## Isolation and Crystal and Molecular Structures of Two Geometric Isomers of a 3N,2S-Pentacoordinate Copper(II) Complex

Sir:

The coordination chemistry of copper ions with thioether ligands is an area of considerable current interest owing to the ligation of the thioether moiety of methionine to the copper ion at the active site of blue copper proteins.[1] X-ray crystal structure studies at 1.6-Å resolution have revealed that the copper ion at the active site of the blue (type 1) protein plastocyanin[2] is coordinated to two imidazole groups of histidine residues, a thioether group of a methionine residue, and a thiolate moiety of a cysteine residue, with a distorted tetrahedral geometry. Similar coordination was suggested for the copper atom in another blue (type 1) protein: azurin, obtained from *Pseudomonas aeruginosa* based on X-ray crystal structure studies at 3.0-Å resolution.[3] More recently, the structure of azurin obtained from *Alcaligenes denitrificans* at 1.8-Å resolution showed distorted trigonal-planar or trigonal-bipyramidal coordination of the copper atom.[4] To better understand the effect of such coordination on the unusual properties of these proteins, complexes of pyridine-,[5] imidazole-,[6] or benzimidazole[7] -thioether ligands with copper(II) have been prepared and studied. We now report the preparation and X-ray crystallographic structure studies on a new tris complex of Cu(II) with 1-methyl-2-(2-(methylthio)ethyl)imidazole (**1**), which crystallizes
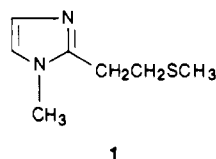
in two forms that have different coordination geometry about the pentacoordinate copper ion and that are markedly different from the previously reported complexes.

Reaction of copper(II) tetrafluoroborae with 1-methyl-2-(2-(methylthio)ethyl)imidazole[8] (**1**) in ethanol gave a complex of molecular formula $CuL_3(BF_4)_2$.[9] Recrystallization from ethanol
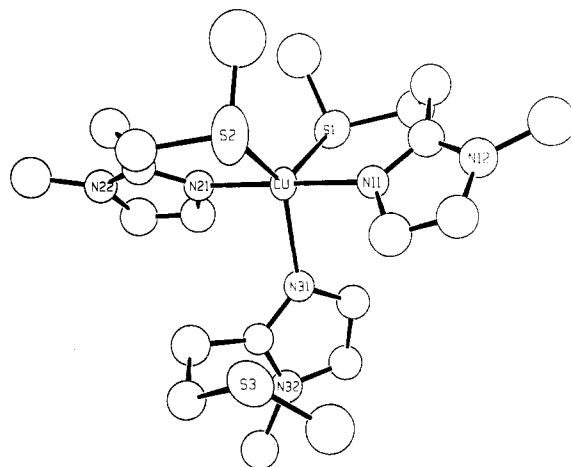

Figure 1. ORTEP[11] drawing of the green form of $CuL_3{}^{2+}$. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

Figure 2. ORTEP[11] drawing of the blue form of $CuL_3{}^{2+}$. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn to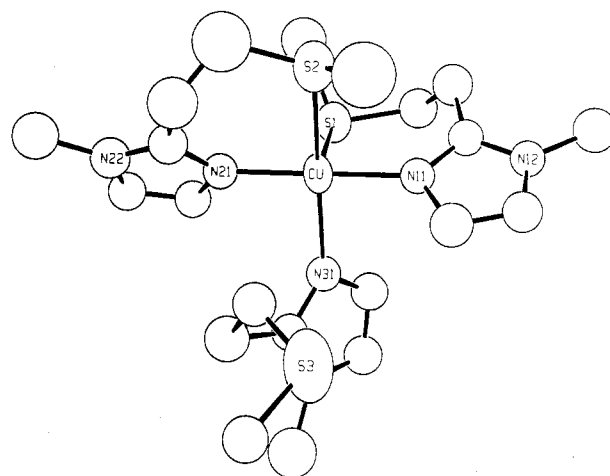 enclose 50% of the probability distribution except for the side chain with the uncoordinated S atom in which there is apparent disorder.

gave green crystals. The crystal and molecular structure of this material was determined by single-crystal X-ray methods.[10] An ORTEP[11] view of the molecule is shown in Figure 1. Recrystallization of $CuL_3(BF_4)_2$ by vapor diffusion of (not further purified) anhydrous commercial reagent grade diethyl ether into a solution of the complex in Spectrograde nitromethane gave blue crystals. The crystal and molecular structure of this complex was also determined by single-crystal X-ray methods.[12] An ORTEP view

(1) Karlin, K. D.; Zubieta, J., Eds. *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Adenine: Guilderland, NY, 1983.

