

oxides of the type  $Ba_3M_2O_6$  with  $BaO_3$  layers involve face-sharing of filled octahedra, their small cations have lower formal charges. Therefore the partial occupancy of the Re(2) sites is expected to be accompanied by some vacancies in the Re(1) sites. The refined site population parameters show that about 6% of the Re(1) sites are vacant. It may be concluded that, within the limit of  $3\sigma$ , for each Re(2) site occupied the occupancy of the two Re(1) sites sharing octahedral faces with it is precluded so as to avoid strong metal-metal repulsion. This results in about 2% deficiency of Re in the structure. It remains speculative whether the required charge balance is achieved by a corresponding deficiency of oxygen or by oxidation of Re(VI) to Re(VII) or both. By way of contrast, it was reported that the compound  $Ba_5Ta_4O_{15}$  could be obtained from oxidizing  $Ba_5Ta_4O_{13}$  without change in structure,<sup>9,10</sup> which is related to the present one in having a five-layer sequence (cchhc) and vacant octahedra sharing opposite faces with filled octahedra.

The strong metal-metal repulsion between face-sharing octahedra may explain why the compound  $BaReO_3$ , which could have all the Re(2) sites filled in the 9R structure, fails to form under normal conditions. It is possible, however, that the occupancy of the octahedral sites and consequently the exact stoichiometry of  $Ba_3Re_2O_9$  is pressure dependent. The nonstoichiometric  $Re_{1+x}O_3$  ( $0.14 < x < 0.21$ ) formed at high pressure was reported to contain hexagonal close-packed oxygen with one type of octahedral site partially filled.<sup>11</sup> Complete filling of these sites would have given the compound  $Re_2O_3$  which is hitherto unknown. Another example of cation deficiency in related structures may be found in the mineral senaite with the general formula  $AM_{21}O_{38}$ , which also features

a nine-layer sequence of close-packed anion lattice where the layer composition is  $AO_{38}$ .<sup>12</sup> It has been suggested<sup>13</sup> that its structure is derived from natural oxidation and leaching of iron and manganese from an original structure of the formula  $AM_{24}O_{28}$ , in which the  $Fe^{2+}$  and  $Mn^{2+}$  occupy the h-M-h octahedral sites that share faces with the h-M-c octahedral sites occupied by Ti.

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**Supplementary Material Available:** A listing of calculated and observed structure amplitudes (1 page). Ordering information is given on any current masthead page.

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## Sulfinato Coordination of Triplet-State Cobalt(III) through Sulfur. Crystal and Molecular Structure of Bis{2-[(2-pyridylmethyl)amino]ethylsulfinato}cobalt(III) Perchlorate Dihydrate

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The crystal and molecular structure of bis{2-[(2-pyridylmethyl)amino]ethylsulfinato}cobalt(III) perchlorate dihydrate,  $[Co(C_8H_{11}N_2SO_2)_2]ClO_4 \cdot 2H_2O$ , has been determined by single-crystal x-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional  $R$  index of 0.043. The bright orange crystals form as rectangular prisms in the monoclinic space group  $C2/c$  with  $a = 23.171$  (4) Å,  $b = 11.397$  (2) Å,  $c = 9.210$  (2) Å, and  $\beta = 96.62$  (2)° and with four molecules per unit cell. The cobalt(III) ion lies at an inversion center and is coordinated octahedrally by two amine nitrogen atoms at 1.974 (3) Å, two pyridyl nitrogen atoms at 1.945 (2) Å, and two sulfur atoms of the sulfinato groups at 2.233 (1) Å—the oxygen atoms do not coordinate to Co(III). The compound was prepared by the reaction of Co(II) with 2-[(2-pyridylmethyl)amino]ethanethiol in the presence of hydrogen peroxide in basic solution and was recrystallized from water-ethanol-ethyl acetate. In the absence of hydrogen peroxide, a cobalt(II) disulfide complex is obtained. The cobalt(III) sulfinato complex is paramagnetic, with Co(III) in an intermediate spin state ( $\mu = 3.27$ , as determined by the Evans NMR method); the occurrence of this unusual spin state is attributed to the presence of  $d_{z^2}$  and  $d_{xy}$  levels of comparable energy as a result of electronic distortion. The preparation of a sulfinate from a thiol in the presence of cobalt has its biological analogue in the formation of cysteinesulfinic acid from cysteine, a reaction most likely catalyzed by a metalloenzyme.

### Introduction

Cobalt(III) sulfinate complexes may be prepared by reacting a sulfinate salt with a Co(III) complex,<sup>1-3</sup> by  $SO_2$  insertion into a Co(III)-C bond,<sup>2-5</sup> or by oxidizing a cobalt(III) thiolato complex by hydrogen peroxide.<sup>6-10</sup> This work appears to exemplify the last method and describes the synthesis and structure of bis{2-[(2-pyridylmethyl)amino]ethylsulfinato}-

cobalt(III) perchlorate dihydrate, obtained from the reaction of cobalt(II) perchlorate with 2-[(2-pyridylmethyl)amino]ethanethiol in the presence of hydrogen peroxide. In the absence of hydrogen peroxide, the reaction product is {2-[(2-pyridylmethyl)amino]ethyl disulfide}cobalt(II) perchlorate.

