used as a secondary standard for all solid-state ^{13}C spectra and Q_8M_8 for all ^{29}Si spectra.

(6) M. Maricq and J. S. Waugh, in press.
(7) E. Lippmaa, M. Alla, and E. Kundla, paper presented at the 18th ENC Conference in Asilomar, April 1977.
(8) A. I. Kitaigorodskii, *Org. Kristallochim., Akad. Nauk, Moscow* (1955).
(9) Compare the solid-state spectra of maleic and fumaric acids; see Table I.
(10) E. F. Rybaczewski, L. S. Smith, A. F. Garito, A. J. Heeger, and B. G. Silbernagel, *Phys. Rev. B*, **14**, 2746 (1976).
(11) For the ^{29}Si NMR spectra of tetramethylsilane silicates in solution, see D. Hoebbel, G. Garco, G. Engelhardt, H. Jancke, P. Franke, and W. Wicke, *Z. Anorg. Allg. Chem.*, **424**, 115 (1976), and R. K. Harris and R. H. Newman, *ibid.*, in press. We want to thank Dr. D. Hoebbel for the silicates used.
(12) G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel, and W. Wieker, *Z. Anorg. Allg. Chem.*, **418**, 17 (1975).
(13) J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin Lead Comp.*, **1**, 235 (1974).
(14) E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966).
(15) Slow molecular motions with correlation times in the range of the sample spinning rate and those at frequencies coinciding with the decoupling rf field strength (A. N. Garroway, in press) must also be considered. Strong dipolar interaction between the tin and chlorine nuclei, not significantly suppressed by the magic angle sample spinning, can lead to severe ^{119}Sn line broadening as well. Although the lines found in the ^{13}C solid-state spectrum of this compound are sharp ($\Delta\nu_{1/2} \simeq 50$ Hz), the ^{13}C lines in solid *p*-dichlorobenzene are broad ($\Delta\nu_{1/2} \simeq 350$ Hz), although by far not so broad as the ^{119}Sn line in Bu_2SnCl_2. Large paramagnetic solid-state ^{119}Sn shifts have recently been found in other R_2SnHal_2 and $RSnHal_3$ compounds (V. Haeberlen and T. Saluvere, *J. Magn. Reson.*, in press), and complicated association–dissociation phenomena, leading to a broad spread of isotropic shifts, provide the best explanation both for the unexpected ^{119}Sn shift value and the large line width.

Endel T. Lippmaa,* Madis A. Alla, Tonis J. Pehk

*Department of Physics, Institute of Cybernetics
of the Estonian Academy of Sciences
Tallinn 200001, U.S.S.R.*

Günter Engelhardt

*Central Institute of Physical Chemistry
of the Academy of Sciences of D.D.R.
Berlin, Adlershof, D.D.R.*

A Unique Two-Electron, Reversible Reduction of a Binuclear Copper(II) Complex. Observation of the Electrochemical Behavior Predicted by Polcyn and Shain for the Sequential Transfer of Two Electrons at the Same Potential

Sir:

Recently there have been reports of electrochemical investigations of systems in which two metal ions are chemically bound in close proximity.[1-3] Presumably, the object of this research is to study and develop systems which (a) exhibit novel multiple-electron redox processes and/or (b) mimic multiple-electron redox processes found in biological systems. Of particular interest in this regard are the enzymatic proteins containing type III coppers, e.g., laccase, tyrosinase, and hemocyanin. The type III copper centers are believed to contain two magnetically coupled Cu(II) ions[4] which undergo a one-step, two-electron, reversible reduction to Cu(I), Cu(I).[5,6] Such multielectron transfer reactions are apparently critical in the biological reductions of dioxygen. To our knowledge, all synthetic binuclear copper complexes that exhibit reversible reductions do so in (a) a one-electron reduction presumably yielding a Cu(I), Cu(II) product[1] or (b) two one-electron steps with a significant potential separation presumably yielding a Cu(I), Cu(I) product.[7]

This paper reports the first example of a synthetic system in which the molecule is reduced in two *sequential* reversible, one-electron steps having *identical* $E_{1/2}$ values. The net result of this process is the transfer of two electrons at the same potential.
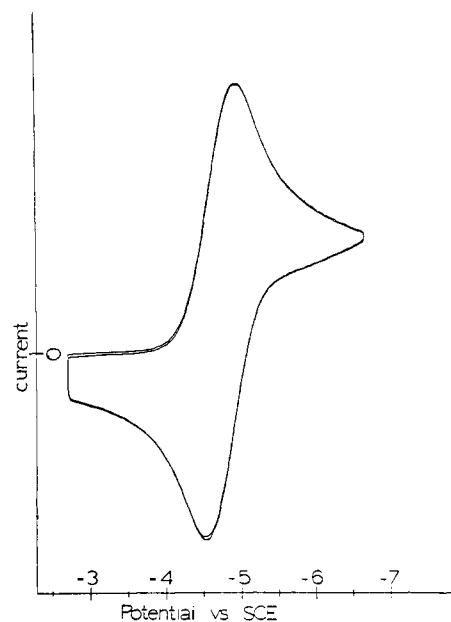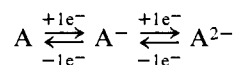

