

neutral alumina and were distilled and stored under N<sub>2</sub> in the dark. The oxidants, 10% NaClO in H<sub>2</sub>O (Carlo Erba), Na<sub>2</sub>BO<sub>3</sub>·4H<sub>2</sub>O (Fluka), 80% *tert*-butyl hydroperoxide (Fluka) and Oxone (Janssen) were commercial products and used without purification. Where necessary the solutions containing the oxidants were titrated iodometrically. Where not available commercially, the epoxide products were prepared by literature procedure.<sup>26</sup> The catalysts [(diphoe)Pt(CF<sub>3</sub>)(CH<sub>2</sub>Cl<sub>2</sub>)](BF<sub>4</sub>) and (diphoe)-Pt(CF<sub>3</sub>)(OH) were prepared according to already described methods.<sup>26</sup> The dmpe derivatives were prepared from (PPh<sub>3</sub>)<sub>2</sub>Pt(CF<sub>3</sub>)Cl<sup>27</sup> according to the following procedure.

**(dmpe)Pt(CF<sub>3</sub>)Cl.** To a suspension of *trans*-(PPh<sub>3</sub>)<sub>2</sub>Pt(CF<sub>3</sub>)Cl (0.40 g, 0.48 mmol) in THF (20 mL) was added in one portion dmpe (0.075 g, 0.50 mmol), and the reaction mixture was stirred at room temperature for 2 days. After this time a white solid formed. The solution was concentrated under reduced pressure to about 10 mL. The solid was filtered off, washed with *n*-pentane (3 × 2 mL), and dried in vacuo. Yield: 60%. Anal. Calcd (found): C, 18.70 (18.75); H, 3.59 (3.62). IR (Nujol): 279 cm<sup>-1</sup> (Pt-Cl). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -25.50, (dd), <sup>3</sup>J<sub>FP<sub>trans</sub></sub> = 10.0 Hz, <sup>3</sup>J<sub>FP<sub>trans</sub></sub> = 58.2 Hz, <sup>2</sup>J<sub>FP<sub>trans</sub></sub> = 566 Hz. <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 29.0 (dq, *trans* CF<sub>3</sub>), <sup>3</sup>J<sub>PF</sub> = 58.2 Hz, <sup>2</sup>J<sub>PP</sub> = 3.7 Hz, <sup>1</sup>J<sub>PP<sub>trans</sub></sub> = 1825 Hz; δ 23.1 (dq, *cis* CF<sub>3</sub>), <sup>3</sup>J<sub>PF</sub> = 10.0 Hz, <sup>2</sup>J<sub>PP</sub> = 3.7 Hz, <sup>1</sup>J<sub>PP<sub>cis</sub></sub> = 3745 Hz.

**(dmpe)Pt(CF<sub>3</sub>)(CH<sub>2</sub>Cl<sub>2</sub>)BF<sub>4</sub>.** (dmpe)Pt(CF<sub>3</sub>)Cl (0.30 g, 0.67 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and the solution was carefully degassed. A 0.68-mL aliquot of a 1 M solution of AgBF<sub>4</sub> in acetone was added dropwise. The mixture was stirred for 1 h, AgCl was filtered off, and the filtrate was brought to dryness in vacuo. The white solid obtained is very hygroscopic and can be stored under a dry N<sub>2</sub> atmosphere. Yield:

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(27) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* 1979, 175, 239.

95%. Anal. Calcd (found): C, 16.40 (16.31); H, 3.10 (3.14).

**Catalytic Reactions.** These were carried out in a 25- or 50-mL round-bottomed flask equipped with a stopcock for vacuum/N<sub>2</sub> operations and a side-arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (25 °C) was maintained by water circulation through an external jacket connected with a thermostat. For reactions at 83 °C the reactors were unjacketed to allow heating through an external oil bath and equipped with a reflux condenser. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer.

Absence of diffusional problems below 1.0 × 10<sup>-4</sup> M s<sup>-1</sup> initial rates was determined by the independence of conversion vs time plots on the stirring rate on experiments randomly selected from Figure 3.

The general procedure here reported was followed in all cases. In a typical experiment the appropriate amount of solid catalyst was placed in the reactor, which was evacuated and placed under N<sub>2</sub> atmosphere. Dry, N<sub>2</sub>-saturated CH<sub>2</sub>Cl<sub>2</sub> was added, followed by 1-octene. After a few minutes of stirring, the oxidant solution was injected and the time was started. In reactions carried out at 83 °C, DCE was used as solvent instead of CH<sub>2</sub>Cl<sub>2</sub>, and after the usual procedure, the reaction mixture was rapidly brought to reflux. The conversion was monitored by sampling periodically the reaction mixture with a microsyringe.

**Acknowledgment.** Financial support from the Consiglio Nazionale delle Ricerche (Rome) through the "Progetto Finalizzato Chimica Fine II" is gratefully acknowledged.

**Registry No.** 1, 98839-55-5; 2, 70504-87-9; dmpe, 23936-60-9; *trans*-(PPh<sub>3</sub>)<sub>2</sub>Pt(CF<sub>3</sub>)Cl, 71581-10-7; (dmpe)Pt(CF<sub>3</sub>)Cl, 118017-52-0; (dmpe)Pt(CF<sub>3</sub>)(CH<sub>2</sub>Cl<sub>2</sub>)BF<sub>4</sub>, 118017-54-2; *tert*-butyl hydroperoxide, 75-91-2; potassium hydroperoxysulfate, 10058-23-8; 1-octene, 111-66-0; 1-hexene, 592-41-6; styrene, 100-42-5; *cis*-4-methyl-2-pentene, 691-38-3; allyl methacrylate, 96-05-9; allyl chloride, 107-05-1; propylene, 115-07-1; cyclooctene, 931-88-4; allylbenzene, 300-57-2; sodium hypochlorite, 7681-52-9; sodium perborate, 7632-04-4.

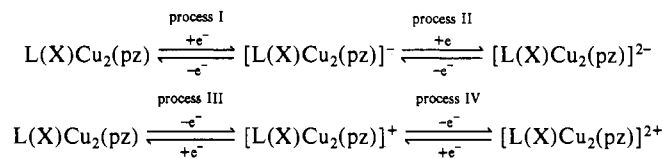
Contribution from the Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds 3217, Victoria, Australia, and Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Victoria, Australia

## Effects of Replacing Oxygen by Sulfur at the Endogenous Bridging Center on the Redox Properties of Binuclear Copper(II) Complexes

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The comparative voltammetry of the binuclear complexes L(O)Cu<sub>2</sub>(pz) and L(S)Cu<sub>2</sub>(pz) at mercury, platinum, gold, and glassy-carbon electrodes in dichloromethane, tetrahydrofuran, dimethylformamide, and propyl cyanide has enabled the influence of the endogenous bridging center on the redox properties to be examined in detail when oxygen (O) is replaced by sulfur (S). Each of the complexes exhibits an extended one-electron-transfer series:



X = O, S; L(X)<sup>3-</sup> = binucleating ligand component; pz = pyrazolate bridge

In the noncoordinating solvent dichloromethane, reduction processes I and II for L(O)Cu<sub>2</sub>(pz) are well separated but are electrolyte- and electrode-dependent. With L(S)Cu<sub>2</sub>(pz), although the first reduction process occurs at a more negative potential than is the case with the oxygen analogue, the separation between processes I and II is significantly less. In dichloromethane, [L(X)Cu<sub>2</sub>(pz)]<sup>2-</sup> is not stable even on the voltammetric time scale. However, in more polar solvents, nonspecific solvent terms provide increased stability. In contrast to the large separation in reduction process I and II, oxidation processes III and IV are not resolved in dichloromethane with L(O)Cu<sub>2</sub>(pz) and barely resolved for L(S)Cu<sub>2</sub>(pz), with the sulfur-bridged species being easier to oxidize than the oxygen-bridged complex. In polar coordinating solvents, the separation in the two oxidation potentials is increased. However, the stability of [L(X)Cu<sub>2</sub>(pz)]<sup>+</sup> and [L(X)Cu<sub>2</sub>(pz)]<sup>2+</sup> is decreased significantly by solvent-specific terms.

