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 ~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.

$$[Cu_2(BAA)_2] \underset{}{\overset{E_{1/2}'}{\rightleftarrows}} [Cu_2(BAA)_2]^{-1} \underset{}{\overset{E_{1/2}''}{\rightleftarrows}} [Cu_2(BAA)_2]^{2-}$$

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.

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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, $[(C_6H_5)_4P]_2[M(SC_6H_5)_4]_2$ (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 $[(C_6H_5)_4P]_2$-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 $K\alpha_{av}$ radiation (λ 0.7107 Å, $2\theta_m$ 12.2°) for I, II, III, and V, Cu $K\alpha_{av}$ 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

Table I. Crystal and Refinement Data

	$[(C_6H_5)_4P]_2\text{-}$ $Cd(SC_6H_5)_4$ (I)	$[(C_6H_5)_4P]_2\text{-}$ $Zn(SC_6H_5)_4$ (II)	$[(C_6H_5)_4P]_2\text{-}$ $Ni(SC_6H_5)_4$ (III)	$[(C_6H_5)_4P]_2\text{-}$ $Co(SC_6H_5)_4$ (IV)	$[(C_6H_5)_4P]_2\text{-}$ $Mn(SC_6H_5)_4$ (V)
Cell dimensions, Å	a = 13.983 (2)	a = 13.735 (2)	a = 13.691 (4)	a = 13.794 (3)	a = 13.828 (2)
	b = 17.572 (4)	b = 17.499 (6)	b = 17.551 (5)	b = 17.583 (4)	b = 17.527 (4)
	c = 24.906 (4)	c = 24.810 (5)	c = 24.873 (5)	c = 24.941 (6)	c = 24.834 (5)
Space group	$Pbc2_1$, z = 4	$Pbc2_1$, z = 4	$Pbc2_1$, z = 4	$Pbc2_1$, z = 4	$Pbc2_1$, z = 4
d_{calcd}, g/cm^3	1.33	1.31	1.30	1.29	1.29
d_{obsd},[a] g/cm^3				1.29 (1)	
μ, cm^{-1}	5.9	6.50	5.57	44.2	4.60
$2\theta_{max}$, deg	40	40	40	95.0[b]	40
Unique reflections	3989	3924	3939	2539	3949
Reflections used $F^2 > 3\sigma(F^2)$	3488	3342	3364	2206	3612
Parameters	268	268	268	268	268
r_1[c]	0.056	0.053	0.070	0.058	0.055
R_2[d]	0.073	0.066	0.090	0.076	0.074

[a] Determined by flotation in CCl_4/pentane. [b] Cu Kα radiation was used. [c] $R_1 = \Sigma|\Delta F|/\Sigma|F_o|$. [d] $R_2 = [\Sigma_w(\Delta F)^2/\Sigma_w|F_o|^2]^{1/2}$.

Table II. Selected Structural Parameters in the $M(SC_6H_5)_4{}^{2-}$ Anions

	$(Cd(SC_6H_5)_4{}^{2-}$	$Zn(SC_6H_5)_4{}^{2-}$	$Ni(SC_6H_5)_4{}^{2-}$	$Co(SC_6H_5)_4{}^{2-}$	$Mn(SC_6H_5)_4{}^{2-}$
			Bond Lengths, Ångstroms		
M–S$_1$	2.540 (4)	2.362 (3)	2.303 (4)	2.326 (4)	2.454 (3)
M–S$_2$	2.546 (4)	2.363 (3)	2.289 (5)	2.342 (4)	2.445 (3)
M–S$_3$	2.517 (3)	2.329 (3)	2.272 (4)	2.316 (4)	2.421 (3)
M–S$_4$	2.535 (3)	2.357 (3)	2.287 (4)	2.328 (4)	2.449 (3)
S$_1$–S$_2$	3.860 (7)	3.530 (6)	3.304 (7)	3.455 (8)	3.708 (6)
S$_3$–S$_4$	3.988 (7)	3.578 (6)	3.300 (7)	3.478 (8)	3.770 (6)
S$_1$–S$_3$	4.380 (8)	4.083 (6)	4.056 (8)	4.037 (8)	4.221 (6)
S$_1$–S$_4$	4.195 (8)	3.924 (6)	3.900 (8)	3.917 (8)	4.053 (6)
S$_2$–S$_3$	4.154 (8)	3.900 (6)	3.855 (8)	3.887 (8)	4.015 (6)
S$_2$–S$_4$	4.273 (8)	3.995 (6)	3.920 (8)	3.959 (8)	4.128 (6)
			Angles, Degrees		
S$_1$–M–S$_2$	98.7 (2)	96.7 (2)	92.0 (2)	95.6 (2)	98.4 (1)
S$_3$–M–S$_4$	108.5 (2)	99.6 (1)	92.7 (2)	97.0 (2)	101.5 (1)
S$_1$–M–S$_3$	120.0 (2)	121.0 (2)	124.9 (2)	121.3 (2)	120.0 (1)
S$_2$–M–S$_4$	114.0 (2)	115.6 (1)	117.9 (2)	116.1 (2)	115.0 (1)
S$_1$–M–S$_4$	110.8 (2)	112.6 (2)	116.3 (2)	114.8 (2)	111.5 (1)
S$_2$–M–S$_3$	110.2 (2)	112.5 (2)	115.4 (2)	113.5 (2)	111.2 (1)
M–S–C[a]	108.8 (2.1)	109.6 (2.2)	108.5 (2.4)	109.9 (2.2)	109.7 (2.2)
			Dihedral Angles, degrees		
(S$_1$–M–S$_3$); (S$_2$–M–S$_4$)		83.7	83.7	75.0 / 81.3	82.4
(S$_1$–M–S$_4$); (S$_2$–M–S$_3$)		102.0	102.0	109.1 / 102.4	102.1
(S$_1$–M–S$_2$); (S$_3$–M–S$_4$)		94.8	94.8	94.4 / 93.8	94.7

