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Paul R. Sharp, and Allen J. Bard

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Contribution from the Department of Chemistry,
University of Texas, Austin, Texas 78712

Electrochemistry in Liquid Sulfur Dioxide. 6. Electrochemical Production and Isolation of Tetrakis(pyridine *N*-oxide)copper(III) Hexafluorophosphate[1]

PAUL R. SHARP*[2] and ALLEN J. BARD

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The electrochemistry of $Cu(pyO)_4^{2+}$ (pyO = pyridine *N*-oxide) in liquid SO_2 was investigated. The complex shows a quasi-reversible oxidation wave corresponding to the production of the 3+ form and a second irreversible, multielectron oxidation wave. At a given scan rate and temperature, the peak separation (ΔE_p) of the quasi-reversible wave depends upon the electrode material. The 3+ form is stable on the coulometric time scale at −30 °C and was isolated as a moisture-sensitive PF_6^- salt. Electrochemical, spectroscopic, and magnetic data support the formulation of the 3+ form as a Cu(III) complex.

Introduction

While still uncommon, a number of Cu(III) complexes have been prepared.[3] Interest in Cu(III) complexes has been stimulated by the implication of Cu(III) intermediates in biological[4] and synthetic[5] systems. A common feature of the known Cu(III) complexes is that each contains either a macrocylic or chelating ligand. No Cu(III) complexes have been reported that contain only monodentate ligands. In addition, although oxygen can be found in the coordination sphere of some Cu(III) complexes, none with only oxygen in the coordination sphere are known.

In this paper we report the electrochemical preparation of $Cu(pyO)_4^{3+}$ (pyO = pyridine *N*-oxide), which contains only oxygen in the coordination sphere and only as a monodentate ligand. The identity of this complex as a Cu(III) species is supported by ^1H NMR, EPR, magnetic, and electrochemical data. The success of the preparation depends upon the unique properties of the electrochemical solvent, SO_2, which we have previously reported.[1] Here, however, the poor coordinating ability of SO_2 is probably an important factor not previously realized.

While pyO has not previously been reported to stabilize high oxidation states, one example with bipyridine *N,N*-dioxide has been reported.[6]

Experimental Section

The electrochemical cells, equipment, electrodes, and procedures have been previously described.[7] The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate ($(TBA)PF_6$), was prepared as previously described.[8] Pyridine *N*-oxide (Aldrich) was vacuum distilled prior to use.[9] The metal complexes were prepared following the method of Carlin;[10] however, the metal salts were generated in situ (ethanol) from $Cu(OH)_2{\cdot}Cu(CO_3)$ and the appropriate acid prior to reaction with the pyridine *N*-oxide. The C, H, and N analyses were performed by Schwarzkopf Microanalytical Laboratory. NMR spectra were recorded on a Nicolet NT200 superconducting instrument. UV-vis spectra were recorded on a Cary 14 spectrophotometer as previously described.[1]

Table I. Peak Separation, ΔE_p (mV), for the Quasi-reversible 2+/3+ Couple[a]

T, °C	electrode material		
	Pt	Au	C
−20	120		100
−30	140	66	110
−40	200		132
−45	204	70	
−50	260		160
−60	350		180
−78	484	156	

[a] Scan rate 200 mV s^{-1}.

Table II. Summary of Voltammetric Parameters for the Oxidation of $Cu(pyO)_4^{2+}$ in Liquid Sulfur Dioxide[a]

diagnostic parameter	scan rate, mV s^{-1}			
	50	100	200	500
$i_p v^{1/2} C^{-1}$, $\mu A\ s^{1/2}\ V^{-1/2}\ mM^{-1}$	7.6[b]	7.5	7.1	6.0
$E_{pa} - E_{pc}$, mV	106	114	120	156
E_{pa}, V vs. AgRE	1.46	1.46	1.47	1.50

[a] 0.1 M $(TBA)PF_6$; −20 °C; Pt working area 0.017 cm^2. [b] Assuming this to be the limiting, reversible value, the diffusion coefficient is 2.3×10^{-6} $cm^2\ s^{-1}$.