### Introduction

The redox properties of binuclear copper complexes, Cu<sub>2</sub>L, have received much attention in recent years, particularly with respect to studies endeavoring to understand and mimic the redox function

of copper proteins.<sup>4</sup> The nature of the coordination environment of the copper is important in determining the redox properties. Oxygen, nitrogen, and sulfur centers have all been considered as

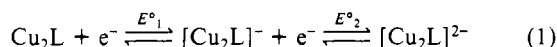
(1) Deakin University.

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(3) University of Melbourne.

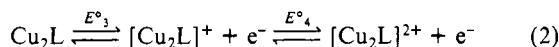
(4) (a) Solomon, E. I. *Copper Proteins*; Spiro, T. G., Ed.; Wiley: New York, 1981; Chapter 2. (b) Karlin, K. D., Zubieta, J., Eds. *Copper Coordination Chemistry, Biochemical and Inorganic Perspectives*; Adenine Press: Guilford, NY, 1983; pp 259, 456. (c) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* 1977, 99, 6730.

possible donors in copper proteins.<sup>4-6</sup> Standard redox potentials ( $E^{\circ}_1$  and  $E^{\circ}_2$ ) for the two one-electron-reduction processes



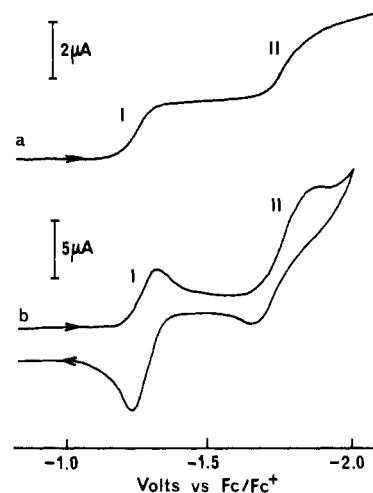
observed for dicopper(II) complexes of binucleating ligands ( $\text{Cu}_2\text{L}$  in eq 1) vary widely depending on the nature of the binucleating ligand, the coligands, and the molecular geometry.<sup>7-17</sup> In some cases  $E^{\circ}_1$  and  $E^{\circ}_2$  are essentially equal while in others they are separated by several hundred millivolts. It has been proposed that the separation between  $E^{\circ}_1$  and  $E^{\circ}_2$  is governed by the degree of interaction between the two metal (copper) centers in the mixed-valence Cu(I)/Cu(II) complex,  $[\text{Cu}_2\text{L}]^-$  in eq 1.<sup>18,19</sup> Voltammetric studies have revealed the effects of the electrolyte<sup>17</sup> and of the nature of the endogenous and exogenous bridging centers<sup>15</sup> upon  $E^{\circ}_1$  and  $E^{\circ}_2$ .

In principle, it would be expected that two oxidation processes (eq 2) as well as the two reduction processes should also be accessible. The separation between  $E^{\circ}_3$  and  $E^{\circ}_4$  would also be



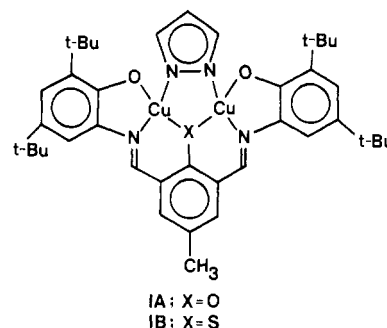
expected to be related to the intermetallic interaction in the Cu(II)/Cu(III) mixed-valence complex,  $\text{Cu}_2\text{L}^+$ . However, to date, the oxidation of dicopper(II) complexes has received little attention, which is surprising in view of the relative accessibility on the voltammetric and even synthetic time scale of mononuclear copper(III) complexes.<sup>20,21</sup> Very recently<sup>22</sup> two successive one-electron oxidations of a dicopper(II) complex of a macrocyclic binucleating ligand were reported.

The present paper describes extensive electrochemical investigations of both the reduction and oxidation of the dicopper(II)



**Figure 1.** Dc polarogram (a) and cyclic voltammogram (b) for the reduction of  $5 \times 10^{-4}$  M  $\text{L}(\text{O})\text{Cu}_2(\text{pz})$  in  $\text{CH}_2\text{Cl}_2$  (0.1 M  $(\text{TBA})\text{ClO}_4$ ) at a dropping mercury electrode at 20 °C: (a) drop time 0.5 s; (b) scan rate 200  $\text{mV s}^{-1}$  commenced 2 s after initiation of drop growth.

complexes IA and IB, which differ only in the nature of the endogenous bridging atom. The binucleating ligand components



of IA and IB will be represented as  $\text{L}(\text{O})^{3-}$  and  $\text{L}(\text{S})^{3-}$ , respectively, so that IA will be referred to as  $\text{L}(\text{O})\text{Cu}_2(\text{pz})$  and IB as  $\text{L}(\text{S})\text{Cu}_2(\text{pz})$ , where pz symbolizes the exogenous pyrazolate bridge. Most previous studies of the electrochemistry of binuclear copper compounds have been restricted to polar, coordinating solvents. The four peripheral *tert*-butyl substituents incorporated into the present complexes provide sufficient solubility in noncoordinating solvents, such as dichloromethane, to allow a wider study of the influence of solvation upon the redox processes. The electrochemistry of the corresponding matched pair of dinickel(II) complexes,  $\text{L}(\text{O})\text{Ni}_2(\text{pz})$  and  $\text{L}(\text{S})\text{Ni}_2(\text{pz})$ , was reported recently.<sup>23</sup>

### Experimental Section

**Synthesis.**  $\text{L}(\text{S})\text{Cu}_2(\text{pz})$  was prepared as described previously.<sup>24</sup>

**$\text{L}(\text{O})\text{Cu}_2(\text{pz})$ .**  $\text{L}(\text{O})\text{H}_3$  (0.60 g, 1.0 mmol), prepared as described previously<sup>23</sup> and dissolved in boiling chloroform (4  $\text{cm}^3$ ), was added to a solution of cupric acetate hydrate (0.45 g, 2.10 mmol) dissolved in boiling methanol (70  $\text{cm}^3$ ). Red crystalline  $\text{L}(\text{O})\text{Cu}_2(\text{CH}_3\text{O})$  separated immediately. The reaction mixture was maintained at the boiling point for 5 min and was then cooled to room temperature. The resulting solid was collected, washed with methanol, and dried at 80 °C under vacuum; yield 0.45 g (62%).  $\text{L}(\text{O})\text{Cu}_2(\text{CH}_3\text{O})$  obtained as described above (0.45 g, 0.62 mmol) and pyrazole (0.29 g, 4.60 mmol) in a mixture of chloroform (30  $\text{cm}^3$ ) and methanol (50  $\text{cm}^3$ ) were heated under refluxing conditions for 2 h. After the mixture had been cooled to room temperature, the suspended red crystalline solid was collected and recrystallized from chloroform/methanol. After the product was dried under vacuum at 80 °C, the yield of  $\text{L}(\text{O})\text{Cu}_2(\text{pz})$  was 0.36 g (77%). Anal. Calcd for  $\text{C}_{40}\text{H}_{50}\text{Cu}_2\text{N}_4\text{O}_3$ : C, 62.0; H, 6.9; N, 7.0%. Found: C, 62.1; H, 6.8; N, 6.6.