The preparation of a sulfinate from a thiol in the presence of a metal ion has its biological analogue in the formation of

cysteinesulfinic acid from cysteine. This is the first step of a major pathway in the metabolic degradation of cysteine in living organisms<sup>11</sup> and is catalyzed by an enzyme whose activity is lost in the presence of metal chelating agents.<sup>12</sup>

Previous crystallographic studies of the sulfinato complexes [Cu(2-pySO<sub>2</sub>)<sub>2</sub>]<sup>13</sup> and [Cu(*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>14</sup> have shown that the sulfinato group bonds to copper through an oxygen atom (sulfinato-*O* complex) in each case. It had been suggested on spectroscopic grounds that the metal atom is bonded to sulfur (sulfinato-*S* complex) in [Co(en)<sub>2</sub>-(NH<sub>2</sub>CH(COO)CH<sub>2</sub>SO<sub>2</sub>)]ClO<sub>4</sub>,<sup>7</sup> [Co(dimethylglyoximate)<sub>2</sub>(RSO<sub>2</sub>)(CH<sub>3</sub>OH)],<sup>1</sup> and Hg(RSO<sub>2</sub>)<sub>2</sub>,<sup>15</sup> and in palladium complexes of the following types: Na[PdCl(RSO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)], [Pd(RSO<sub>2</sub>)<sub>2</sub>L<sub>2</sub>], [AsPh<sub>4</sub>][Pd<sub>2</sub>Cl<sub>4</sub>(PhSO<sub>2</sub>)<sub>2</sub>].<sup>16</sup> Sulfinato-*S* and sulfinato-*S* coordination of Co(III) have recently been observed in the crystal structures of [Co(en)<sub>2</sub>-(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)](NO<sub>3</sub>)(ClO<sub>4</sub>)<sup>6</sup> and [Co(en)<sub>2</sub>-(HO<sub>2</sub>CCH(NH<sub>2</sub>)CH<sub>2</sub>SO)](ClO<sub>4</sub>)<sub>2</sub>.<sup>8</sup>

### Experimental Section

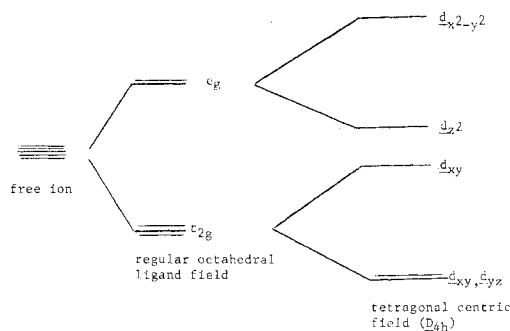
Reagent grade Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (G. Frederick Smith Chemical Co.) was used. Analytical reagent grade 30% H<sub>2</sub>O<sub>2</sub> solution (Mallinckrodt Chemical Works) was diluted to 15% with distilled water. A 0.3 N solution of NH<sub>3</sub> was prepared from analytical reagent grade concentrated ammonia solution (Mallinckrodt). All other chemicals were of reagent grade quality. Elemental analyses were performed by Galbraith Laboratories, Inc., and University of California Chemical Analytical Services. Infrared spectra were obtained using a Beckman IR-10 spectrometer. The magnetic moment was measured by the Evans NMR method;<sup>17,18</sup> a Varian XL-100 NMR spectrometer using coaxial NMR tubes was employed. A 1%-by-volume solution of tetramethylsilane in deuterated dimethyl sulfoxide was used as the solvent (99.5% D; Norell Chemical Co.).

**Preparation of [2-[(2-Pyridylmethyl)amino]ethyl disulfide]cobalt(II) Perchlorate.** The preparation of the parent thiol has been described.<sup>19</sup> It was reacted with 0.001 mol of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in a 2:1 ratio of thiol to metal in ammoniacal ethanol solution. A reddish brown powder was filtered the next day. Its chemical analysis corresponds to the formula [Co(2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. Anal. Calcd for C<sub>16</sub>H<sub>22</sub>Cl<sub>2</sub>CoN<sub>4</sub>O<sub>8</sub>S<sub>2</sub>: C, 32.44; H, 3.74; Co, 9.82; N, 9.46. Found: C, 33.80; H, 3.90; Co, 9.82; N, 9.90. The percentage of carbon is high, possibly indicating the presence of organic solvent as impurity.

