L_2(ClO_4)_2 \cdot 2H_2O$		1585	1532	505
(Pr,Pr)HL	1650	1628		
$Cu(Pr,Pr)L_2 \cdot H_2O$	1650	1570	1520	
$Cu_2(Pr,Pr)L_2(ClO_4)_2 \cdot 2H_2O$		1585	1530	505
(Ph,Ph)HL	1655	1620		
$Cu(Ph,Ph)L_2 \cdot H_2O$	1645	1570	1505	
$Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$		1580	1520	495
(Ph,Me)HL	1660	1630		
$Cu(Ph,Me)L_2 \cdot H_2O$	1640	1585	1525	
$Cu_2(Ph,Me)L_2(ClO_4)_2 \cdot 2H_2O$		1590	1530	505

bridged copper(II) complexes. In the visible region the mononuclear complexes in DMF and chloroform solutions display an asymmetric band, which can be deconvoluted into two maxima near 660 and 710 nm. The spectral features of these compounds in solid state are essentially the same although the broad maxima at 660 nm could not be resolved. The electronic spectra of the mononuclear complexes may be compared with copper(II) bis(β-diketonates), several of which show broad absorption bands in the range 500–700 nm. Their polarized spectra have been explained in terms of planar C_{2h} or D_{2h} symmetry.[32,33] The axial EPR spectra of copper(II) β-diketonates, however, have been interpreted in terms of D_{4h} symmetry.[34] The EPR spectra of undiluted $Cu(R,R')L_2 \cdot H_2O$ do not show any hyperfine splitting, but the values of g tensors ($g_\perp$ = 2.054–2.059; $g_\parallel$ = 2.25–2.27) are very close to those reported for a number of copper(II) β-diketonates. The binuclear complexes in acetone in DMF, and in solid state show a single absorption band in the region 750–770 nm, the position of which remains unaffected due to the change of medium. The displacement of the absorption band in the binuclear complexes to a higher wavelength relative to that in the mononuclear complexes indicates that the steric environments in these two type of compounds are not exactly same. It appears that while the mononuclear complexes are square planar, there is slight tetrahedral distortion in the binuclear compounds. This is supported by the fact that the introduction of tetrahedral distortion in square-planar copper(II) complexes causes a shift in the absorbance to a higher wavelength.[35]

Infrared Spectra. Pertinent IR data of the complexes are shown in Table III. All of the complexes show a broad band around 3400 cm^{-1} due to the water molecules. Of particular interest are the C═O stretchings, which are diagnostic of the purity of the complexes. The ligands show two C═O stretchings, one due to free C═O and the other due to hydrogen-bonded C═O. In $Cu(R,R')L_2 \cdot H_2O$ also, two such bands are observed. The metal-bound carbonyl is shifted to lower frequency with respect to the hydrogen-bonded one by about 40–60 cm^{-1}, whereas the free carbonyl is at 10–15 cm^{-1} lower energy in the complexes. As expected in $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$, the two carbonyl bands coalesce into one, which, however, is consistently shifted to a slightly higher frequency by 5–15 cm^{-1} from the corresponding bonded carbonyl of the mononuclear chelates. This implies more double-bond character of C┄O in $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$. A phenyl ring vibration at 1600 cm^{-1} is observed in the ligands as well as in complexes. Another strong band in the region 1505–1540 cm^{-1} is observed in both types of complexes, but not in the ligands. This band is found to be present in the binuclear macrocyclic chelates obtained by condensing (R,R')HL with 1,3-diaminopropane but vanishes when the double bonds of the macrocyclic ring systems are fully reduced.[36] On the basis of this observation we confidently assign this band as due to C┄O of the phenolic part, which becomes partially double bonded as a sequel of conjugation in the chelate ring. It may be noted that this band is located at a frequency 5–15 cm^{-1} higher in $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$ relative to that in $Cu(R,R')L_2 \cdot H_2O$. The positive shift in frequency is expected because of the augmentation of double-bond character of the phenolic C—O due to conjugation from both compartments of the chelate rings. However, the shift is not that much, as one would expect if delocalization occurs to the same extent as in the mononuclear complexes. In $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$, bands related to ionic perchlorate are present in the region 1100 cm^{-1} (broad) and at 620 cm^{-1} (sharp) but the intense absorption band around 930 cm^{-1}, indicative of coordinated perchlorate,[37] is absent. An interesting feature in the binuclear complexes is the presence of a sharp new band at 500–510 cm^{-1}, which probably arises due to a certain mode of



vibration.