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**Table I.** Cyclic Voltammetric Data<sup>a</sup> for Reduction and Oxidation of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C Using a Scan Rate of 100 mV s<sup>-1</sup>

electrode	supporting electrolyte	process	$E_p$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_p$ , mV	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_{1/2}$ , V
Hg	0.1 M (TBA)ClO <sub>4</sub>	redn I	-1.310 <sup>c</sup>	80	-1.270	} 0.43
		red II	-1.805 <sup>c</sup>	210	-1.700	
GC <sup>d</sup>	0.1 M (TBA)BF <sub>4</sub>	redn II	-1.270	115	-1.215	} 0.48
		redn II	-1.780	170	-1.695	
		oxidn (III + IV)	+0.490	95	+0.445	≤0.05
		oxidn V	+1.085	irrev	(+0.975) <sup>b</sup>	
GC <sup>d</sup>	0.1 M (TBA)ClO <sub>4</sub>	redn I	-1.285	140	-1.215	
		redn II	-1.820	irrev	...	
		oxidn (III + IV)	+0.470	120	+0.410	≤0.05
		oxidn V	+1.000	irrev	...	
Pt	0.1 M (TBA)BF <sub>4</sub>	redn I	-1.415	400	-1.215	
		redn II	-2.000	irrev	...	
		oxidn (III + IV)	+0.475	85	+0.445	≤0.05
		oxidn V	+1.140	irrev	...	
Pt	0.1 M (TBA)ClO <sub>4</sub>	redn I	-1.400	320	-1.240	
		redn II	-1.930	irrev	...	
		oxidn (III + IV)	+0.470	105	+0.420	≤0.05
		oxidn V	+0.970	irrev	...	
Au	0.1 M (TBA)BF <sub>4</sub>	redn I	-1.335	250	-1.210	
		redn II	-1.845	irrev	...	
		oxidn (III + IV)	+0.475	85	+0.430	≤0.05
		oxidn V	+1.120	irrev	...	

<sup>a</sup>  $E_p$  = peak potential,  $\Delta E_p$  = peak separation for the oxidation peak and reduction peak potential,  $E_{1/2}$  = half-wave potential, calculated with the assumption that it is equal to the average of the oxidation and reduction peak potentials.  $\Delta E_{1/2}$  = separation in  $E_{1/2}$  for processes I and II or processes III and IV. TBA = tetrabutylammonium, denoted as Bu<sub>4</sub>N in the text. irrev = chemically irreversible process. <sup>b</sup> Value of  $E_{1/2}$  obtained from differential pulse voltammetry at a scan rate of 4 mV s<sup>-1</sup> and a pulse width of 60 ms and with the assumption that  $E_p = E_{1/2} - \Delta E/2$ , where  $\Delta E$  = pulse amplitude. <sup>c</sup> Dc polarography shows two one-electron-reduction steps at  $E_{1/2} = -1.260$  V vs Fc/Fc<sup>+</sup> ( $E_{3/4} - E_{1/4} = 60$  mV) and  $-1.700$  V vs Fc/Fc<sup>+</sup> ( $E_{3/4} - E_{1/4} = 100$  mV). <sup>d</sup> GC = glassy carbon.

**Reagents.** Dichloromethane of HPLC grade was used without further purification. Acetone was dried over Drierite (CaSO<sub>4</sub>). Tetrahydrofuran (THF) was dried over lithium aluminum hydride, and propyl cyanide (or butyronitrile, PrCN) was dried over phosphorus pentoxide. Dimethylformamide (DMF) was allowed to stand over alumina for 24 h, decanted, and distilled under vacuum prior to use.

Electrochemical grade tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) and tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) were purchased from Southwestern Analytical Chemicals Inc. and dried under vacuum at 70 °C for at least 8 h prior to use.

**Instrumentation.** Electrochemical measurements (cyclic voltammetry and hydrodynamic voltammetry) were performed with a BAS-100 electrochemical analyzer or a Princeton Applied Research (PAR) Model 174 polarographic analyzer connected to a Houston Instruments 2000 X-Y recorder. The working electrodes were platinum disk (Pt), glassy-carbon disk (GC), gold disk (Au), and dropping mercury (Hg). The disk working electrodes were frequently polished with an alumina/water slurry, after which they were washed with water and then with the solvent being used. This cleaning treatment is required to obtain reproducible results, particularly for the reduction processes. A Metrohm rotating-disk-electrode assembly, Model 628-10, was used for the hydrodynamic voltammetry.

A platinum-wire auxiliary electrode was used, and the Ag/AgCl (saturated LiCl in acetone) reference electrode was separated from the test solution by a salt bridge containing the same solvent and supporting electrolyte as the test solution. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) oxidation process was used as a reference standard by frequently measuring the potential for oxidation of a  $5 \times 10^{-4}$  M solution of ferrocene, and all potentials are reported vs Fc/Fc<sup>+</sup>.

Coulometry was performed at a platinum-gauze working electrode using a PAR Model 173 potentiostat and a PAR Model 179 digital coulometer. The reference electrode was the same Ag/AgCl electrode used in voltammetric experiments, and the auxiliary electrode was platinum gauze separated from the test solution by a salt bridge containing the solvent/electrolyte mixture.

## Results and Discussion

(a) **Reduction of L(O)Cu<sub>2</sub>(pz) and L(S)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub>.** Tables I and II summarize the electrochemical data.

(i) **L(O)Cu<sub>2</sub>(pz).** Figure 1 shows a dc polarogram at a dropping mercury electrode at 20 °C with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. Two reduction waves are observed with equal limiting currents per unit concentration (after background correction). The first reduction step (process I) corresponds to a reversible, diffusion-controlled one-electron transfer under con-

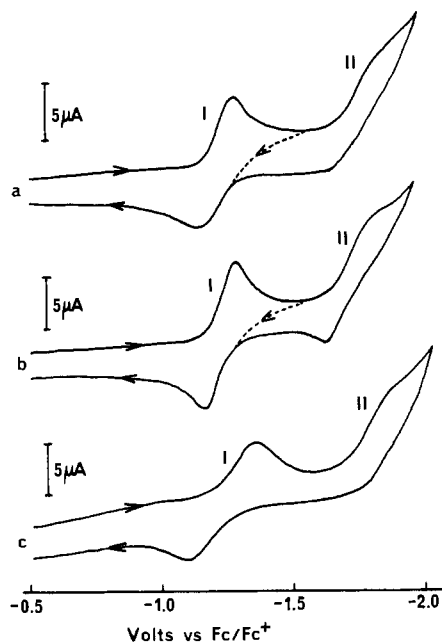
**Table II.** Cyclic Voltammetric Data<sup>a</sup> for Reduction and Oxidation of  $5 \times 10^{-4}$  M L(S)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C Using a Scan Rate of 100 mV s<sup>-1</sup>

electrode	supporting electrolyte	process	$E_p$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_p$ , mV	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_{1/2}$ , V
Hg	0.1 M (TBA)ClO <sub>4</sub>	redn I	-1.255	110	-1.200	} 0.23
		redn II	-1.510	irrev	(-1.230) <sup>b</sup>	
GC <sup>d</sup>	0.1 M (TBA)BF <sub>4</sub>	redn I	-1.315	90	-1.270	} 0.21
		redn II	-1.555	irrev	(-1.290) <sup>b</sup>	
		oxidn III	+0.375	70	+0.340	} 0.08
		oxidn IV	+0.485	70	+0.450	
		oxidn V	+1.190	irrev	(+1.150) <sup>b</sup>	
Pt	0.1 M (TBA)BF <sub>4</sub>	redn I	-1.325	110	-1.270	} 0.25
		redn II	-1.590	irrev	(-1.540) <sup>b</sup>	
		oxidn III	+0.380	65	+0.345	} 0.09
		oxidn IV	+0.485	60	+0.455	
		oxidn V	+1.210	irrev	(+1.190) <sup>b</sup>	