(2) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, *272*, 319–324. Guss, J. M.; Freeman, H. C. *J. Mol. Biol.* **1983**, *169*, 521–563.

(3) Adman, E. T.; Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1978**, *123*, 35–47.

(4) Norris, G. E.; Anderson, B. F.; Baker, E. N. *J. Am. Chem. Soc.* **1986**, *108*, 2784.

(5) (a) Brubaker, G. R.; Brown, J. N.; Yoo, M. K.; Kinsey, R. A.; Kutchan, T. M.; Mottel, E. A. *Inorg. Chem.* **1979**, *18*, 299–302. (b) Karlin, K. D.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 906–908. (c) Ainscough, E. W.; Baker, E. N.; Brodie, A. M.; Larsen, N. G. *J. Chem. Soc., Dalton Trans.* **1981**, 2054–2058.

(6) (a) Prochaska, H. J.; Schwindinger, W. F.; Schwartz, M.; Burk, M. J.; Bernarducci, E.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 3446–3455. (b) Birker, P. J. M. W. L.; Godefroi, E. F.; Helder, J.; Reedijk, J. *Ibid.* **1982**, *104*, 7556–7560.

(7) (a) Rietmeijer, F. J.; Birker, P. J. M. W. L.; Gorter, S.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1191–1198. (b) Birker, P. J. M. W. L.; Helder, J.; Henkel, G.; Krebs, B. *Inorg. Chem.* **1982**, *21*, 357–363. (c) Dagdigian, J. V.; McKee, V.; Reed, C. A. *Ibid.* **1982**, *21*, 1332–1342. (d) Addison, A. W.; Burke, P. J.; Henrick, K.; Rao, T. N.; Sinn, E. *Ibid.* **1983**, *22*, 3645–3653. (e) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(8) *Chem. Abstr.* **1982**, *97*, 72359z. We developed a new synthesis of this compound, which will be reported subsequently.

(9) The experiment was carried out as follows. A solution of copper(II) tetrafluoroborate monohydrate (128 mg, 0.50 mmol) in commercial absolute ethanol (3 mL) not further dried, was added to a solution of ligand **1** (156 mg, 1.00 mmol) in commercial absolute ethanol (3.0 mL) at room temperature. A turquoise blue precipitate formed rapidly. After being stirred at room temperature for 2 h, the mixture was filtered to obtain $[CuL_3](BF_4)_2$ as a light blue solid (196 mg, 55% yield).

(10) The material crystallized from ethanol as plates in the orthorhombic space group $Pna2_1$ with $a = 14.424$ (3) Å, $b = 10.790$ (2) Å, $c = 20.127$ (3) Å, $Z = 4$, and $V = 3132$ Å^3. The data were collected on a crystal measuring 0.10 × 0.27 × 0.23 mm at room temperature by using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. A Nicolet P2$_1$ diffractometer was used with $\theta/2\theta$ scan type over the range 2.5–55.0° in 2θ. The $+h,+k,+l$ octants were collected, and a total of 4073 reflections were collected. No reflections were averaged because they were all unique. The structure was solved by using Patterson heavy-atom techniques for locating the copper atom, and the other atoms were found by difference Fourier maps. The structure was refined by using 1965 reflections with $I > 3\sigma(I)$ to the final value of the residual $R = 0.073$. The calculated absorption coefficient, μ, was 9.6, and absorption corrections were not made. Anomalous scattering factors were obtained from: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. No corrections were made for extinction. The Cu, S, and F atoms were refined anisotropically and all other atoms isotropically.

(11) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory: Oak Ridge, TN, 1965, revised 1971.