Table IV. Electrochemical Data of Copper(II) Complexes

complex[a]	$E_{1/2}$,[b] V (vs. SCE)	ΔE_p,[c] mV	$I_{p,c}/I_{p,a}$
$Cu_2(H,H)L_2(ClO_4)_2 \cdot 2H_2O$	−0.038	95[d]	0.88
$Cu_2(Me,Me)L_2(ClO_4)_2 \cdot 2H_2O$	−0.046	95[d]	0.92
$Cu_2(Pr,Pr)L_2(ClO_4)_2 \cdot 2H_2O$	−0.049	75[d]	0.92
$Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$	−0.041	42[d]	0.97
$Cu_2(Ph,Me)L_2(ClO_4)_2 \cdot 2H_2O$	−0.045	42[d]	0.95
$Cu(Ph,Ph)L_2 \cdot H_2O$	−0.43	100[e]	1.05
$Cu(Pr,Pr)L_2 \cdot H_2O$	−0.43	130[e]	1.08

[a] 1 mmol of the complex in DMF (0.1 M TEAP) was used. [b] $E_{1/2} = 0.5(E_{p,c} + E_{p,a})$. [c] $\Delta E_p = (E_{p,a} - E_{p,c})$. [d] Scan rate 200 mV/s. [e] Scan rate 50 mV/s.

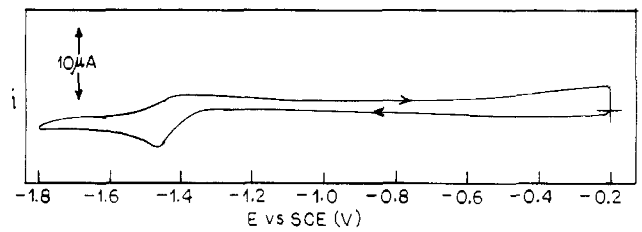


Figure 1. Cyclic voltammogram of $Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$ (~1 mM) in DMF at 200 mV/s.

Electrochemistry. All electrochemical results presented here (Table IV) were obtained in DMF solutions (in 0.1 M TEAP) with use of a HMDE, and the potentials reported are vs. SCE. Figure 1 shows the cyclic voltammogram (CV) of $Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$ scanned in the potential range −0.2 to −1.8 V. In this region the CV is characterized by single irreversible reduction at ≃−1.45 V. A similar irreversible wave was ob-

(31) Nishida, Y.; Kida, S. *J. Inorg. Nucl. Chem.* **1976**, *38*, 451. Nishida, Y.; Numata, F.; Kida, S. *Inorg. Chim. Acta* **1974**, *11*, 189.
(32) Belford, R. L.; Carmaichael, J. W. *J. Chem. Phys.* **1967**, *46*, 4515.
(33) Hathaway, B. J.; Billig, D. E.; Dudley, R. J. *J. Chem. Soc. A* **1970**, 1420.
(34) Fackler, J. P.; Levy, J. D.; Smith, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2436.
(35) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968; p 355.
(36) Mandal, S. K.; Nag, K., to be submitted for publication.
(37) (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd. ed.; Wiley-Interscience: New York, 1978. (b) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331.