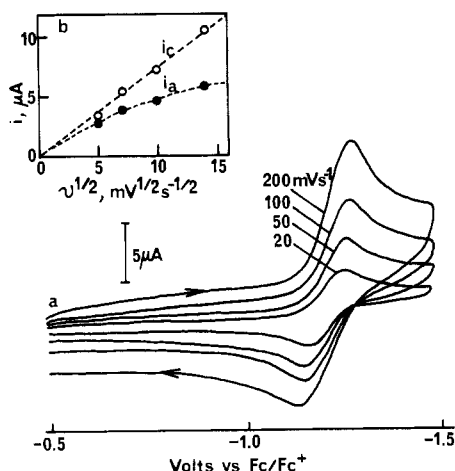
<sup>a</sup> Footnotes, symbols, and experimental parameters are the same as used in Table I.

ditions of dc polarography. That is, a plot of  $E$  versus  $\log [(i_d - i)/i]$  ( $E$  = potential,  $i$  = current,  $i_d$  = diffusion-controlled limiting current) is linear with a slope of  $60 \pm 2$  mV at 20 °C. In contrast, the second reduction step (process II) is drawn out with a plot of  $E$  versus  $\log [(i_d - i)/i]$  having a slope of  $100 \pm 10$  mV. Nevertheless, as Figure 1b demonstrates, process II has a considerable degree of chemical but not electrochemical reversibility, under conditions of cyclic voltammetry. The cyclic voltammograms at the mercury electrode were obtained at a slowly growing mercury drop electrode, so that peak heights on the reverse (oxidative) scan are larger than on the forward (reductive) scan because of the larger electrode area. Data are essentially independent of electrolyte at the dropping mercury electrode.

At a glassy-carbon electrode, cyclic voltammograms are different from those obtained at a mercury electrode and are dependent on the electrolyte. Figure 2a reveals that while process

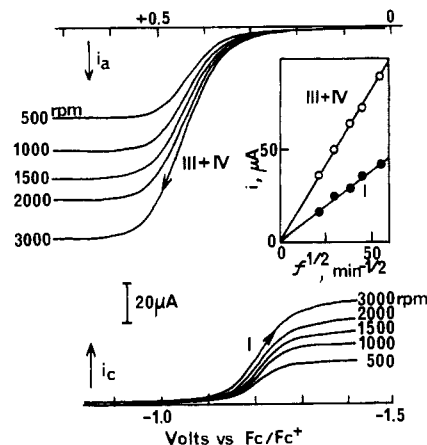


**Figure 2.** Cyclic voltammograms for the reduction of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C using a scan rate of 100 mV s<sup>-1</sup>: (a) supporting electrolyte 0.1 M (TBA)ClO<sub>4</sub>, glassy-carbon electrode; (b) supporting electrolyte 0.1 M (TBA)BF<sub>4</sub>, glassy-carbon electrode; (c) supporting electrolyte 0.1 M (TBA)BF<sub>4</sub>, Au electrode.



**Figure 3.** (a) Cyclic voltammograms for the first reduction process of L(O)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M (TBA)BF<sub>4</sub>) at a glassy-carbon electrode (scan rates indicated on the curves) and (b) plot of the peak current vs the square root of the scan rate.

I is well defined in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, it is not completely reversible with a scan rate of 100 mV s<sup>-1</sup>. Process II occurs near the solvent limit, but in contrast to the situation at a mercury electrode, the process is almost irreversible at a scan rate of 100 mV s<sup>-1</sup>. With 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> as the electrolyte, substantial differences are observed compared with the case when 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> is the electrolyte. Process II is now found to be almost chemically reversible at slow scan rates at a glassy-carbon electrode (Figure 2b). However, the scan rate dependence of the reverse oxidation peak for process I is inconsistent with a simple electron-transfer process (Figure 3) and the process becomes more irreversible in the chemical sense at faster scan rates. The data are consistent with a chemical step accompanying the electron-transfer processes at the glassy-carbon electrode surface. This process may or may not be reversible depending on the conditions. At a rotating glassy-carbon electrode processes I and II exhibit identical limiting currents per unit concentration in both perchlorate and tetrafluoroborate electrolytes and in this sense parallel the situation at the dropping mercury electrode. The dependence of the limiting



**Figure 4.** Rotating-disk voltammograms for oxidation and reduction of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M (TBA)BF<sub>4</sub>) at a glassy-carbon electrode at a scan rate of 20 mV s<sup>-1</sup> (rotation rates are shown on the curves). Plots of limiting current vs the square root of the rotation rate,  $\nu^{1/2}$ , are shown as an insert.

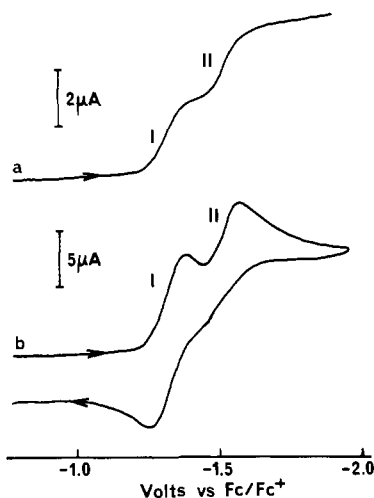
current on the rotation rate is that expected for diffusion control (see Figure 4) and is exactly half the magnitude of the well-defined two-electron-oxidation process (see later). Similarly, the linear dependence of the reduction peak heights at solid electrodes on the square root of scan rate (Figure 3) and limiting current  $t^{1/6}$  ( $t$  = drop time) polarographic drop time dependence indicate diffusion control of the mass-transfer process to the electrodes at glassy-carbon and mercury electrodes, respectively, for the reduction processes I and II.

At platinum or gold electrodes (Figure 2c) process I is very drawn out (Table I) and process II is completely irreversible in either Bu<sub>4</sub>NClO<sub>4</sub> or Bu<sub>4</sub>NBF<sub>4</sub> electrolyte. Apparently, the electron transfer rate for reduction of L(O)Cu<sub>2</sub>(pz) is slower at solid electrodes than is the case at mercury electrodes and is electrode- and electrolyte-dependent.