**Infrared Spectrum of [Co(2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.** There have been several studies of the shifts of  $\nu$ (C=C) and  $\nu$ (C=N) stretching frequencies in the infrared region of coordinated 2-pyridyl groups.<sup>13,20-22</sup> In the parent ligand 2-[(2-pyridylmethyl)amino]ethanethiol these frequencies occur at 1587, 1568, 1455, and 1428 cm<sup>-1</sup>. In the cobalt disulfide complex the C=N stretch is shifted to 1612 cm<sup>-1</sup>, indicating strong pyridine coordination. The C=C bands occur at 1574, 1458, and 1429 cm<sup>-1</sup>. The approximate equivalence of the pyridine rings is indicated by the presence of four bands.<sup>13,20</sup>

The ring breathing mode that occurs at 988 cm<sup>-1</sup> in the parent ligand is shifted to 998 cm<sup>-1</sup> in the disulfide complex. The strong band at 742 cm<sup>-1</sup> and the shoulder at 720 cm<sup>-1</sup> which occur in the parent ligand are assigned to the  $\gamma$ (C-H) and  $\phi$ (C-C) modes, respectively.<sup>20</sup> These bands occur in the disulfide complex at 761 and 720 cm<sup>-1</sup>. The ring deformation vibration at 395 cm<sup>-1</sup> in the parent ligand is shifted in the disulfide complex to 428 cm<sup>-1</sup>, again indicating strong pyridine coordination. A trans configuration of the pyridine rings is indicated by the presence of a single deformation band.<sup>13,20</sup> As expected, the S-H stretch at 2500 cm<sup>-1</sup> in the parent ligand disappears in the complex. The N-H stretch at 3300 cm<sup>-1</sup> in the parent ligand is shifted in the complex to 3210-3230 cm<sup>-1</sup>; thus the secondary amine group is also coordinated. The broad, symmetric band with a peak at 1090 cm<sup>-1</sup> and the single sharp band at 620 cm<sup>-1</sup> indicate uncoordinated perchlorate.<sup>23</sup>

**Preparation of Bis[2-[(2-pyridylmethyl)amino]ethylsulfinato]cobalt(III) Perchlorate Dihydrate.** A 0.001-mol sample of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was reacted with 0.002 mol of 2-[(2-pyridylmethyl)amino]ethanethiol in the presence of 15% H<sub>2</sub>O<sub>2</sub> in ammoniacal ethanol solution. A small amount of reddish brown precipitate was filtered off. On the next day, an orange powder was isolated by filtration, but the chemical analysis indicated that ammonium perchlorate had coprecipitated with a cobalt complex. For this reason, a reliable



**Figure 1.** The tetragonal splitting of a  $d^6$  ion in a centric field.

analysis could not be obtained. The powder was recrystallized successively from 95% ethanol and from water to give small orange crystals. These were redissolved in 50% aqueous ethanol and recrystallized by slow evaporation of ethyl acetate into the ethanol-water solution in a closed system.<sup>24</sup> Well-formed single crystals (mp 220 °C) were obtained by this method in 5 weeks. The molecular weight was established from the unit cell volume and density and corresponds to [Co(2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O. The crystal structure determination confirms this formula.

**Magnetic Moment of [Co(2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O.** The magnetic moment of bis[2-[(2-pyridylmethyl)amino]ethylsulfinato]cobalt(III) perchlorate dihydrate was determined by the Evans NMR method.<sup>17,18</sup> In this method, a very small sample is required; single crystals of the complex were used. The magnetic susceptibility,  $\chi$ , of the complex is obtained from

$$10^6 \chi = \frac{3\Delta f}{2\pi f} \frac{M}{c}$$

where  $M$  = molecular weight of the complex,  $c$  = concentration of the solution (g/mL),  $f$  = field strength (Hz), and  $\Delta f$  = shift in the tetramethylsilane signal due to the presence of the paramagnetic ion (Hz). The measured susceptibility was then corrected for the diamagnetic susceptibilities of the tetramethylsilane, the dimethyl sulfoxide, and the cobalt sulfinato complex, using Pascal's constants.<sup>25</sup> With these corrections, the molar susceptibility of the cobalt sulfinato complex is  $4467 \times 10^{-6}$  in cgs units. The magnetic moment,  $\mu$ , is given by

$$\mu = 2.829(T\chi)^{1/2}$$

Therefore,  $\mu = 3.27$  at approximately 26 °C.