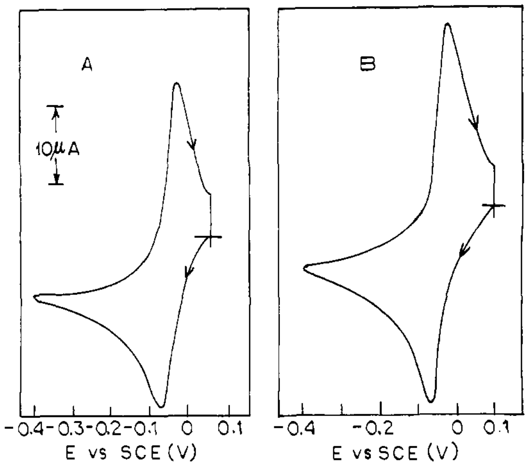


Figure 2. (A) Cyclic voltammogram of $Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$ (~1 mM) in DMF at 200 mV/s. (B) Cyclic voltammogram of $Cu_2(Ph,Me)L_2(ClO_4)_2 \cdot 2H_2O$ (~1 mM) in DMF at 200 mV/s.

served for $Cu(Ph,Ph)L_2 \cdot H_2O$ and (Ph,Ph)HL in the vicinity of −1.5 V, showing that at this potential reductions of the copper(I) species and the ligand moiety take place concurrently.

Figure 2 shows the cyclic voltammograms of $Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$ (A) and $Cu_2(Ph,Me)L_2(ClO_4)_2 \cdot 2H_2O$ (B) in the potential range +0.10 to −0.4 V. In each case, the electron-transfer process is reversible, as is evident from the equal heights of the cathodic and anodic waves and a separation of 42 mV of the peak potentials (ΔE_p) that remains invariant with scan rate. A good linear correlation obtained between the cathodic peak current and the square root of the scan rate when varied from 20 to 500 mV/s corroborated the reversible behavior.[38]

In a binuclear copper(II) complex, if the sequential electron-transfer processes are represented as

$$Cu^{II}\text{–}Cu^{II} + e^- \underset{}{\overset{E^f_1}{\rightleftharpoons}} Cu^{II}\text{–}Cu^{I} \quad (1)$$

$$Cu^{II}\text{–}Cu^{I} + e^- \underset{}{\overset{E^f_2}{\rightleftharpoons}} Cu^{I}\text{–}Cu^{I} \quad (2)$$

the net result would be the transfer of two electrons at a single potential when $E^f_1 \simeq E^f_2$. The electrochemical behavior of molecules that contain two or more chemically equivalent electroactive sites has been the subject of a number of studies.[39-41] Polcyn and Shain[39] predicted that for reversible sequential transfer of two electrons the ΔE_p in the CV will be 42 mV. In contrast, according to Anson et al.,[41] CV's for molecules with multiple, noninteracting redox centers will be similar to those of the corresponding species with a single center, and ΔE_p should be 58 mV. However, they pointed out[41] that departures from the above generalization may occur due to a variety of reasons; among these, electronic interaction between two centers will be a major one.

The gross redox behavior of the other three binuclear complexes are similar and is exemplified by the voltammogram of $Cu_2(Me,Me)L(ClO_4)_2 \cdot 2H_2O$ (Figure 3). However, they are not truly reversible systems as evident from larger ΔE_p values (Table IV). In these compounds the ratio of cathodic and anodic currents deviates slightly from 1 in the slow scanning range (≤200 mV/s). The voltammograms become symmetric at higher scan rates (≥500 mV/s), but in the case of $Cu_2(H,H)L_2(ClO_4)_2 \cdot 2H_2O$ it is difficult to get rid of the

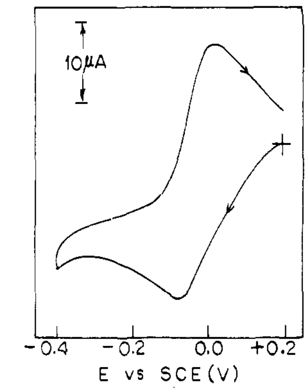


Figure 3. Cyclic voltammogram of $Cu_2(Me,Me)L_2(ClO_4)_2 \cdot 2H_2O$ (~1 mM) in DMF at 200 mV/s.