A possible interpretation of the electrochemical data is that the mixed-valence species [L(O)Cu<sup>I</sup>Cu<sup>II</sup>(pz)]<sup>-</sup> undergoes a secondary process after electron transfer, which for example could consist of the loss of the terminal donor of L(O)<sup>3-</sup> from the coordination sphere of the newly formed Cu(I) center. This would result in a T-shaped three-coordinate Cu(I) environment, as has been observed in a closely related system.<sup>25</sup> The two Cu(I) centers in [L(O)Cu<sub>2</sub>(pz)]<sup>2-</sup> could also have the T-shaped three-coordinate environment. A structural change not involving bond breaking is also feasible. For example, distortion to a less planar geometry of the ligand system around the copper atoms could occur after reduction. Alternatively, L(O)Cu<sub>2</sub>(pz) may have weakly bound axial electrolyte or solvent that could be lost on reduction and contribute to the complex response. Chronocoulometric data provided no evidence for reactant adsorption. Cyclic voltammetric, rotating-disk, and polarographic data are also not consistent with any strong product or reactant adsorption, so that alternative mechanisms to structural change seem less plausible. Unfortunately, no definitive structural information is available on the reduced forms of the binuclear complexes so that further speculation is unwarranted.

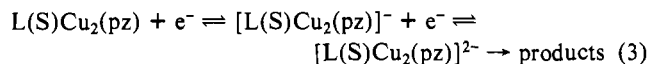
The polarographic  $E_{1/2}$  values,  $E_{1/2}$  values calculated as the average of  $(E_p^{\text{red}} + E_p^{\text{ox}})/2$  from cyclic voltammetry, and  $E_{1/2}$  calculated from the relationship  $E_{1/2} = E_p - \Delta E/2$  under conditions of differential pulse voltammetry where  $E_p$  = peak potential and  $\Delta E$  = pulse amplitude are included in Table I. The electrode and electrolyte dependences indicate that the processes are not simple reversible one-electron-reduction processes in dichloromethane.

(ii) L(S)Cu<sub>2</sub>(pz). In contrast to reduction of L(O)Cu<sub>2</sub>(pz), data contained in Figure 5 and Table II show that both processes



**Figure 5.** Dc polarogram (a) and cyclic voltammogram (b) for the reduction of  $5 \times 10^{-4}$  M  $L(S)Cu_2(pz)$  in  $CH_2Cl_2$  (0.1 M  $(TBA)ClO_4$ ) at a dropping mercury electrode at 20 °C: (a) drop time 0.5 s; (b) scan rate  $200 \text{ mV s}^{-1}$  commenced 2 s after initiation of drop growth.

I and II are essentially independent of electrode material and electrolyte. The reaction scheme can be presented as in eq 3.

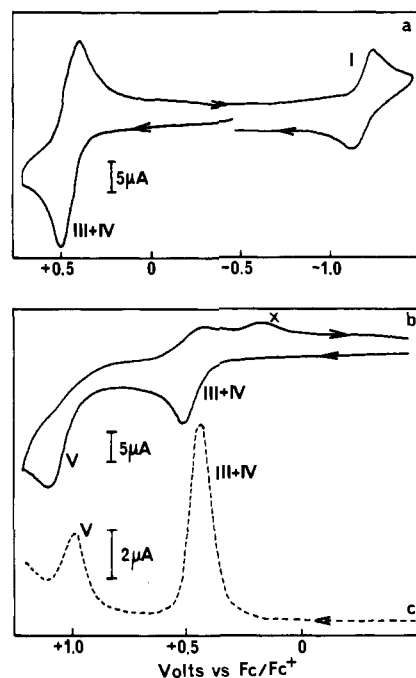


For process I under conditions of cyclic voltammetry, the ratio  $i_p^{\text{red}}/i_p^{\text{ox}}$  is close to unity at all scan rates, temperatures, and electrodes. On substitution of sulfur for oxygen, process I is shifted to a slightly more negative potential. However, process II becomes much less separated from process I in the sulfur case, leading to  $E_{1/2}$  values for process II being at a less negative potential than is the case with the oxygen analogue. Unfortunately, the irreversibility of process II means that  $E_{1/2}$  does not have direct thermodynamic significance and the significance of the differing values of  $E_{1/2}$  is therefore uncertain.

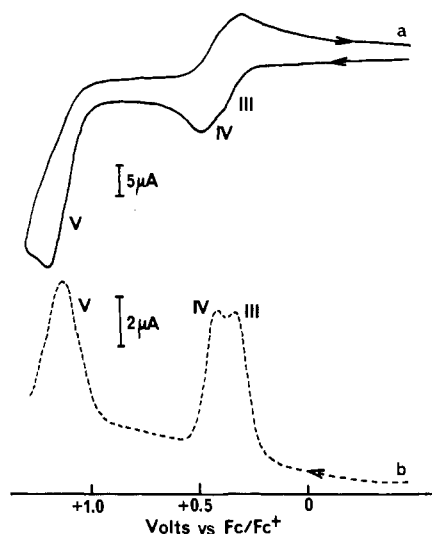
**(b) Oxidation of  $L(O)Cu_2(pz)$  and  $L(S)Cu_2(pz)$  in  $CH_2Cl_2$ .** Data are summarized in Table I and II. No strong electrode or electrolyte dependence is observed in dichloromethane. Figures 4 and 6 show that for  $L(O)Cu_2(pz)$  a chemically reversible two-electron-oxidation step (process III + process IV) at approximately 0.4 V vs  $Fc/Fc^+$  is followed by a chemically irreversible two-electron oxidation at the more positive potential of approximately 1.1 V vs  $Fc/Fc^+$  (process V). On the reverse scan (reduction scan) a new peak marked with a cross (x) in Figure 6b is observed at about 0.16 V vs  $Fc/Fc^+$  if the potential is switched at potentials more positive than in process V for the  $L(O)Cu_2(pz)$  compound. Process V is attributed to an overall ligand-based oxidation step involving fragmentation of the binuclear complex and is not discussed any further.

Evidence that the first oxidation step is a two-electron process is obtained by comparison of the relative heights of the diffusion-controlled limiting current with the one-electron-reduction steps at the rotating-disk electrode (see Figures 4 and 6a). The shape of a plot of  $E$  versus  $\log [(i_d - i)/i]$  is indicative of two unresolved one-electron-oxidation processes. The fact that two one-electron steps are present is clearly revealed in the case of oxidation of  $L(S)Cu_2(pz)$  (Figure 7), where two distinctly separated processes be directly observed by small-amplitude differential pulse voltammetry. The first one-electron-oxidation process is postulated to produce  $[L(X)Cu_2(pz)]^+$  and the second process to generate  $[L(X)Cu_2(pz)]^{2+}$  ( $X = O, S$ ).  $L(O)Cu_2(pz)$  is harder to oxidize than  $L(S)Cu_2(pz)$ .

Replacement of O by S at the endogenous bridging center has been demonstrated to have structural and/or electronic consequences that significantly influence the reduction processes. Replacement of oxygen by sulfur also influences the oxidation processes. The crystal structure of the complex analogous to  $L(O)Cu_2(pz)$  with the four *tert*-butyl groups replaced by hydrogens



**Figure 6.** Cyclic voltammograms (a, b) and differential pulse voltammogram (c) for oxidation and reduction of  $5 \times 10^{-4}$  M  $L(O)Cu_2(pz)$  in  $CH_2Cl_2$  (0.1 M  $(TBA)BF_4$ ) at a glassy-carbon electrode at 20 °C: (a, b) scan rate  $100 \text{ mV s}^{-1}$ ; (c) scan rate  $4 \text{ mV s}^{-1}$ , pulse width 60 ms, pulse amplitude 50 mV.