Magnetic moments ranging from 4.47 to 5.66 have been reported for the high-spin Co(III) complexes [Co(H<sub>2</sub>O)<sub>3</sub>F<sub>3</sub>] and CoF<sub>6</sub><sup>3-</sup>.<sup>26</sup> An intermediate magnetic moment of 3.27 may arise from (1) an admixture of high-spin and low-spin complex, (2) thermal equilibrium between high- and low-spin states, (3) antiferromagnetic interactions between high-spin Co<sup>3+</sup> ions, or (4) a triplet ground state as a result of tetragonal distortion. It is doubtful that ferromagnetic impurities could account for the magnetic moment of 3.27. The possibility that antiferromagnetic interactions may be responsible for the magnetic moment is rejected on the basis of the crystal structure determination. Similar in coordination environment to the cobalt sulfinato complex is the series of halogeno(quadridentate ligand)cobalt(III) complexes where the quadridentate ligand is a nitrogen-donor anionic Schiff base, reported by Gerloch and co-workers.<sup>27</sup> The magnetic moments of these compounds range from 2.7 to 3.15; this paramagnetism is attributed to the discrepancy between the strong in-plane ligand field of the anionic Schiff base and the weak axial field of the halogen. Similarly, the nonequivalence of the ligand fields of the axial sulfur atoms as compared to the nitrogen donors in the  $xy$  plane may lead to the energy level splitting in the complex described in Figure 1. If, as a result of the electronic distortion, the  $d_{z^2}$  and  $d_{xy}$  levels become of comparable energy, the complex would be in a triplet ground state. Alternatively, a thermal equilibrium may be set up between these two states. The room temperature magnetic moment of 3.27, compared to the spin-only magnetic moment of  $2.83 (\mu_{s.o.} = [n(n+2)]^{1/2})$  for two unpaired spins, indicates that almost all of the complex must be in the triplet state at room temperature. Griffith<sup>28</sup> has shown that the <sup>3</sup>T<sub>1</sub> state of the  $t_2^2e$  configuration cannot be the ground term of

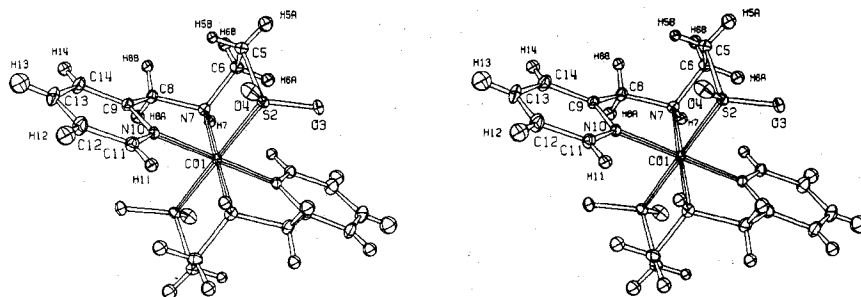


Figure 2. A stereoview<sup>39</sup> of the  $[\text{Co}(\text{C}_8\text{H}_{11}\text{N}_2\text{SO}_2)_2]^+$  complex with ellipsoids of 20% probability.

a  $d^6$  ion in a regular octahedral field but allows that this may not be true in a tetragonal field.

Triplet spin states are more common for Fe(II) than Co(III).<sup>29-34</sup> However, intermediate magnetic moments have been observed for Co(III) complexes,<sup>27,35,36</sup> and a stable triplet ground state has been found in bis(toluene-3,4-dithiolato)cobalt(III).<sup>35</sup>

**X-Ray Data Collection.** The crystal used was a rectangular prism with extreme dimensions  $0.08 \times 0.20 \times 0.22$  mm. It was mounted about an axis approximately parallel to its longest dimension.

Reflections are observed only when the conditions ( $hkl$ ;  $h + k = 2n$ ), ( $h0l$ ;  $l = 2n$ ), and ( $0k0$ ;  $k = 2n$ ) are satisfied. The space group is therefore  $C2/c$  or  $Cc$ . The centric space group  $C2/c$  was indicated by the density of peaks on Harker elements of the Patterson function and was verified by the successful refinement of the structure.<sup>37</sup>

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\text{K}\alpha_1$ ,  $\lambda$  0.70930 Å;  $\text{K}\alpha_2$ ,  $\lambda$  0.71359 Å) and with a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections for which  $7 < 2\theta < 25^\circ$ . The temperature was constant throughout at 25 (1) °C. The  $\theta$ - $2\theta$  scan mode with a scan rate ( $\omega$ ) in  $2\theta$  of  $1^\circ \text{ min}^{-1}$  was used. The total background counting time, equal to the scan time, was equally spent at each end of the scan range, which varied from  $2.0^\circ$  at low  $2\theta$  to  $2.3^\circ$  at  $55^\circ$ ; that is, from  $1^\circ$  in  $2\theta$  below the  $\text{K}\alpha_1$  maximum to  $1^\circ$  above that of  $\text{K}\alpha_2$ . The intensities of three reflections from diverse regions of reciprocal space, which were remeasured after every 100 during data collection, showed only a small decrease in intensity of 1.5%, for which the appropriate correction was applied.