Isolation of $Cu(pyO)_4(PF_6)_3$. A 0.5-g (0.68-mmol) sample of $Cu(pyO)_4(PF_6)_2$ was coulometrically oxidized at 1.5 V vs. AgRE in the presence of 0.5 g of $(TBA)PF_6$ in 20 mL of SO_2 at −30 °C. The SO_2 was removed at −30 °C by trap-to-trap distillation leaving a purple residue in the working-electrode compartment. The temperature was maintained at −30 °C, and the sample was exposed to a dynamic vacuum of 1×10^{-5} torr for 12 h after which time the sample was allowed to warm to room temperature still under vacuum. If this procedure is not followed, SO_2 occluded in the residue decomposes the product at room temperature. Dinitrogen is then admitted into the cell, and the residue is washed with dry CH_2Cl_2 to remove any remaining starting material and the supporting electrolyte. Analytical pure $Cu(pyO)_4(PF_6)_3$ remains as a moisture-sensitive, deep purple, microcrystalline solid. All manipulations of this complex must be performed in a dry, nonreducing atmosphere; yield 0.42 g (65%).

^1H NMR (SO_2/C_6D_6, 200 MHz, −40 °C): 8.43 (s, 2 H, H_α or H_β), 8.05 (s, 1 H, H_γ), 7.62 ppm (s, 2 H, H_α or H_β). J_{HH} was not observed because of paramagnetic impurity broadening.

Anal. Calcd for $CuC_{20}H_{20}N_4O_4P_3F_{18}$: C, 27.33; H, 2.39; N, 6.37; Cu, 7.22. Found: C, 27.26; H, 2.42; N, 5.80; Cu, 7.23. No EPR signal (Varian E-9) was observed in a solid sample at 30 °C nor was

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(1) Part 5: Gandiello, J. G.; Bradley, P. G.; Norton, K. A.; Woodruff, W. A.; Bard, A. J., submitted for publication in *J. Am. Chem. Soc.* Part 4: Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689–2693.

(2) Present address: Department of Chemistry, University of Missouri, Columbia, MO 65211.

(3) (a) Fabbrizzi, L.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1980**, 646–647. (b) Keyes, W. E.; Dunn, J. B. R.; Loehr, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 4527–4529. (c) Bossu, F. P.; Chellappa, K. L.; Margerum D. W. *Ibid.* **1977**, *99*, 2195–2203. (d) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126. (e) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Ibid.* 1976, *15*, 2115–2119. (f) Bour, J. J.; Birker, P. J. M. W. L.; Steggerda, J. J. *Ibid.* **1971**, *10*, 1202–1205. (g) Olson, D. C. Vasilevskis, J. *Ibid.* **1971**, *10*, 463–470. (h) Beurskens, P. T.; Cras, J. A.; Steggerda, J. J. *Ibid.* **1968**, *7*, 810–813. (i) Bour, J. J.; Steggerda, J. J. *Chem. Commun.* **1967**, *85*.

(4) Dyrkacz, G R.; Libby, R. D.; Hamilton, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 626–628.

(5) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215. Saloman, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1137.

(6) Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 338–339.

(7) (a) Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373. (b) Tinker, L. A.; Bard, A. J. *Ibid.* **1979**, *101*, 2316–2319.

(8) Geiger, W. E., personal communications as described in ref 7a.

(9) Moshor, H. S.; Turner, L.; Carlsmith, A. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 828.

(10) Carlin, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 3773–3775.

0020-1669/83/1322-3462$01.50/0

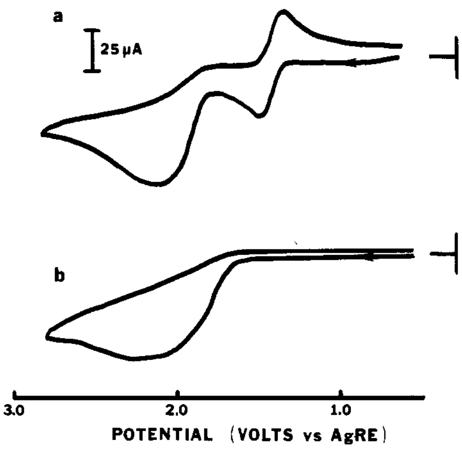

Figure 1. Cyclic voltammograms at a Pt disk electrode in liquid SO_2 (−75 °C, scan rate 500 mV s^{-1}, 0.1 M $(TBA)PF_6$): (a) $Cu(pyO)_4(ClO_4)_2$, 8 mM; (b) pyO.

any paramagnetism detected by the Evans method[11] (C_6H_6 reference, −40 °C).