**Figure 7.** Cyclic voltammogram (a) and differential pulse voltammogram (b) for the oxidation of  $5 \times 10^{-4}$  M  $L(S)Cu_2(pz)$  in  $CH_2Cl_2$  (0.1 M  $(TBA)BF_4$ ) at a glassy-carbon electrode at 20 °C: (a) scan rate  $100 \text{ mV s}^{-1}$ ; (b) scan rate  $4 \text{ mV s}^{-1}$ , other parameters as in Figure 6c.

reveals an arrangement of the seven donor atoms and the two copper centers that is close to coplanar.<sup>26</sup> A similar approximately planar arrangement for  $L(O)Cu_2(pz)$  is highly likely. Copper(III),  $d^8$ , complexes often adopt a planar four-coordinate arrangement, and therefore conversion of Cu(II) to Cu(III) in forming  $[L(O)Cu_2(pz)]^+$  and  $[L(O)Cu_2(pz)]^{2+}$  need not involve significant structural change. The very similar  $E_{1/2}$  values for processes III and IV are consistent with this hypothesis.

The crystal structure of a pyrazolato-bridged dicopper(II) complex of a binucleating ligand containing an endogenous bridging thiophenoxide center very closely related to  $L(S)^3-$  but having different terminal oxygen donors was reported recently.<sup>24</sup> In this case, one copper is four-coordinate and approximately

(26) Vince, D. G. Ph.D. Thesis, University of Melbourne, 1973.

**Table III.** Voltammetric Data for Reduction of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in Different Solvents at 20 °C

solvent	supporting electrolyte	electrode	process	cyclic voltammetry				differential pulse voltammetry	
				$E_p$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_p$ , mV	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_{1/2}$ , V	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$W_{1/2}$ , mV
CH <sub>2</sub> Cl <sub>2</sub>	0.1 M (TBA)BF <sub>4</sub>	GC	I	-1.270	115	-1.215	0.48	-1.200	100
			II	-1.780	170	-1.695		-1.715	160
PrCN	0.1 M (TBA)ClO <sub>4</sub>	GC	I	-1.280	65	-1.250	0.50	-1.260	105
			II	-1.780	90	-1.735		-1.740	110
		Au	I	-1.350	230	-1.235	0.53	-1.265	225
			II	-1.900	280	-1.760		-1.785	180
		Pt	I	-1.530	485	-1.285	0.54	-1.215	250
			II	-1.935	225	-1.820		-1.815	200
DMF	0.1 M (TBA)ClO <sub>4</sub>	GC	I	-1.280	80	-1.240	0.45	-1.240	100
			II	-1.755	140	-1.685		-1.695	130
		Pt	I	-1.351	330	-1.185		<i>b</i>	<i>b</i>
			II	-1.834	irrev	irrev		<i>b</i>	<i>b</i>

<sup>a</sup>  $W_{1/2}$  is the width at half-wave height. Other symbols and experimental parameters are the same as used in Table I. In THF, the presence of adsorption precluded the calculation of accurate values of voltammetric parameters. <sup>b</sup> Broad, ill-defined response.

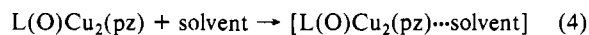
**Table IV.** Voltammetric Data<sup>a</sup> for Reduction of  $5 \times 10^{-4}$  M L(S)Cu<sub>2</sub>(pz) in Different Solvents at 20 °C

solvent	supporting electrolyte	electrode	process	cyclic voltammetry			differential pulse voltammetry	
				$E_p$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_p$ , mV	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$W_{1/2}$ , mV
CH <sub>2</sub> Cl <sub>2</sub>	0.1 M (TBA)BF <sub>4</sub>	GC	I	-1.315	90	-1.270	-1.290	110
			II	-1.555	irrev	irrev	-1.500	150
PrCN	0.1 M (TBA)ClO <sub>4</sub>	GC	I	-1.280	80	-1.240	-1.275	100
			II	-1.580	irrev	irrev	-1.530	150
THF	0.1 M (TBA)ClO <sub>4</sub>	GC	I	-1.360	115	-1.300	-1.295	140
			II	-1.645	irrev	irrev	-1.510	160
DMF	0.1 M (TBA)ClO <sub>4</sub>	GC	I	-1.250	90	-1.205	-1.200	100
			II	-1.520	irrev	irrev	-1.480	135
		Au	I	-1.315	65	-1.280	-1.275	90
			II	-1.700	irrev	irrev	-1.665	110
		Pt	I	-1.320	75	-1.280	-1.280	110
			II	-1.760	irrev	irrev	-1.650	190

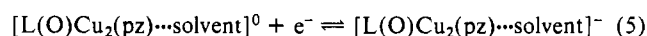
<sup>a</sup> Symbols and experimental parameters are the same as those used in Tables I and III.

planar, the other is approximately square pyramidal with a weakly coordinated apical methanol, and the sulfur center is pyramidal. It is highly likely the sulfur center in L(S)Cu<sub>2</sub>(pz) is also pyramidal, especially since pyramidal sulfur centers are to the best of our knowledge invariably observed in complexes in which simple thiolate anions, RS<sup>-</sup>, bridge two metal centers. The relatively large separation of the two one-electron-oxidation processes for L(S)Cu<sub>2</sub>(pz) compared with those for L(O)Cu<sub>2</sub>(pz) suggests that [L(S)Cu<sub>2</sub>(pz)]<sup>+2+</sup> has to undergo a greater structural rearrangement to achieve an acceptable copper(III) environment than is the case with [L(O)Cu<sub>2</sub>(pz)]<sup>+2+</sup>.

**(c) Reduction of L(O)Cu<sub>2</sub>(pz) and L(S)Cu<sub>2</sub>(pz) in Polar and Coordinating Solvents.** Figure 8, and data in Table III, and a comparison with results presented earlier reveal that a significant increase in the kinetic stability of [L(O)Cu<sub>2</sub>(pz)]<sup>2-</sup> occurs in the more polar PrCN and DMF solvents. In these solvents, process I is a simple one-electron step and process II is chemically reversible even in perchlorate electrolyte. Calculated reversible half-wave potentials ( $E_{1/2}^r$  values), which have direct thermodynamic significance, are almost independent of solvent so that the origin of the increased stability must be associated with kinetic terms arising from weak solvent interaction. Electronic spectra of L(O)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub> and DMF are only slightly different so that interactions of the kind

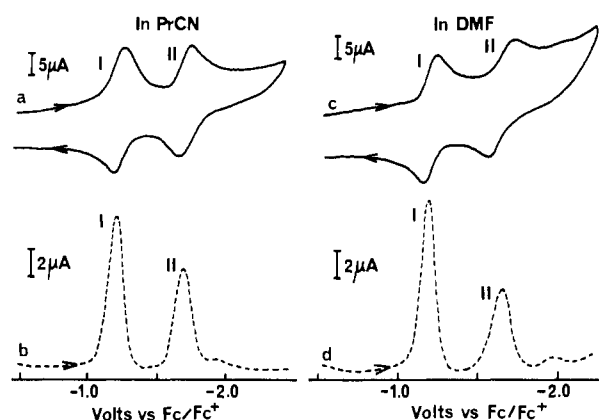


must be weak. The reduction processes in coordinating solvents can therefore be written as



with solvent effects stabilizing the reduced complexes.<sup>7</sup>

Data (Table IV) demonstrate that reduction of L(S)Cu<sub>2</sub>(pz) is essentially solvent, electrolyte, and electrode-independent in both



**Figure 8.** Cyclic voltammograms (a, c) and differential pulse voltammograms (b, d) for the reduction of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in (a, b) PrCN (0.1 M (TBA)ClO<sub>4</sub>) and (c, d) DMF (0.1 M (TBA)ClO<sub>4</sub>) at a glassy-carbon electrode: (a, c) scan rate 100 mV s<sup>-1</sup>; (b, d) scan rate 4 mV s<sup>-1</sup>, other parameters as in Figure 6c.

the kinetic and thermodynamic senses within the limit of uncertainty of the measurements and calculations. This result is consistent with the conclusion that [L(S)Cu<sub>2</sub>(pz)]<sup>-2-</sup> is less amenable to either specific or nonspecific solvent, electrolyte, and/or electrode interactions than [L(O)Cu<sub>2</sub>(pz)]<sup>-2-</sup>.