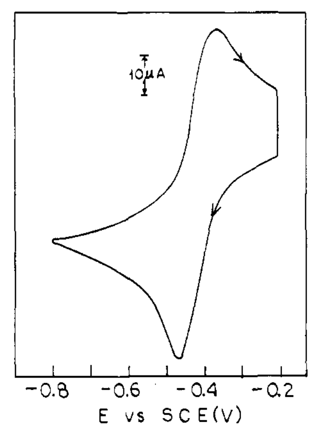
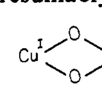


Figure 4. Cyclic voltammogram of $Cu(Ph,Ph)L_2 \cdot H_2O$ (~1 mM) in DMF at 100 mV/s.

asymmetric currents even at 1 V/s. Nevertheless, the coulometric studies (at −0.3 V) have established $n = 2 \pm 0.1$ for these compounds, including the diformyl derivative. The green solution of $Cu_2(Ph,Ph)L_2(ClO_4)_2 \cdot 2H_2O$ and $Cu_2(H,H)L_2(ClO_4)_2 \cdot 2H_2O$ on constant-otential electrolysis at −0.3 V turned to a straw color, which lacked absorbance in the range 1000–500 n, thus indicating the absence of any copper(II) center. A new band presumably due to



was observed at 470 nm (ϵ = 1750 M^{-1} cm^{-1} for the dibenzoyl derivative and ϵ = 1100 M^{-1} cm^{-1} for the diformyl compound).

The substituents seemingly show little effect on the $E_{1/2}$ values of the complexes. The small variations that exist in the series may be compared with the change in pK_a of the ligands. The pK_a values[42] are as follows: (H,H)HL, 6.94; (Me,Me)HL, 9.78; (Pr,Pr)HL, 10.15; (Ph,Me)HL, 9.63; (Ph,Ph)HL, 9.29. A close inspection of these values reveals that, except for the case with (H,H)HL (for which the pK_a is rather too low), $E_{1/2}$ values of the complexes increase with increase in pK_a values of the ligands.

The electrochemical studies of $Cu(Ph,Ph)L_2 \cdot H_2O$ and $Cu(Pr,Pr)L_2 \cdot H_2O$ were carried out to delineate their difference in redox behavior vis-à-vis the coupled systems. Figure 4 shows the cyclic voltammogram of $Cu(Ph,Ph)L_2 \cdot H_2O$. The results (shown in Table IV) indicate that the mononuclear complexes undergo quasi-reversible reduction at a relatively more negative potential. The peak separations vary from 100 to 125 mV (Ph,Ph), and from 130 to 160 mV (Pr,Pr) at the scan rates

(38) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(39) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.
(40) Ammer, F.; Saveant, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 115, 215.
(41) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(42) The pK_a values were determined spectrophotometrically at 25 °C in aqueous solution (containing 2% of acetone) at an ionic strength of 0.05 M (KCl).

of 50 and 200 mV/s, respectively.

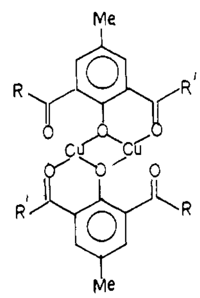
In a discussion of the redox behavior of binuclear copper(II) complexes, the conproportionation constant, K_{con}, which is related as follows, is taken into consideration.[12]

$$Cu^{II}-Cu^{II} + Cu^{I}-Cu^{I} \xrightleftharpoons{K_{con}} 2Cu^{II}-Cu^{I}$$

$$\log K_{con} = (E^{f}_{1} - E^{f}_{2})/0.0591$$

When the mixed-valent species is highly unstable with respect to disproportionation, K_{con} tends to zero and $E^{f}_{1} \simeq E^{f}_{2}$. It has been pointed out[12] that, for such a case to occur, the two copper centers during reduction should undergo a change either chemically or geometrically. Since a chemical change is unlikely to take place in the system under consideration, we are left with the possibility of geometrical change.