Results

Cyclic Voltammetry. A blue-green solution results when $Cu(pyO)_4X_2$ ($X = ClO_4$, PF_6, BF_4) is dissolved in liquid SO_2. A typical cyclic voltammogram observed for the oxidation of $Cu(pyO)_4^{2+}$ at a Pt disk electrode is shown in Figure 1a. The anodic and cathodic peak separation (ΔE_p) for the first oxidation is scan rate (v = 20–500 mV s^{-1}) and temperature dependent.

At −20 °C, ΔE_p approaches the expected Nernstian value for a one-electron transfer and the peak current ratios (i_{pa}/i_{pc}) become essentially unity, typical behavior for a quasi-reversible electron transfer in a chemically stable system. Under these nearly Nerstian conditions, $E_{1/2}$ = 1.41 V vs. AgRE or approximately 1.6 V vs. SCE.[7] Other data are summarized in Table II. Similar behavior was observed at a Au and a C electrode; however, ΔE_p was up to 60% smaller at these electrodes at a given scan rate and temperature (Table I).

$Cu(pyO)_6^{2+}$ gave identical results; however, this compound is known to lose pyO in solution to give $Cu(pyO)_4^{2+}$.[10] Interestingly, both $Mn(pyO)_6^{2+}$ and $Ni(pyO)_6^{2+}$, which do not lose pyO in solution, showed only irreversible multielectron waves in SO_2 at about the same potential as that for the oxidation of free pyO (Figure 1b). The second oxidation wave for $Cu(pyO)_4^{2+}$ (Figure 1a), an irreversible, multielectron process, also occurs at about the same potential as that for the oxidation of free pyO. When 25 equiv of MeCN is added to a solution of $Cu(pyO)_4^{2+}$, the second oxidation wave remains unchanged while the first quasi-reversible wave completely disappears. This behavior is most readily explained by assigning the first oxidation wave to a metal-centered process, altered by coordination of MeCN, and the second oxidation wave to a ligand-centered process, unaffected by the presence of MeCN (see Discussion).

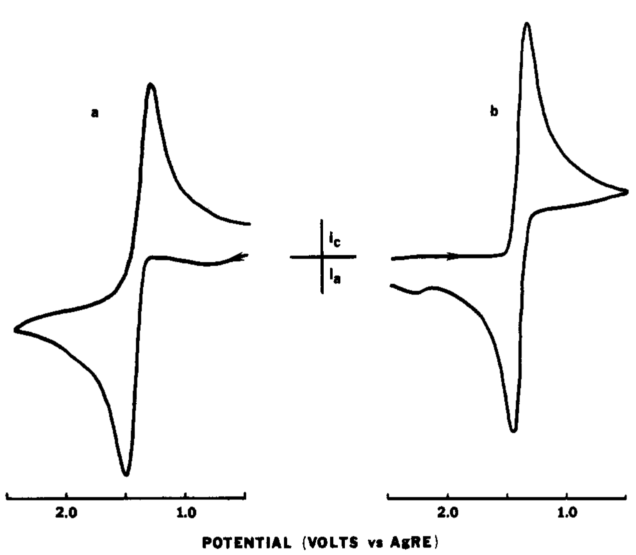

Figure 2. Cyclic voltammograms at a Pt disk of $Cu(pyO)_4(PF_6)_2$, 35 mM (−40 °C, scan rate 100 mV s^{-1}, 0.1 M $(TBA)PF_6$): (a) before and (b) after coulometric oxidation at 1.5 V vs. AgRE.