The electrode and solvent effects for reduction of L(O)Cu<sub>2</sub>(pz) are different from those reported for essentially planar dipositive copper binuclear macrocyclic ligand complexes.<sup>27,28</sup> Data reported

(27) Gagné, R. R.; Henling, L. M.; Kistenmacher, T. J. *Inorg. Chem.* **1980**, *19*, 1226.

**Table V.** Voltammetric Data<sup>a</sup> for Oxidation of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in Different Solvents at a Glassy-Carbon Electrode at 20 °C

solvent	supporting electrolyte	process	cyclic voltammetry			differential pulse voltammetry	
			$E_p$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_p$ , mV	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$W_{1/2}$ , mV
CH <sub>2</sub> Cl <sub>2</sub>	0.1 M (TBA)BF <sub>4</sub>	III + IV	+0.490	95	+0.440	+0.450	110
		V	+1.085	irrev	irrev	+0.975	105
PrCN	0.1 M (TBA)ClO <sub>4</sub>	III + IV	+0.440	140	+0.370	+0.370	145
		V	+0.870	irrev	irrev	+0.830	80
THF	0.1 M (TBA)ClO <sub>4</sub>	III + IV	+0.400	230	+0.285	+0.315	235
		V	+0.840	irrev	irrev	+0.705	140
DMF	0.1 M (TBA)ClO <sub>4</sub>	III + IV	+0.405	irrev	irrev	+0.315	135

<sup>a</sup>Symbols and experimental parameters are the same as those used in Tables I and III.

**Table VI.** Voltammetric Data<sup>a</sup> for Oxidation of  $5 \times 10^{-4}$  M L(S)Cu<sub>2</sub>(pz) in Different Solvents at a Glassy-Carbon Electrode at 20 °C

solvent	supporting electrolyte	process	cyclic voltammetry			differential pulse voltammetry		
			$E_p$ , V vs Fc/Fc <sup>+</sup>	$\Delta E_p$ , mV	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$E_{1/2}$ , V vs Fc/Fc <sup>+</sup>	$W_{1/2}$ , mV	$\Delta E_{1/2}$ , mV
CH <sub>2</sub> Cl <sub>2</sub>	0.1 M (TBA)BF <sub>4</sub>	III	+0.375	70	+0.340	+0.350	<i>b</i>	} 80
		IV	+0.485	70	+0.450	+0.430	<i>b</i>	
		V	+1.190	irrev	irrev	+1.150	170	
PrCN	0.1 M (TBA)ClO <sub>4</sub>	III	0.425 <sup>c</sup>	155 <sup>c</sup>	+0.345 <sup>c</sup>	+0.310	<i>b</i>	} 60
		IV				+0.370	<i>b</i>	
		V	+1.110	irrev	irrev	+1.060	<i>d</i>	
THF	0.1 M (TBA)ClO <sub>4</sub>	III	+0.360	80	+0.320	+0.315	<i>b</i>	} 70
		IV	+0.475	130	+0.410	+0.390	<i>b</i>	
DMF	0.1 M (TBA)ClO <sub>4</sub>	III+IV	+0.370	irrev	irrev	+0.215	135	

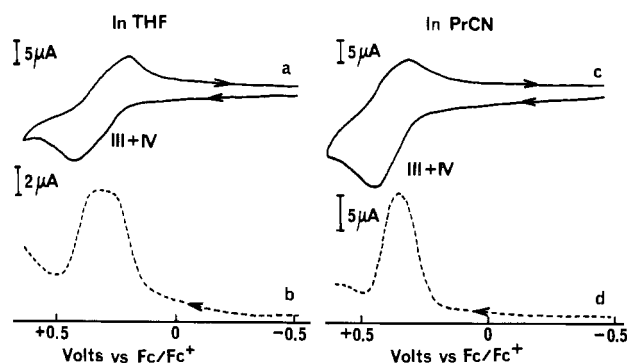
<sup>a</sup>Symbols and experimental parameters are the same as those used in Tables I and III. <sup>b</sup>Two overlapping peaks were observed so that accurate  $W_{1/2}$  values could not be obtained. <sup>c</sup>Unresolved two-electron-oxidation process. <sup>d</sup>Broad and ill-defined.

by Drago et al.<sup>7</sup> on a neutral complex, in which an oxygen bridging center is also present, show some similarities to the reduction of L(O)Cu<sub>2</sub>(pz) with respect to the electrolyte effect. However, the considerable solvent dependence of process II (thermodynamic sense) reported by Drago<sup>7</sup> is not found with the present complexes. Clearly, the bridging center and its environment plays an important role in the reduction of binuclear copper complexes.

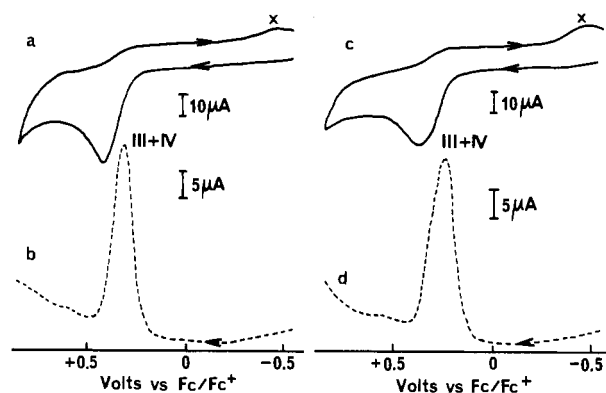
**(d) Oxidation of L(O)Cu<sub>2</sub>(pz) and L(S)Cu<sub>2</sub>(pz) in Polar and Coordinating Solvents.** Unlike the reduction processes, oxidation processes for L(O)Cu<sub>2</sub>(pz) and L(S)Cu<sub>2</sub>(pz) are significantly altered in the thermodynamic sense on changing from noncoordinating CH<sub>2</sub>Cl<sub>2</sub> to the coordinating solvents of PrCN, THF, and DMF. Additionally, changes in kinetic stability of the products of the electron-transfer processes occur.

Whereas oxidation processes III and IV are unresolved for oxidation of L(O)Cu<sub>2</sub>(pz) in CH<sub>2</sub>Cl<sub>2</sub>, the two processes are partially resolved in some coordinating solvents. Figure 9 shows this situation in PrCN and THF for oxidation of L(O)Cu<sub>2</sub>(pz), where separation occurs but with the processes remaining chemically reversible. However, in DMF, the two processes are chemically irreversible for both complexes and new processes (marked with a cross) are observed on the reverse scan of cyclic voltammograms (Figure 10). With PrCN as the solvent, the degree of chemical reversibility for oxidation of L(S)Cu<sub>2</sub>(pz) actually depends on the scan rate. At a slow scan rate of 20 mV s<sup>-1</sup>, irreversibility is observed in the chemical sense and process V is not observed. At faster scan rates, both processes III and IV become reversible, although the processes occur at slightly less positive potentials than in CH<sub>2</sub>Cl<sub>2</sub>. At scan rates in excess of 1 V s<sup>-1</sup>, process V is evident, and apart from a small shift in potential, data are similar to that in CH<sub>2</sub>Cl<sub>2</sub>.