Table I. Selected Bond Distances and Bond Angles[a] for Green (Trigonal-Bipyramidal) and Blue (Square-Pyramidal) Complexes, CuL₃(BF₄)₂
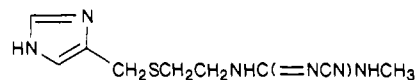
parameter	green crystals	blue crystals
Cu–S, Å	2.478 (3), 2.394 (3)[a]	2.398 (2),[b] 2.614 (2)[c]
Cu–N, Å	2.119 (7), 1.985 (7), 1.997 (7)	1.960 (5), 1.966 (5), 2.030 (5)
N(11)–Cu–N(21), deg	178.9 (3)	176.8 (2)
N(1)–Cu–S(1), deg	101.6 (2)	99.3 (2)
N(31)–Cu–S(2), deg	127.1 (2)	159.7 (2)
S(1)–Cu–S(2), deg	131.2 (1)[d]	100.66 (9)
N(11)–Cu–N(31), deg	89.7 (3)	88.2 (2)
N(11)–Cu–S(1), deg	91.5 (2)	92.3 (2)
N(11)–Cu–S(2), deg	86.7 (2)	87.0 (2)
N(21)–Cu–N(31), deg	90.2 (3)	92.9 (2)
N(21)–Cu–S(1), deg	89.6 (2)	90.5 (2)
N(21)–Cu–S(2), deg	92.5 (2)	90.9 (2)

[a] The standard deviation of the least significant figure is given in parentheses. [b] These values are within the expected range for equatorial copper(II) to thioether Cu–S bonds: References 5, 6b, and 7. Glick, M. D.; Gavel, D. P.; Diaddario, L. L., Jr.; Rorabacher, D. B. *Inorg. Chem.* **1976**, *15*, 1190. Cohen, B.; Ou, C. C.; Lalancette, R. A.; Borowski, W.; Potenza, J. A.; Schugar, H. S. *Ibid.* **1979**, *18*, 217–220. Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Ibid.* **1981**, *20*, 151–157. Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Ibid.* **1983**, *22*, 266–271. Pett, V. B.; Diaddario, L. L., Jr.; Dockal, E. R.; Cornfield, P. W.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Ibid.* **1983**, *22*, 3661–3670. Musker, W. K.; Olmstead, M. M.; Kessler, R. M. *Ibid.* **1984**, *23*, 1764–1768. Diaddario, L. L., Jr.; Dockal, E. R.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Ibid.* **1985**, *24*, 356–363. Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Moy, I. W.-Y.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1985**, *107*, 2399–2404. [c] This value is in the range reported for apical copper(II) to thioether Cu–S bonds: References 6a and 7d. [d] Previously reported values centered on 90° for the S–Cu–S bond angles for equatorially disposed sulfur atoms[5a,6b,7a,b] in a trigonal bipyramid. These considerably smaller values than expected are ascribed to rigidity in the bridging groups. One larger value, 108°, has also been reported.[5b]

of the molecule is shown in Figure 2.

This complex, in contrast to those pentacoordinate complexes previously reported,[13] has only N and S in the coordination sphere of the copper(II).[14] No solvent molecule or counterion is coordinated by the copper ion. In addition, the previously reported pentacoordinate copper(II) complexes involve sterically congested and/or polydentate ligands. Ligand constraints and steric effects have been cited as important in favoring pentacoordinate geometries over the more usual square-planar or tetragonal geometries. It should also be noted that cimetidine **2** also acts as a bidentate ligand, using imidazole N(2) and thioether sulfur atoms, toward copper(II) but the copper atom is six-coordinate with distorted octahedral geometry.[15]

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Furthermore, two different geometries are observed in the green and blue crystals although both involve 3N,2S-ligation. The approximate geometry about the copper atom in the green crystals is trigonal bipyramidal with 2S,N in the equatorial plane and 2N apical.[16] The bond distances and bond angles are shown in Table I. The UV/vis absorption spectrum of this compound in nitromethane shows maxima at (extinction coefficients in parentheses) 386 (800) and 660 nm (200). A powdered sample of this material has a rhombic EPR spectrum with $g_1 = 2.048$, $g_2 = 2.098$, and $g_3 = 2.173$. The approximate geometry about the copper atom in the blue crystals is square pyramidal with 3N,S in the plane and S(1) apical.[17] The in-plane S(2) and N(31) trans to it are a little below the 3N,S plane, and the nitrogen atoms trans to each other, N(11) and N(21), and the copper atom, are a little above this plane. The bond distances and bond angles are shown in Table I. The UV/vis absorption spectrum of this compound in nitromethane exhibits maxima at (extinction coefficients in parentheses) 389 (200) and 613 nm (500). A powdered sample of this material shows a broad absorption in its EPR spectrum with $g_{av} = 2.081$.