Controlled-Potential Coulometry. Controlled-potential coulometry at 1.5 V vs. AgRE on a 10 mM solution of $Cu(pyO)_4(PF_6)_2$ at −40 °C gave an n_{app} (faradays per mole of reactant consumed) of 0.97, confirming the one-electron nature of the oxidation. The chemical stability of the product is evident from the cyclic voltammograms before and after coulometry (Figure 2). The initially pale blue-green solution darkens to deep purple as the oxidation proceeds. The resulting solution of $Cu(pyO)_4^{3+}$ is stable to significant decomposition to the boiling point of SO_2 (−10 °C). However, if the temperature increases above this point in the presence of SO_2, the purple residue rapidly turns pale blue. A cyclic voltammogram of this blue product, after refilling the cell with SO_2 was identical with that of the starting Cu(II) complex, $Cu(pyO)_4^{2+}$. Similar reductions by SO_2 but at a more rapid rate have been observed in other systems.[1,7a]

Decomposition can be avoided by removing the SO_2 in vacuo at −30° C. The resulting microcrystalline, purple solid can be separated from the supporting electrolyte ($(TBA)PF_6$) by washing with dry CH_2Cl_2. The complex must be totally insoluble in CH_2Cl_2, since it reacts rapidly with CH_2Cl_2 in SO_2 solution. The purple complex also reacts rapidly with H_2O, CH_3CN, Me_2SO, CH_3NO_2, and THF both in the solid state and in solution. Decomposition occurs in minutes in moist air. The isolated complex analyzes (Cu, C, H, N) as $Cu(pyO)_4(PF_6)_3$. No EPR signal was detected in a solid sample at 30 °C, and no paramagnetism was detected by the Evans method[11] at −40 °C. In addition, the ^1H NMR of the complex in SO_2 at −40 °C showed signals for equivalent pyO ligands at shifts similar to those of the free ligand (although these signals were broadened by some residual paramagnetic starting material). Solid $Cu(pyO)_4(PF_6)_3$ is stable at 25 °C for weeks provided that care is taken to remove all traces of SO_2 by prolonged exposure to high vacuum. Heating a sample (melting point capillary in vacuo) at ~4 °C/min showed no decomposition up to 100 °C where the solid turned dark green.

The UV-vis spectrum in liquid SO_2 at −20 °C showed a single intense band centered at λ = 650 nm. The extinction coefficient, ϵ, could only be assigned a lower limit of 1×10^4 L mol^{-1} cm^{-1} because of extensive decomposition of the dilute solution at the temperature of our apparatus. Such a large ϵ indicates that this is probably a pyO to Cu charge-transfer band.

Discussion

The site of electron loss in an oxidation or electron addition in a reduction of a metal complex is frequently difficult to determine. Some oxidations previously thought to be metal centered have now been shown to be ligand centered.[12] However, the above experimental observations do suggest that the first oxidation of $Cu(pyO)_4^{2+}$ to the 3+ form is metal centered; i.e., $Cu(pyO)_4^{3+}$ is best formulated as $Cu^{III}(pyO)_4^{3+}$. The alternative possibility, that the first oxidation is ligand

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(11) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(12) (a) Phillipi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6026–6034. (b) Gans, P.; Marchon, J.-C.; Reed, C. A.; Regnard, J.-R. *Nouv. J. Chim.* **1981**, *5*, 203–204.

centered, can be argued against for the following reasons:

(1) The first oxidation of the 2+ form occurs at a potential less positive than that of the free ligand. The potential for oxidation of the coordinated ligand should be equal to or more positive than that of the free ligand because of the electrostatic effect of the 2+ charge on the complex and the stabilization of the ligand by coordination. The first oxidation therefore does not appear to be ligand centered. In addition, the second oxidation of the 2+ form occurs at a potential nearly identical with that of the oxidation of the free ligand and of the Ni(II) and Mn(II) complexes with pyO. This suggests that the second oxidation of the 2+ form is the ligand-centered oxidation.

(2) With few exceptions, Cu(III) complexes are diamagnetic, low-spin, d^8 complexes. Thus, the "normal" ^{1}H NMR spectrum, the absence of an EPR signal and the absence of any detectable paramagnetism for the 3+ form again supports its formulation as the metal-centered oxidation product, $Cu^{III}(pyO)_4^{3+}$. The alternative, ligand-centered oxidation product, $Cu^{II}(pyO^{+}\cdot)(pyO)_3^{2+}$, should be paramagnetic. However, this argument is weakened by recent work which shows that antiferromagnetic coupling of a ligand radical cation, such as $pyO^{+}\cdot$, with a paramagnetic metal center can occur, leading to an $S = 0$ spin state.[13]