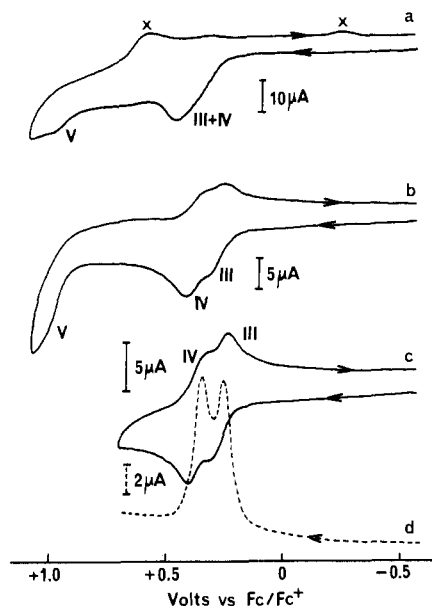
The temperature dependence of the voltammetry of L(S)Cu<sub>2</sub>(pz) in PrCN is shown in Figure 11. At ambient temperatures (Figure 11a) processes in addition to those found in CH<sub>2</sub>Cl<sub>2</sub> are present and are marked with a cross (X). At -60 °C, data parallel those observed in CH<sub>2</sub>Cl<sub>2</sub> (Figure 11b,c).



**Figure 9.** Cyclic voltammograms (a, c) and differential pulse voltammograms (b, d) for the oxidation of  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) in (a, b) THF (0.1 M (TBA)ClO<sub>4</sub>) and (c, d) PrCN (0.1 M (TBA)ClO<sub>4</sub>) at a glassy-carbon electrode: (a, c) scan rate 100 mV s<sup>-1</sup>; (b, d) scan rate 4 mV s<sup>-1</sup>, other parameters as in Figure 6c.

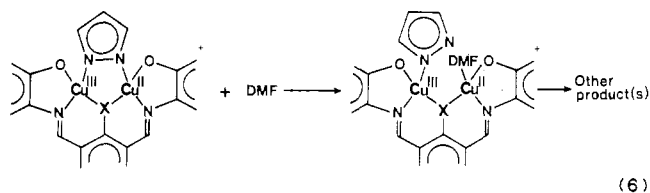


**Figure 10.** Cyclic voltammograms (a, c) and differential pulse voltammograms (b, d) for the oxidation of (a, b)  $5 \times 10^{-4}$  M L(O)Cu<sub>2</sub>(pz) and (c, d)  $5 \times 10^{-4}$  M L(S)Cu<sub>2</sub>(pz) in DMF (0.1 M (TBA)ClO<sub>4</sub>) at a glassy-carbon electrode: (a, c) scan rate 100 mV s<sup>-1</sup>; (b, d) scan rate 4 mV s<sup>-1</sup>, other parameters as in Figure 6c.

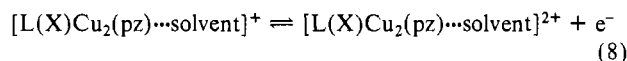
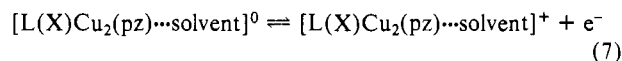


**Figure 11.** Cyclic voltammograms (a-c) and differential pulse voltammogram (d) for the oxidation of  $5 \times 10^{-4}$  M  $L(S)Cu_2(pz)$  in PrCN (0.1 M  $(TBA)ClO_4$ ) at a glassy-carbon electrode at (a) 20 °C and (b-d) -61 °C: (a-c) scan rate  $100 \text{ mV s}^{-1}$ ; (d) scan rate  $4 \text{ mV s}^{-1}$ , other parameters as in Figure 6c.

In contrast to the reduction studies, where only nonspecific solvent terms are operating, the introduction of a coordinating solvent produces significant solvent-specific terms that influence both the thermodynamic and kinetic stability of  $[L(X)Cu_2(pz)]^+$  and  $[L(X)Cu_2(pz)]^{2+}$  ( $X = O, S$ ). At ambient temperatures, the presence of a range of new processes (Figures 10a,b and 11a) suggests that fragmentation of the  $[L(X)Cu_2(pz)]^+$  occurs at the longer time scales. Equation 6 is an example of a proposed



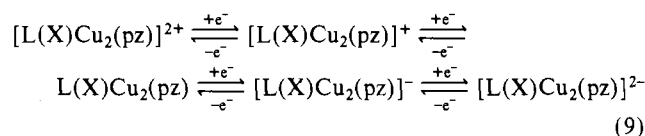
mechanism that would be consistent with the observed data. Equations 7 and 8 represent the oxidation processes at shorter



time scales, where no fragmentation occurs. Possibly, the solvent terms become more important for the copper(III) complexes than for copper(II) complexes.

**(e) Controlled-Potential Electrolysis.** Exhaustive controlled-potential electrolysis experiments at platinum-gauze working electrodes in  $CH_2Cl_2$ , THF, PrCN, and DMF showed no evidence for the formation of any of the  $[L(X)Cu_2(pz)]^{2+/-/-2-}$  complexes or other voltammetrically identified species on the synthetic time scale. That is, after long-time-scale reduction or oxidation experiments, decomposition of the products relevant to the voltammetric time scale occurs. Products of electrolysis experiments therefore bear no direct relationship on the results reported within much shorter time scale voltammetric technique. Attempts to isolate and characterize the products of controlled potential electrolysis experiments have been unsuccessful.

**(f) Conclusions.** The work described in this paper demonstrates the importance of the endogenous bridging center on the redox properties of copper binuclear complexes. For the  $L(X)Cu_2(pz)$  complexes, an extended electron-transfer series exists as in eq 9.



Substitution of oxygen for sulfur in the endogenous bridging center leads to considerable thermodynamic and kinetic differences, which can be electrolyte-, solvent-, and electrode-dependent.

**Registry No.** THF, 109-99-9; DMF, 68-12-2;  $(TBA)ClO_4$ , 1923-70-2;  $(TBA)BF_4$ , 429-42-5; Hg, 7439-97-6; GC, 7440-44-0; Pt, 7440-06-4; Au, 7440-57-5;  $CH_2Cl_2$ , 75-09-2; PrCN, 109-74-0;  $L(O)Cu_2(CH_3O)$ , 118457-98-0;  $L(O)Cu_2(pz)$ , 118457-99-1;  $L(S)Cu_2(pz)$ , 110340-79-9;  $[L(O)Cu_2(pz)]^-$ , 118458-00-7;  $[L(O)Cu_2(pz)]^{2-}$ , 118458-01-8;  $[L(S)Cu_2(pz)]^-$ , 118458-02-9;  $[L(S)Cu_2(pz)]^{2-}$ , 118458-03-0;  $[L(O)Cu_2(pz)]^+$ , 118458-04-1;  $[L(O)Cu_2(pz)]^{2+}$ , 118458-05-2;  $[L(S)Cu_2(pz)]^+$ , 118458-06-3;  $[L(S)Cu_2(pz)]^{2+}$ , 118458-07-4.