A conformal change can be brought about inter alia by bond breaking or rotation about a bond. The possiblity of bond breaking in $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$ cannot be ruled out in view of the fact that carbonyl oxygen is a poor donor for copper(I). If bond breaking does occur, the reduced species would be **3**. Unfortunately we could not isolate the cuprous



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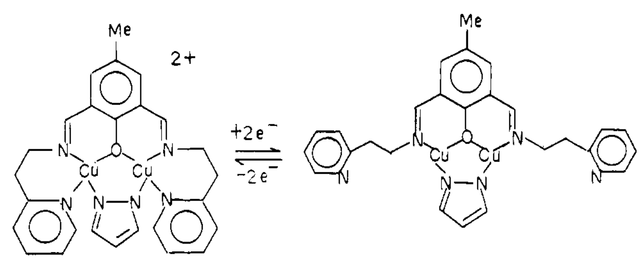
complexes in solid state from DMF solution as generated by constant-potential electrolysis. The formation of **3** could have been easily verified from their IR spectra. On the other hand, even in systems related to **4** where bond breaking is believed



4

to take place during electron transfer, two distinct, one-electron redox processes have been observed.[13] This shows that bond breaking does not necessarily lead to a single-step two-electron reduction of $Cu^{II}-Cu^{II}$ complex. It is possible, however, that a much faster rate of electron transfer compared to that of the bond-breaking process decides the nature of redox behavior.

In the case of $Cu_2(TKO)_2$ Fenton and Lintvedt[15] suggested that each triketonate moiety undergoes rotation in opposite directions on going from $Cu^{II}-Cu^{II}$ to $Cu^{I}-Cu^{I}$; as a result, significant tetrahedral character develops about the copper. The known preference of copper(I) for a tetrahedral site is well documented.[43] We have already indicated (see Electronic Spectra) that in $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$ the copper atoms are in slightly tetrahedrally distorted planar environment. Therefore, further distortion during electron transfer seems quite probable. Moreover, bond distortion may even cause the rupture of copper(I)–oxygen (carbonyl) bond leading to the formation of **3**.

A relevant question that needs to be answered is why the redox potentials of the binuclear chelates are less negative than the mononuclear chelates, even though they contain the same donor atoms. The answer may be 2-fold. In the first place, the binuclear complexes are cationic; therefore, purely on electrostatic grounds one would expect easier reduction of these species. Second, as we have pointed out earlier, the electron transfer will be more facile in the binuclear complexes due to their favored stereochemical configuration.

The present study has established that the $Cu^{II}{}_2O_6$ core is indeed responsible for the sequential two-electron transfer at a single potential. Another significant aspect is the relatively less negative redox potentials of these compounds. The difference in the redox potentials between $Cu_2(R,R')L_2(ClO_4)_2 \cdot 2H_2O$ ($E_{1/2} = -0.05$ V) and $Cu_2(TKO)_2$ ($E_{1/2} = -0.45$ to -0.65 V) is remarkable. Our values may be compared with the known redox potentials of type 3 coppers in copper proteins:[2] for example, 0.36 V for mushroom tyrosinase, 0.46V for *Rhus* laccase, and 0.76 V for fungal laccase.

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Registry No. **2** (R = R' = H), 86373-06-0; **2** (R = R' = Me), 86373-07-1; **2** (R = R' = Pr), 86373-09-3; **2** (R = R' = Ph), 86373-11-7; **2** (R = Ph, R' = Me), 86373-13-9; Cu(H,H)L_2, 30222-96-9; Cu(Me,Me)L_2, 30012-27-2; Cu(Pr,Pr)L_2, 86373-02-6; Cu(Ph,Ph)L_2, 86373-03-7; Cu(Ph,Me)L_2, 86373-04-8.

(43) Jardine, F. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.