Standard deviations were assigned to individual reflections according to the formula

$$\sigma(I) = [\omega^2(\text{CT} + B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count,  $B_1$  and  $B_2$  are the background counts, and the intensity  $I = \omega(\text{CT} - B_1 - B_2)$ . A value of 0.02, appropriate to the instrumentation used, was assigned to the empirical parameter<sup>38</sup>  $p$  to account for instrument instability. The weights,  $w$ , used in least squares were the reciprocal squares of  $\sigma(F_o)$ . Of the 2945 symmetry-independent reflections measured, all those for which  $2\theta < 55^\circ$ , 2147 had intensities greater than three times their standard deviations, and only these were included in subsequent calculations. The intensities were corrected for Lorentz and polarization effects;<sup>37</sup> the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. An absorption correction<sup>37,39</sup> ( $\mu = 15.92 \text{ cm}^{-1}$ ) was applied which approximated the crystal shape by a  $6 \times 10 \times 10$  grid; the calculated transmission coefficients ranged from 0.772 to 0.887. The atomic scattering factors<sup>40</sup> for  $\text{Co}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{S}^0$ ,  $\text{O}^0$ ,  $\text{N}^0$ ,  $\text{C}^0$ , and H (bonded)<sup>41</sup> were used. The first three were modified to include the real part of the anomalous dispersion correction.<sup>42</sup>

**Crystal Data.** Bis[2-[(2-pyridylmethyl)amino]ethylsulfinato]cobalt(III) perchlorate dihydrate,  $[\text{Co}(\text{C}_8\text{H}_{11}\text{N}_2\text{SO}_2)_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ :  $C2/c$ ,  $a = 23.171$  (4) Å,  $b = 11.397$  (2) Å,  $c = 9.210$  (2) Å,  $\beta = 96.62$  (2)°,  $V = 2416$  (1) Å<sup>3</sup>, mol wt 592.5 amu,  $d_{\text{obsd}}$  (floatation) = 1.649  $\text{g cm}^{-3}$ ,  $d_{\text{calcd}} = 1.629 \text{ g cm}^{-3}$ ,  $Z = 4$ , and  $F(000) = 1184$ . Figures in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

**Structure Determination.** The position of the cobalt atom was determined using a three-dimensional Patterson function.<sup>37</sup> A conventional  $R_1$  value of 0.452 was obtained based on the cobalt atom

Table I. Final Positional Parameters and Their Standard Deviations<sup>a</sup>

	$x$ ( $\delta(x)$ )	$y$ ( $\delta(y)$ )	$z$ ( $\delta(z)$ )
Co(1)	2500	2500	0
S(2)	2135.9 (4)	848.7 (7)	830.8 (9)
O(3)	2557 (1)	277 (2)	1926 (3)
O(4)	1852 (1)	46 (2)	259 (3)
C(5)	1587 (2)	1475 (4)	1819 (4)
C(6)	1848 (2)	2583 (4)	2516 (4)
N(7)	2060 (1)	3358 (3)	1375 (3)
C(8)	1585 (2)	4032 (3)	519 (4)
C(9)	1414 (1)	3464 (3)	-915 (4)
N(10)	1790 (1)	2668 (2)	-1332 (3)
C(11)	1657 (2)	2124 (3)	-2635 (4)
C(12)	1166 (2)	2388 (4)	-3554 (4)
C(13)	793 (2)	3221 (5)	-3149 (5)
C(14)	906 (2)	3746 (4)	-1798 (5)
Cl(15)	0	3257 (2)	2500
O(16)	168 (2)	4017 (5)	1366 (5)
O(17)	479 (2)	2662 (6)	3081 (6)
O(18)	4664 (10)	4438 (23)	1488 (24)
O(19)	4882 (11)	4904 (23)	4087 (21)
H(5A)	150 (2)	95 (4)	249 (4)
H(5B)	129 (2)	170 (3)	127 (4)
H(6A)	221 (2)	241 (3)	319 (4)
H(6B)	157 (2)	296 (3)	296 (4)
H(7)	228 (2)	380 (3)	178 (4)
H(8A)	173 (2)	477 (4)	35 (4)
H(8B)	127 (2)	412 (3)	103 (4)
H(11)	191 (2)	159 (3)	-291 (4)
H(12)	112 (2)	202 (4)	-438 (5)
H(13)	47 (2)	343 (4)	-369 (5)
H(14)	69 (2)	430 (3)	-148 (4)

<sup>a</sup> Values for nonhydrogen atoms are given  $\times 10^4$ ; values for hydrogen atoms are given  $\times 10^3$ . See Figures 2 and 3 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

alone, where  $R_1 = \sum(|F_o - |F_{\text{cl}}||) / \sum F_o$ . All other nonhydrogen atoms were located in successive Fourier syntheses using the fast-Fourier algorithm. Hydrogen atom positions were calculated assuming C-H and N-H distances of 0.95 and 0.87 Å, respectively.<sup>43</sup> These positions were also clearly observed on a difference Fourier function. The hydrogen atoms of the disordered water molecules were not located.