Detailed comparison of the molecular structures for the two crystalline forms of complex **2** reveals the following similarities and differences. The Cu–S bond distance involving the apical S in the blue crystals is longer by 0.2 Å than those in the green crystals. To convert the square-pyramidal geometry of the blue complex to the trigonal-bipyramidal geometry of the green complex, the bond angles involving the two sulfur atoms and N(31) change as follows: N(31)–Cu–S(1) increases slightly (99 → 102°), N(31)–Cu–S(2) decreases substantially (160 → 127°), and S-(1)–Cu–S(2) increases substantially (101 → 131°). This results in an increase in the nonbonded S(1)⋯S(2) distance from 3.86 to 4.43 Å. The overall geometries of the chelated ligands in both complexes are very similar except that the side chain in one of them differs, resulting in a marked difference in the orientation of the S–CH₃ groups on each of these ligands relative to each other,[18] and the geometries of the uncoordinated side chains are substantially different from each other in the blue and green complexes.

The blue material converts slowly to the green material on standing in nitromethane solution at room temperature but converts more rapidly on heating. This can be monitored by the change in the absorption spectrum. The initial absorption spectrum of the blue material slowly changes to that of the green material.

In summary, these are the first reported complexes of copper(II)

(12) The blue material crystallized as rectangular blocks in the monoclinic space group P2₁/n with a = 12.796 (6) Å, b = 12.742 (3) Å, c = 19.788 (3) Å, β = 95.38 (3)°, Z = 4, and V = 3212 Å³. The data were collected at room temperature on a crystal measuring 0.17 × 0.15 × 0.54 mm by using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. A Nicolet P2₁ diffractometer was used with θ/2θ scan type over the range 2.5–50.0° in 2θ. The +h,+k,±l octants were collected, and a total of 6262 reflections were collected. The agreement factors for the average of 309 observed and accepted reflections was 2.5% on the basis of intensity and 4.7% on the basis of F_o. The structure was solved by using Patterson heavy-atom techniques for locating the copper atom, and the other atoms were found by difference Fourier maps. The structure was refined by using 2888 reflections with $I > 3\sigma(I)$ to the final value of the residual $R = 0.098$. The calculated absorption coefficient, μ, was 9.4, and absorption corrections were not made. Anomalous scattering factors were obtained from: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. No corrections were made for extinction. The Cu, S, and F atoms were refined anisotropically and all other atoms isotropically.

(13) A complex reported in ref 6a has tetragonal N₄S₂ coordination about copper(II).

(14) The other pentacoordinate copper(II) complexes have N₂S₂O,[5a,b,7a] N₂S₂Br,[6b] N₂S₂Cl,[7b] SN₂O₂[7c,d] and NSBr₃[5c] donor atom sets.

(15) Sofo, L.; Borrás, J.; Sancho, A.; Fuertes, A.; Miravitlles, C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1431. Sancho, A.; Borrás, J.; Soto-Tuero, L.; Esteban-Calderon, C.; Martinez-Ripoll, M.; Garcia-Blanco, S. *Polyhedron* **1985**, *4*, 539.

(16) To provide a systematic way to compare structures intermediate between idealized square-pyramidal and trigonal-bipyramidal extremes, Addison et al.[7e] defined a structural index parameter τ. For a five-coordinate atom M to which A–E atoms are coordinated, atom A is designated as the axial ligand. The greater basal angle, BMC, is defined as β and the angle DME (measured away from A) is defined as α. The index τ = $(\beta - \alpha)/60$ between the degree of trigonality between perfect trigonal bipyramid (τ = 1) and perfect square pyramid (τ = 0). Thus, for the green crystals, designating S(1) as A, the N(11)–Cu–N(21) angle (178.9°) as β, and the N(31)–Cu–S(2) angle (127.1°) as α leads to τ = 0.863.

(17) The τ value[7e] for the blue crystals is calculated as follows by using the definitions in the preceeding footnote.[16] Designating S(1) as A, the N(11)–Cu–N(21) angle (176.8°) as β, and the N(31)–Cu–S(2) angle (159.7°) as α leads to τ = 0.285.