[a] Average value, $\sigma = [(\Sigma_{i=1}^N (s_i - \bar{x})^2)/(N - 1)]^{1/2}$ where x_i is the size of the angle and $\bar{x}$ is the mean value for the N equivalent bond angles.

included were given fixed temperature factors equal to those of the carbon atoms attached to them and the individual carbon temperature factors refined (C–C = 1.390, C–H = 0.95 Å). Nongroup atoms were refined anisotopically. Structural details for the complex anions are presented in Table II. See paragraph at end of paper regarding supplementary material.

The M(II) ions in I, II, III, IV, and V are four coordinate. The MS$_4$ units are distorted tetrahedra and the distortions present are very similar to those observed in the structure of the Fe(II) complex.[2] The distortions consist of compressions of each of the tetrahedra along one of their twofold axes. The deviations of the MS$_4$ units from T_d symmetry are evident in the small S$_1$–M–S$_2$ and S$_3$–M–S$_4$ angles and the opening up of the remaining S–M–S angles (Table I). The deviations of the S–M–S angles from tetrahedral symmetry (109.5°) in the *least* distorted Cd(II) complex range from −10.8 to +10.5°. In all structures two of the sulfur atoms are compressed to a greater extent than the other two. This is evident in the difference between the S$_1$–M–S$_3$ and S$_2$–M–S$_4$ angles and the S$_1$–S$_3$ and S$_2$–S$_4$ distances, respectively. In all structures the M–S$_3$ bond length appears to be slightly shorter than the other
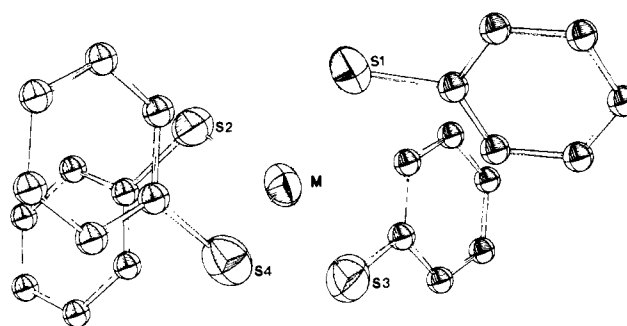

Figure 1. Structures and labeling of the MS$_4$ core of the $M(SC_6H_5)_4{}^{2-}$ complex anions. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces.

M–S bond lengths. The similarity of the deviations of the MS$_4$ units from T_d symmetry, observed in I, II, III, IV, and V suggests that the origin of these distortions very likely arises from crystal packing forces which are expected to be similar

in the x-ray isomorphous series.

The structure of polymeric $Cd(SCH_2CH_2OH)_2$ contains both tetrahedral and trigonal bipyramidal, CdS_4 and CdS_5 sites.[11] The CdS_4 site is distorted with a range in the S–Cd–S angles from 102 to 123°. The average Cd–S bond length of 2.56 Å is comparable with that observed in I. A distorted CdS_4 unit also is found in the tetrahedral site of the $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ cluster[12] and shows a range in the S–Cd–S angles of 100–118°. The Cd–S bond lengths in this site are 2.50 and 2.53 Å.

The Zn–S bond lengths in II compare with the values reported for synthetic sphalerite[13] (2.340 Å) and the tetrahedral ZnS_4 units[14] in the dimeric bis(dimethyldithiocarbamato)-zinc(II) (2.312 (6) to 2.429 (6) Å). In this severely distorted tetrahedron, S–Zn–S angles range from 76.4 to 136.5°. A ZnS_4 geometry similar to that found in the present structure has been reported[15] for the bis(trithioperoxycumato)zinc(II) complex, where the Zn–S bond lengths are 2.316 (3) and 2.327 (2) Å, and the S–Zn–S angles range from 117.9 (1) to 96.7 (1)°. A less distorted ZnS_4 tetrahedron is found[16] in the structure of the polymeric bis(ethylxanthato)zinc(II) complex. In this molecule the Zn–S bond lengths range from 2.337 (10) to 2.369 (8) Å and the S–Zn–S angles range from 112.1 (3) to 102.6 (3)°.