Full-matrix least-squares refinement with isotropic thermal parameters for the hydrogen atoms and the disordered water oxygens, and anisotropic thermal parameters for all other nonhydrogen atoms, led to the final error indices,  $R_1 = 0.043$  and  $R_2 = 0.048$ , where  $R_2 = [\sum w(F_o - |F_{\text{cl}}|)^2 / \sum w F_o^2]^{1/2}$ . The final "goodness-of-fit",  $[\sum w(F_o - |F_{\text{cl}}|)^2 / (m - s)]^{1/2} = 5.04$ , remains high, presumably because of the ill-defined positions of the water molecules and their unlocated hydrogen atoms. The number of observations used in least squares is  $m$  (2147), and  $s$  (199) is the total number of parameters. The overdetermination ratio ( $m/s$ ) is therefore 10.8.

In the final cycle of least-squares refinement, the shift in each nonhydrogen positional parameter was less than 5% of its esd, and the largest shift in a nonhydrogen thermal parameter was less than 7% of its esd. For the hydrogen atoms, all shifts were less than 50% of their esd's, with the largest shifts being oscillatory in nature. The largest peak on the final difference Fourier function, whose esd was calculated to be  $0.1 \text{ e } \text{Å}^{-3}$ , is  $0.6 \text{ e } \text{Å}^{-3}$  in height, and is located near

Table II. Thermal Vibrational Parameters and Their Standard Deviations<sup>a</sup>

1. Nonhydrogen Atoms						
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$						
	$\beta_{11}$ or $B_{\text{iso}}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co(1)	7.3 (1)	23.7 (5)	41.4 (7)	1.7 (4)	0.6 (4)	1.7 (10)
S(2)	11.4 (2)	29.9 (6)	63.8 (10)	-2.6 (5)	9.7 (6)	15.0 (13)
O(3)	14.5 (5)	48 (2)	105 (4)	10 (2)	10 (2)	77 (5)
O(4)	24.0 (7)	47 (2)	95 (4)	-27 (2)	15 (3)	-32 (5)
C(5)	10.5 (7)	51 (3)	79 (5)	-1 (3)	14 (3)	20 (7)
C(6)	13.2 (7)	56 (3)	60 (4)	4 (3)	20 (3)	-3 (7)
N(7)	9.4 (6)	37 (2)	57 (3)	1 (2)	2 (2)	-19 (5)
C(8)	11.3 (7)	41 (3)	83 (5)	13 (3)	7 (3)	-8 (6)
C(9)	9.3 (6)	40 (3)	73 (4)	5 (2)	4 (3)	9 (6)
N(10)	8.4 (5)	35 (2)	54 (3)	5 (2)	-1 (2)	11 (4)
C(11)	11.3 (7)	50 (3)	64 (4)	4 (2)	-5 (3)	-7 (6)
C(12)	14.6 (8)	85 (4)	70 (5)	4 (3)	-19 (3)	-25 (8)
C(13)	12.2 (8)	108 (5)	104 (6)	13 (3)	-27 (4)	31 (9)
C(14)	11.1 (8)	72 (4)	107 (6)	21 (3)	-3 (3)	8 (8)
Cl(15)	11.6 (3)	102 (2)	133 (2)	0.0	-8 (1)	0.0
O(16)	46 (1)	251 (8)	207 (7)	-71 (6)	66 (5)	47 (12)
O(17)	34 (1)	354 (11)	290 (10)	144 (6)	-13 (6)	26 (16)
O(18)	22.6 (9) <sup>b</sup>					
O(19)	22.4 (9) <sup>b</sup>					

2. Hydrogen Atoms					
	$B, \text{\AA}^2$		$B, \text{\AA}^2$		$B, \text{\AA}^2$
H(5A)	3 (1)	H(6B)	3 (1)	H(8B)	2 (1)
H(5B)	2 (1)	H(7)	2 (1)	H(11)	2 (1)
H(6A)	3 (1)	H(8A)	3 (1)	H(12)	4 (1)
				H(13)	5 (1)
				H(14)	3 (1)

<sup>a</sup> The  $\beta$ 's are  $\times 10^4$ . See Figures 2 and 3 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter. <sup>b</sup> Isotropic  $B$  in  $\text{\AA}^2$ .