(3) If the first oxidation were ligand centered, a series of oxidation waves, associated with each pyO, might be expected much like the bpy oxidation waves observed for $Fe(bpy)_3^{3+}$[7a] and the bpy reduction waves observed for many bpy complexes.[14]

(4) While the exact nature of the $MeCN/Cu(pyO)_4^{2+}$ interaction in SO_2 is not known, a reasonable expectation would be coordination of MeCN at the axial sites.[15] Such an interaction should not strongly affect a ligand-centered oxidation but could strongly affect a metal-centered one.[12a,16] Therefore, the complete disappearance of the first oxidation wave and the absence of any significant effect on the second oxidation wave when MeCN is added to an SO_2 solution of $Cu(pyO)_4^{2+}$ again supports the assignment of the first wave as a metal-centered oxidation and the second as a ligand-centered one.

Finally, electron transfer involving aromatic systems are usually rapid because structural changes are small upon electron trasfer.[17] Thus, a ligand-centered oxidation of $Cu(pyO)_4^{2+}$ might be expected to be rapid. On the other hand, metal-centered oxidations, with the possibility of bond length and coordination changes, show, at times, slow electron-transfer kinetics.[18] While it is tempting to ascribe the quasi-reversibility of the first oxidation of $Cu(pyO)_4^{2+}$ to such changes following a metal-centered oxidation, the variability of ΔE_p with electrode material (Table I) suggests that interfacial phenomena are at least partially involved. It should be emphasized that had the oxidation not been studied with more than one electrode material, the slow electron-transfer kinetics might have been incorrectly attributed totally to intrinsic solution properties of the complex.

A final comment concerns the use of SO_2 as an electrochemical solvent for the study of transition-metal complex oxidations. Ideally, the solvent for such studies should not interact strongly with the metal or displace ligands; i.e., the solvent should not enter the primary coordination sphere of the metal. While transition-metal complexes of SO_2 are known, these are generally complexes with the metals in their lower oxidation states.[19] This observation has been rationalized in terms of π-back-bonding from the metal to SO_2.[20] Higher oxidation states do not have the electron density to bond in this manner. Thus, we have the fortuitous and perhaps related observation that SO_2 does not interact strongly with metals in their higher oxidation states, yet it is precisely these types of complexes that can be electrochemically studied in SO_2. Indeed, it is probably these properties that have allowed the observation of the $Cu(pyO)_4^{2+/3+}$ couple, which is unobservable in the presence of MeCN, a relatively good ligand independent of oxidation state.

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Registry No. $Cu(pyO)_4(PF_6)_2$, 87249-35-2; $Cu(pyO)_4(PF_6)_3$, 87249-37-4; $Cu(pyO)_4(ClO_4)_2$, 14076-96-1; Cu, 7440-50-8; SO_2, 7446-09-5.

---

(13) Buisson, G.; Deronzier, A.; Duee, E.; Gans, P.; Marchon, J.-C.; Regnard, J.-R. *J. Am. Chem. Soc.* **1982**, *104*, 6793–6796. Scholtz, W.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R.; Lang, G. *Ibid.* **1982**, *104*, 6791–6793.

(14) Creutz, C. *Comments Inorg. Chem.* **1982**, *1*, 293.

(15) The ions $Cu(pyO)_4L_2^{2+}$ (L = MeCN and DMF) have been observed in $Cu(pyO)_6^{2+}$ crystals: Keijzers, C. P.; McMullan, R. K.; Wood, J. S.; van Kalkeren, G.; Srinivasan, R.; de Boer, E. *Inorg. Chem.* **1982**, *21*, 4275–4284. Wood, J. S.; de Boer, E.; Keijzers, C. P. *Ibid.* **1979**, *18*, 904–906.

(16) Phillippi, M. A.; Shimomura, E. T.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1322–1325.

(17) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; Chapter 3.

(18) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779 and other papers in the series on "Structural Consequences of Electron Transfer Reactions". Heubert, B. J.; Smith, D. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *31*, 333.

(19) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182 and references cited therein.

(20) Mingos, D. M. P. *Transition Met. Chem.* (*Weinheim, Ger.*) **1978**, *3*, 1.