(18) The syn relationship of the S-methyl groups in the green complex, in which the nonbonded CH₃⋯CH₃ distance is 4.00 Å,[19] would result in severe interaction in the blue complex if they were also syn because the nonbonded S⋯S distance is less. The other major differences between the two structures involve the ligand with the uncoordinated side chain.

(19) Twice the van der Waals distance for a methyl group is 4.00 Å: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 261.

with only thioether sulfur and imidazole nitrogen coordination. Although both pentacoordinate geometries have been found before for copper(II) complexes, this is the first reported example of the isolation and structural characterization of both square-pyramidal and trigonal-bipyramidal coordination geometries for the same complex.

Supplementary Material Available: Tables of final atom positional and thermal parameters, bond distances, and bond angles for both the green and blue forms of [CuL₃](BF₄)₂ (8 pages). Ordering information is given on any current masthead page.

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Electrocatalytic Reduction of HSO₃⁻ to H₂S Based on a Water-Soluble Iron Porphyrin

Sir:

The reduction of HSO₃⁻ to H₂S occurs in nature via a stepwise, catalytic process that is carried out by the sulfite reductase enzymes.[1] They contain an iron isobacteriochlorin prosthetic group, which is known to bind sulfite. We have recently shown that the water-soluble iron porphyrin $[Fe^{III}(TPPS)(H_2O)_n]^{3-}$ (n = 1 or 2; TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine)[2] mimics the action of the enzyme nitrite reductase in its ability to reduce NO_2^- to NH_3 catalytically.[3,4] We report here that the same iron porphyrin complex is also an effective electrocatalyst for the reduction of HSO₃⁻ to H₂S and that possible mechanistic insight into the reduction can be gained from the results of electrochemical studies on the reduction of $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ [5] to $[Ru^{II}(NH_3)_5(H_2S)]^{2+}$ [6] where the sulfur ligand remains bound through the net six-electron change. The iron porphyrin appears to be the first example of a well-defined chemical system for the catalytic reduction of HSO₃⁻ to H₂S.

In Figure 1 is shown a cyclic voltammogram[7] of $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ at pH 2.00. The wave at $E_{1/2}$ = +0.26 V (vs. SCE) arises from the pH-dependent $[Ru^{III}(NH_3)_5(HSO_3)]^{2+}/[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ couple.[8] The process occurring at $E_{p,a}$ = +1.15 V is an irreversible oxidation to give $[Ru^{III}(NH_3)_5(SO_4)]^+$, as shown chemically by Isied and Taube.[9] However, of more interest is the appearance of the multielectron, irreversible reduction at $E_{p,c}$ = –0.74 V. Electrolysis[10a] at E_{appl} = –0.75 V (appl

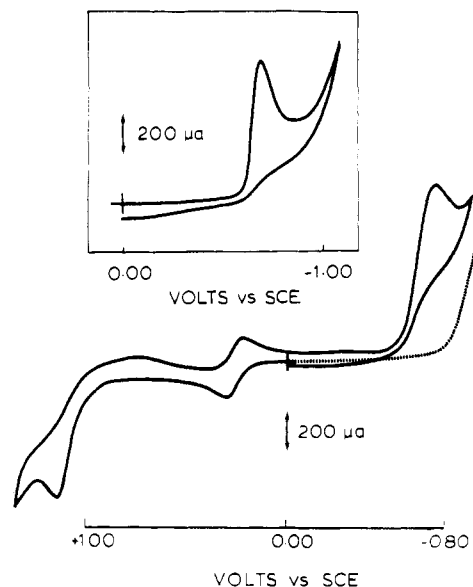(1) Postgate, J. R. In *Inorganic Sulfur Chemistry*; Nickless, G., Ed.; Elsevier: New York, 1968; Chapter 8, pp 259–279.
(2) Taniguchi, V. T. Ph.D. Dissertation, University of California, Irvine, CA, 1978.
(3) Barley, M. H.; Takeuchi, K. J.; Murphy, W. R., Jr.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 507–508.
(4) Barley, M. H.; Takeuchi, K. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 5876–5885.
(5) Gleu, K.; Rehm, K. *Z. Anorg. Allg. Chem.* **1938**, *235*, 211–219.
(6) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689–702.
(7) All cyclic voltammetry experiments were performed with a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel (SCE) reference electrode.
(8) Gleu, K.; Rehm, K. *Z. Anorg. Allg. Chem.* **1938**, *235*, 211–219.
(9) Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 8198–8200.
(10) (a) All coulometric reductions were performed with a reticulated-carbon working electrode, a platinum-gauze auxiliary electrode, and a saturated calomel reference electrode. (b) The electrolyses were carried out to n > 5 with the initial current having fallen to 15–20% of its initial value. The value of n greater than the expected value of n = 4 for the $[(NH_3)_5RuSSRu(NH_3)_5]^{2+} \rightarrow 2[Ru(NH_3)_5(SH_2)]^{2+}$ reduction and the continuing background current are probably the result of the catalytic production of H_2 by the complex.[6,12]