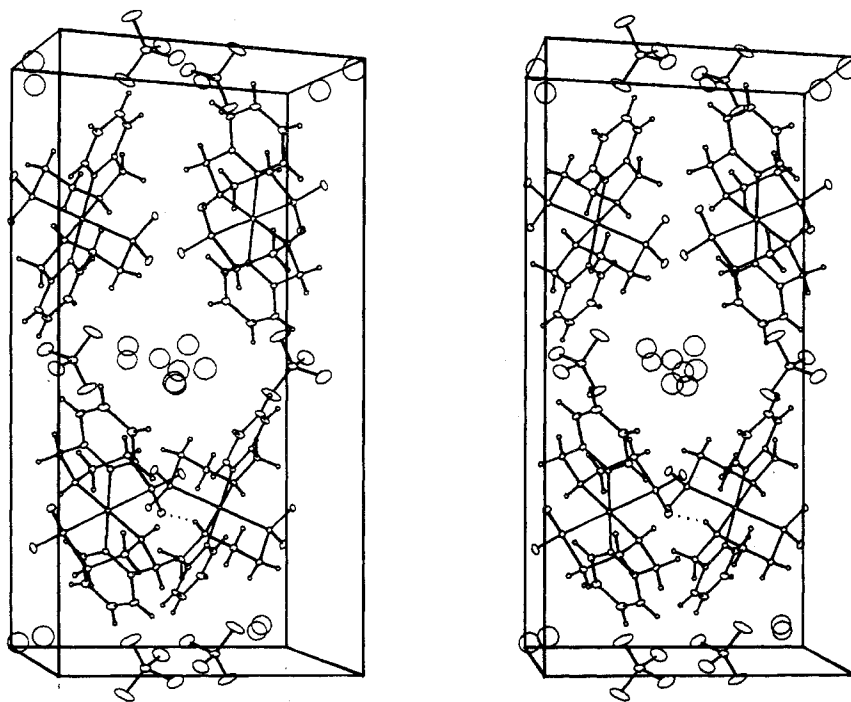


Figure 3. A stereoview<sup>39</sup> of the structure of  $[\text{Co}(\text{C}_8\text{H}_{11}\text{N}_2\text{SO}_2)]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ , bis[2-[(2-pyridylmethyl)amino]ethylsulfonato]cobalt(III) perchlorate dihydrate, with its unit cell, showing ellipsoids of 20% probability. Hydrogen atoms have been assigned isotropic thermal parameters of  $1.0 \text{\AA}^2$ . The view is approximately along  $c$ , with  $a$  vertical and  $b$  horizontal in the plane of the page.

the middle of the close  $\text{O}(18)\cdots\text{O}(19)$  contact between the two disordered water molecules.

The final positional and thermal parameters, together with their standard deviations, are presented in Tables I and II.

### Discussion

The  $\text{Co}(\text{III})$  ion lies at an inversion center in a near octahedral environment. The angles about  $\text{Co}(1)$  are within  $6^\circ$  of  $90^\circ$  (see Table III).  $\text{Co}(1)$  participates in four five-

membered chelate rings involving coordination by two amine nitrogens, two pyridyl nitrogens, and two sulfurs of the sulfonato groups (see Figures 2 and 3).  $\text{Co}(1)$ ,  $\text{N}(7)$ , and  $\text{C}(8)$  lie within  $0.3 \text{\AA}$  of the plane of the pyridine ring (see Figure 2 and Table IV). With angles about it ranging from  $108.0$  to  $113.9^\circ$ , the sulfur atom,  $\text{S}(2)$ , is nearly tetrahedral.

One intermolecular hydrogen bond is observed between the amine nitrogen and a sulfato oxygen atom (see Figure 3 and