Figure 1. The cyclic voltammogram of $Cu_2(BAA)_2$ in DMF, 0.1 M tetraethylammonium perchlorate at a hanging mercury drop electrode. Two scans are represented.

$$A \underset{-1e^-}{\overset{+1e^-}{\rightleftarrows}} A^- \underset{-1e^-}{\overset{+1e^-}{\rightleftarrows}} A^{2-}$$

The molecule exhibiting the peculiar electrochemical properties described here is the neutral, binuclear copper(II) chelate of 1-phenyl-1,3,5-hexanetrionate(−2), $Cu_2(BAA)_2$. A schematic drawing is shown. The synthesis, structure, and

$Cu_2(BAA)_2$
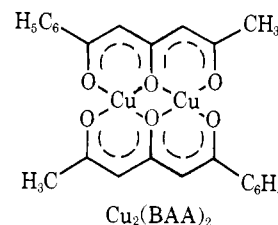
magnetic properties of this compound have been previously reported.[8] Structurally, the compound is best described as planar triketonate moieties with the two Cu(II) ions nearly in the plane and bridged by two ketonic oxygens forming a four-membered Cu_2O_2 ring. The two Cu(II) ions are strongly antiferromagnetically coupled with a singlet–triplet separation of 800 cm^{-1}. Thus, the compound is nearly diamagnetic at room temperature.

The cyclic voltammogram shown in Figure 1 is for the reduction of $Cu_2(BAA)_2$ in DMF solution containing 0.1 M tetraethylammonium perchlorate at a hanging drop mercury electrode.[9] Additional irreversible reductions are observed below −1.5 V. The reduction appears entirely reversible with a potential separation for the cathodic and anodic peaks of 42 mV. The peak separation is unaffected by changing the scan rates between 10 and 200 mV.s. The cathodic and anodic waves are of equal height regardless of the scan rate. A plot of the cathodic peak current vs. the square root of the scan rate yields a straight line ($r = 1.00$). The scan rate results are in agreement with the theoretical treatment of Nicholson and Shain[10] for a reversible process. In addition, the waves are invariant as to whether the scan is begun from the anodic or cathodic side of the waves. All of these results are consistent with a reversible reduction but with a peak separation of 42 mV. The theory for multielectron transfer in stationary-electrode cyclic voltammetry has been developed by Polcyn and Shain.[11] For the case

in which the oxidized species (A) and the partially reduced species (A^{-1}) are both reduced in reversible one-electron steps at the same potential the peak separation is predicted to be 42 mV.[11] The peak heights are predicted to be intermediate between those expected for one- and two-electron reversible waves[10,11] and, indeed, that is found for the cyclic voltammogram shown in Figure 1. These characteristics have not been experimentally observed up until this time. They do, however, adhere to the predictions of the Polcyn and Shain theory extremely well.

As an additional check on the system, the polarographic reductions for the same solutions at a dropping mercury electrode were recorded. The results yield a log $[i/(i_d - i)]$ slope of $\sim$46 mV and a diffusion current corresponding to the transfer of two electrons according to the Lingane–Loveridge equation using $D = 4.5 \times 10^{-6}$ cm^2/s as determined from the cyclic voltammogram.[12] The $E_{1/2} = -0.47$ V vs. a saturated calomel electrode. From the boundary value problem utilized by Polcyn and Shain,[11] an expression describing the current-potential relationship for the polarography of a system involving two sequential one-electron reversible reductions at the same potential may be derived.[13] A result of the solution of this yields

$$\frac{i}{i_d} = \frac{1 + \theta/2}{1 + \theta + \theta^2}, \theta = 10^{16.903(E-E^\circ)}$$

where i is the observed current, i_d is the diffusion current, E is the applied potential, and E° is the formal half-reaction potential. The common "log plot" (E vs. log $[i/(i_d - i)]$), as obtained from the above expression is not linear but appears so near $E_{1/2}$. The value of the slope near $E_{1/2}$ is approximately 45 mV which is very close to our observed value of 46 mV.

All the electrochemical experiments were performed in cells utilizing a DMF-Et$_4$NClO$_4$ bridge joining an aqueous-NaNO$_3$ bridge connected with saturated calomel electrode. No attempt has been made to adjust the measured potentials for the effects of the junction potential. The three-electrode system was connected to a potentiostat capable of full iR drop compensation.

All the results are consistent with the following two-step reduction in which $E_{1/2}' = E_{1/2}'' = -0.47$ V vs. SCE.

$$[\text{Cu}_2(\text{BAA})_2] \overset{E_{1/2}'}{\rightleftharpoons} [\text{Cu}_2(\text{BAA})_2]^{-1} \overset{E_{1/2}''}{\rightleftharpoons} [\text{Cu}_2(\text{BAA})_2]^{2-}$$

The experimental observation of two sequential one-electron transfers at identical potentials is unprecedented. However, careful examination of the experimental data and the incredibly good agreement with the theory of Polcyn and Shain can lead to no other reasonable conclusion.