Figure 1. Cyclic voltammogram of a solution containing 1.3 × 10⁻³ M $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ at pH 2.0 in a 0.1 M sulfate buffer at a scan rate of 100 mV/s. The irreversible wave at E_p = –0.74 V is also observed if the scan is begun in the negative direction; the dashed curve shows the reductive background. The surface area of the glassy carbon electrode was 7.1 mm². Insert: Cyclic voltammogram of 9.9 × 10⁻⁴ M $[(NH_3)_5Ru^{III}SSRu^{III}(NH_3)_5]^{4+}$, which is the initial reduction product, at pH 2.0 in a 0.1 M sulfate buffer at a scan rate of 100 mV/s.

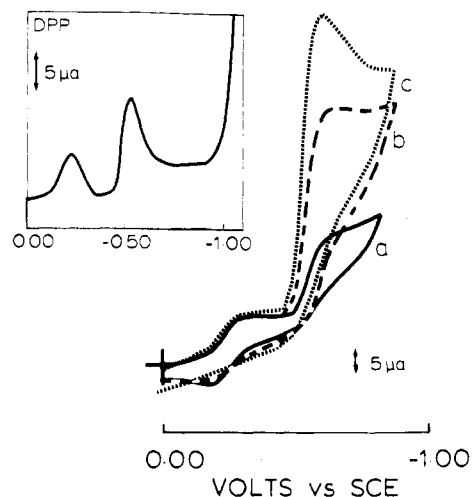**Figure 2.** (a) Cyclic voltammogram of a solution containing 1.6 × 10⁻³ M $[Fe^{III}(TPPS)(H_2O)_n]^{3-}$ and a less than stoichiometric amount of HSO₃⁻ (1 × 10⁻³ M) in a phosphate buffer (0.1 M KH₂PO₄ with 0.6 M Na₂SO₄ added; pH 3.48) at a scan rate of 50 mV/s. (b, c) Cyclic voltammograms of solutions 1.6 × 10⁻³ M in $[Fe^{III}(TPPS)(H_2O)_n]^{3-}$ containing 3.0 × 10⁻³ and 6.0 × 10⁻³ M HSO₃⁻, respectively, at pH 3.48 in a phosphate buffer (0.1 M KH₂PO₄ with 0.6 M Na₂SO₄ added) at a scan rate of 50 mV/s. The surface area of the glassy carbon electrode was 7.1 mm². Insert: Differential-pulse polarogram of a solution containing 2.0 × 10⁻³ M Na₂S₂O₅ and 7.6 × 10⁻⁴ M $[Fe^{III}(TPPS)(H_2O)_n]^{3-}$ at pH 2.74 (0.1 M phosphate buffer with 0.6 M Na₂SO₄ added); the scan rate is 10 mV/s.

= applied) until the initial current falls to ~15% of its initial value occurs with n = 3.60 (±0.06) per monomer to give $[(NH_3)_5Ru^{III}SSRu^{III}(NH_3)_5]^{4+}$ nearly quantitatively, as shown by spectral and electrochemical comparisons with a known sample prepared by the reaction between $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ and $H_2S(g)$.[11] The cyclic voltammogram of the dimer at pH 2 is shown as an inset in Figure 1. The dimer itself undergoes an additional, kinetically slower reduction at the electrode at E_{appl}

(11) Brulet, C. R.; Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758–4759.