The only reported four-coordinate nickel(II) complex with sulphur ligands that assumes a tetrahedral structure is the bis(imidotetramethyldithiodiphosphino-*S*,*S*)nickel(II) complex.[17] The structure of this compound has been determined.[18] The mean Ni–S distance of 2.282 (12) Å is very similar to that found in III, 2.287 (12) Å. Both distances are significantly longer than the corresponding distances 2.10–2.24 Å found in nickel(II) chelate complexes containing a square-planar center.[18]

The angular distortions in III are more pronounced than all of the other complexes, with a span in the S–Ni–S angles from 124.9 (2) to 92.0 (2)°. By comparison the S–Ni–S angles in the bis(imidotetramethyldithiophospino-*S*,*S*)nickel(II) complex range from 117.0 (1) to 106.0 (1)°.

The Mn–S bond lengths in V are similar to those reported in the MnS_4 tetrahedron in bis(tetraphenyldithiomido-phosphinato)manganese(II), for which an average Mn–S bond length of 2.443 (12) Å was reported.[19] In the latter complex the MnS_4 unit is only slightly distorted and the deviations of the S–Mn–S angles from 109.5° range from +2.6 to –3.2°.

Ligand yield or charge-transfer absorptions in the electronic spectra of metalloenzymes and their metal substituted analogues have been used for the identification of both the environment and geometry at the active site. In Co–LADH absorptions maxima associated with ligand field transitions have been observed[8] at 655 nm (ϵ 1330), 730 (800), and between 1000 and 1800 (270–540). A charge-transfer absorption also is observed at 340 nm (ϵ 6500). In the electronic spectrum of the $Co(SC_6H_5)_4^{2-}$ in acetonitrile solution, similar absorptions are observed at 635 nm (sh, $\epsilon \simeq 500$), 690 (920), 730 (770), and 1450 (211). Two charge-transfer absorptions are observed at 285 nm (sh, ϵ 31 500) and 420 (3000). The position of the 420 nm absorption is lower in energy than bands of similar intensity found in bis(*O*-xylyl-α,α'-dithiolato)cobaltate(II)[20] (355 nm (ϵ 3450)), Co(II) substituted stellacyanin[9] (355 nm ($\epsilon \sim$1200)), and the 3,5-dimethyl-1-pyrazolyl borate-5-cys-teinylcobalt(II) complex[21] (388 nm). In all of these complexes the absorptions near 350 nm are assigned to S → Co charge transfer.

The electronic spectrum of the $Cd(SC_6H_5)_4^{2-}$ complex shows a band at 340 nm (ϵ 4200) with a shoulder at 355 nm.

The absorptions attributed to the phenyl groups obscure the region between 260 and 280 nm. The unusually high intensity ($\epsilon \sim$58 000) and broad shape of the phenyl multiplet, compared

with those observed in the Co(II) complex ($\epsilon \sim$40 000) suggest the underlying presence of a charge-transfer band in this region. In Cd–LADH the Cd–S absorption is centered[8] at 245 nm (ϵ 10 200). In cadmium metallothionein the same absorption is observed[7] as a pronounced shoulder at 250 nm ($\epsilon \sim$14 000). The unusually intense (ϵ 48 000) and broad phenyl ring absorptions observed in the spectrum of the $Zn(SC_6H_5)_4^{2-}$ complex also suggest the presence of a charge-transfer absorption in that region. In Zn–LADH the Zn–S charge-transfer absorption occurs[8] at 275 nm.

Further studies are directed toward the synthesis and structural characterization of aliphatic mercaptide complexes of the type $M(SR)_4^{2-}$ with optically and sterically acceptable counterions. It is anticipated that such studies will assess the importance of packing forces in the structures of the $M(SR)_4^{2-}$ complexes and at the same time will allow for the unobstructed detection of charge-transfer electronic absorptions.

Supplementary Material Available: Observed structure factors for $[(C_6H_5)_4P]_2M(SC_6H_5)_4$ complexes with Cd(II), Zn(II), and Mn(II) (45 pages). Ordering information is given on any current masthead page.

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Nitroxide Spin Labels as Surface and Structural Probes for Wood and Cellulose and Its Derivatives

Sir:

As a renewable source of carbon and a substance with numerous important industrial applications, cellulose has been widely investigated;[1] nevertheless, its properties and, in particular, its mode of interaction with solvents (including water)