References and Notes

(1) A. W. Addison, *Inorg. Nucl. Chem. Lett.*, **12**, 899 (1976).
(2) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1969); **95**, 1086 (1973).
(3) G. M. Brown, T. J. Meyer, D. O. Cowan, C. Levanda, F. Kaufman, P. V. Roling, and M. D. Rausch, *Inorg. Chem.*, **14**, 506 (1975).
(4) R. Lontie, "Inorganic Biochemistry", G. I. Eichorn, Ed., Elsevier, Amsterdam, 1973, p 344.
(5) N. Makino, P. McMahill, H. S. Mason, and T. H. Moss, *J. Biol. Chem.*, **249**, 6062 (1974).
(6) B. R. M. Reinhammer and T. I. Vanngard, *Eur. J. Biochem.*, **18**, 463 (1971); *Biochem. Biophys. Acta*, **275**, 245 (1972).
(7) R. R. Gagné and R. P. Kreh, private communication; R. R. Gagné, C. A. Koval, and T. J. Smith, *J. Am. Chem. Soc.*, **99**, 8367 (1977).
(8) R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Kuszaj, *Inorg. Chem.*, **15**, 1633 (1976).
(9) Experiments run under the same conditions, but with a platinum electrode, yielded poor voltammograms presumably owing to adsorption on the platinum surface.
(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 705 (1964).
(11) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966).
(12) See L. Meites, "Polarographic Techniques", 2nd ed, Interscience, New York, N.Y., 1965, p 115.
(13) The equation presented is identical with equation 18 in O. H. Muller, *Ann. N.Y. Acad. Sci.*, **40**, 91 (1940), where $\omega = \theta$ and $\rho = 1/\theta$.

D. Earl Fenton, R. R. Schroeder,* R. L. Lintvedt*

Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received October 11, 1977

Tetrahedral Mercaptide Complexes. Crystal and Molecular Structures of [(C$_6$H$_5$)$_4$P]$_2$M(SC$_6$H$_5$)$_4$ Complexes (M = Cd(II), Zn(II), Ni(II), Co(II), and Mn(II))

Sir:

Recently we reported[1] on the synthesis and characterization of a new series of monomeric thiophenolate complexes. The electronic spectra and magnetic properties of certain of these complexes suggested that all members of the x-ray isomorphous series, [(C$_6$H$_5$)$_4$P]$_2$[M(SC$_6$H$_5$)$_4$]$_2$ (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II)), contained tetrahedral complex anions with MS$_4$ cores. The electronic and Mössbauer spectra of the Fe(II) complex[2] have established this molecule as a successful analogue for the active site in reduced Rubredoxin (Rd). A subsequent crystal structure determination[3] revealed a distorted tetrahedral coordination for the Fe(II) ion. A tetrahedral FeS$_4$ site has been observed by x-ray crystallography in Rd$_{ox}$ from *Clostridium Pasteurianum*.[4]

The presence of metal–sulfur coordination has been implicated by chemical studies or demonstrated by x-ray crystallography in several other metalloenzymes. In horse liver alcohol dehydrogenase, LADH, two catalytic and two structural sites of the composition Zn(S-Cys)$_2$(His)(H$_2$O) and Zn(S-Cys)$_4$, respectively, have been found by a crystallographic study.[5] The coordination geometry at both sites is distorted tetrahedral. In the mammalian proteins, metallothioneins, which generally contain six or seven Zn and/or Cd atoms per molecule, nuclear magnetic resonance[6] and chemical[7] studies indicate metal-(II)–crysteinate binding. An average of three cysteine residues per metal atom has been found available; however, there is no information concerning Cd(II) or Zn(II) coordination. Various derivatives of metalloenzymes have been obtained when the naturally occurring metal ions are removed and the apoenzymes are reconstituted with other transition metal ions. Thus Cd(II) and Co(II) have been introduced in LADH with an apparent retention of catalytic activity.[8] Similarly, copper has been substituted by Co(II) in stellacyanin.[9]

Primary, precise, crystallographic data on tetrahedral thiolate complexes that contain the MS$_4$ chromophore are not available for M = Zn(II), Cd(II), Ni(II), Co(II), and Mn(II). The need for such data in mechanistic and structural studies of various metalloenzymes prompted us to determine the crystal and molecular structures of the [(C$_6$H$_5$)$_4$P]$_2$-M(SC$_6$H$_5$)$_4$ complexes for M = Cd(II), Zn(II), Ni(II), Co(II), and Mn(II) (I, II, III, IV, and V, respectively).

Crystal and refinement data for the five structures are shown in Table I. Intensity data were obtained on a Picker FACS I automatic diffractometer using a step-scan technique employing graphite monochromatized Mo Kα_{av} radiation (λ 0.7107 Å, $2\theta_m$ 12.2°) for I, II, III, and V, Cu Kα_{av} for IV (λ 1.5418 Å, $2\theta_m$ 25.0°). Refinement of the coordinates, determined previously for the x-ray isomorphous Fe(II) complex, was carried out by full-matrix least-squares calculations for all of the structures (Table I). All phenyl groups in the four structures were treated as rigid bodies.[10] The hydrogen atoms