Table III. Molecular Dimensions and Esd's<sup>a</sup>

A. Bond Lengths, Å			
Co(1)-S(2)	2.233 (1)	C(5)-H(5A)	0.90 (4)
Co(1)-N(7)	1.974 (3)	C(5)-H(5B)	0.85 (4)
Co(1)-N(10)	1.945 (2)	C(6)-H(6A)	0.99 (4)
S(2)-O(3)	1.473 (3)	C(6)-H(6B)	0.90 (4)
S(2)-O(4)	1.457 (3)	N(7)-H(7)	0.78 (4)
S(2)-C(5)	1.796 (4)	C(8)-H(8A)	0.93 (4)
C(5)-C(6)	1.512 (3)	C(8)-H(8B)	0.93 (4)
C(6)-N(7)	1.497 (5)	C(11)-H(11)	0.90 (4)
N(7)-C(8)	1.490 (5)	C(12)-H(12)	0.87 (4)
C(8)-C(9)	1.483 (5)	C(13)-H(13)	0.88 (4)
C(9)-N(10)	1.344 (4)	C(14)-H(14)	0.88 (4)
N(10)-C(11)	1.355 (4)	Cl(15)-O(16)	1.445 (5)
C(11)-C(12)	1.370 (5)	Cl(15)-O(17)	1.356 (4)
C(12)-C(13)	1.364 (7)	O(18)···O(19)	2.45 (4)
C(13)-C(14)	1.378 (6)	N(7)···O(3) <sup>b</sup>	2.778 (4)
C(14)-C(9)	1.388 (5)		
B. Bond Angles, Deg			
N(7)-Co(1)-N(10)	83.91 (12)	O(16)-Cl(15)-O(16')	106.3 (4)
N(7)-Co(1)-S(2)	87.37 (8)	O(17)-Cl(15)-O(17')	120.0 (4)
N(10)-Co(1)-S(2)	88.48 (8)	O(16)-Cl(15)-O(17)	108.0 (3)
Co(1)-S(2)-O(3)	111.1 (1)	H(5A)-C(5)-H(5B)	112 (3)
Co(1)-S(2)-O(4)	116.8 (1)	S(2)-C(5)-H(5A)	108 (2)
Co(1)-S(2)-C(5)	99.0 (1)	S(2)-C(5)-H(5B)	113 (2)
Co(1)-N(7)-C(8)	108.6 (2)	H(6A)-C(6)-H(6B)	113 (3)
Co(1)-N(10)-C(9)	114.5 (2)	C(5)-C(6)-H(6A)	111 (2)
Co(1)-N(7)-C(6)	113.1 (3)	C(5)-C(6)-H(6B)	108 (2)
O(3)-S(2)-O(4)	113.9 (2)	C(6)-N(7)-H(7)	107 (3)
O(3)-S(2)-C(5)	106.3 (2)	Co(1)-N(7)-H(7)	106 (3)
O(4)-S(2)-C(5)	108.0 (2)	H(8A)-C(8)-H(8B)	108 (3)
S(2)-C(5)-C(6)	105.9 (3)	N(7)-C(8)-H(8A)	107 (2)
C(5)-C(6)-N(7)	110.0 (3)	N(7)-C(8)-H(8B)	111 (2)
N(7)-C(8)-C(9)	110.6 (2)	N(10)-C(11)-H(11)	118 (2)
C(8)-C(9)-N(10)	115.6 (3)	H(11)-C(11)-C(12)	120 (2)
C(9)-N(10)-C(11)	118.2 (3)	C(11)-C(12)-H(12)	117 (3)
N(10)-C(11)-C(12)	122.3 (3)	H(12)-C(12)-C(13)	124 (3)
C(11)-C(12)-C(13)	119.4 (4)	C(12)-C(13)-H(13)	124 (3)
C(12)-C(13)-C(14)	119.2 (4)	H(13)-C(13)-C(14)	117 (3)
C(13)-C(14)-C(9)	119.3 (4)	C(13)-C(14)-H(14)	123 (2)
C(14)-C(9)-N(10)	121.5 (3)	H(14)-C(14)-C(9)	117 (3)
		N(7)-H(7)···O(3) <sup>b</sup>	151 (3)
C. Selected Torsion Angles, Deg			
Co(1)-N(7)-C(8)-C(9)	26.3		
Co(1)-N(10)-C(9)-C(8)	3.2		
N(10)-C(9)-C(8)-N(7)	15.8		
Co(1)-S(2)-C(5)-C(6)	37.8		
N(7)-C(6)-C(5)-S(2)	54.6		
Co(1)-N(7)-C(6)-C(5)	45.2		
N(10)-Co(1)-S(2)-O(3)	176.9		

<sup>a</sup> The esd is in the units of the least significant digit given for the corresponding parameter. The coordinates of the primed atoms are related to those given in Table I by an intramolecular twofold axis at Cl(15). <sup>b</sup> Intermolecular hydrogen bond.

Tables IIIA and IIIB). The only other hydrogen bond in the structure occurs between the disordered water molecules (Figure 3 and Table IIIA); its severe foreshortening can be ascribed to the large thermal motions of the two water molecules.

The Co(III)-N coordination distance to amine N of 1.974 (3) Å is very similar to the *cis* Co(III)-N distance of 1.978 (3) Å in [Co(en)<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)](ClO<sub>4</sub>)(NO<sub>3</sub>).<sup>6</sup> This distance is 1.956 (4) Å in (±)-tris[(ethylenediamine)cobalt(III)] trichloride trihydrate<sup>44</sup> and about 1.96 Å in most octahedral cobalt(III)-amine complexes.<sup>45-47</sup>

The Co-pyridyl N coordination length of 1.945 (2) Å can be compared to those observed in the strained complex, [aqua(2,2':6',2'':6'',2''':-quaterpyridyl)sulfitecobalt(III)] nitrate monohydrate, 1.854, 1.860, 1.960, and 1.979 Å.<sup>48</sup> As expected, the Co(III)-pyridyl N bond length is 0.031 Å shorter than Co(III)-amine N, probably due to back-bonding from the metal ion to the empty π\* orbitals of the pyridine ring.

Table IV. Deviations of Atoms from Least-Squares Planes (Å × 10<sup>3</sup>)<sup>a</sup>

	Plane 1	Plane 2	Plane 3	Plane 4
Co(1)	-166	0	0	0
S(2)		0	0	0
N(7)	311	0	0	
N(10)	-9	0		0
O(3)			1356	-73
O(4)			-1026	-902
C(5)			-381	
C(6)			362	
C(8)	-28	-543		
C(9)	4	-318		
C(11)	14			
C(12)	2			
C(13)	-25			
C(14)	14			
<i>q<sub>a</sub></i>	-5455	-3751	7062	-4946
<i>q<sub>b</sub></i>	-7183	-8675	-650	5247
<i>q<sub>c</sub></i>	4317	3266	7050	6928
<i>D</i>	-5	-5	4	-1
<i>δ</i>	14	0	0	0

<sup>a</sup> Deviations in italics indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with coordinates given in Table I lies between that plane and the origin. The direction cosines (×10<sup>4</sup>), *q*, are with respect to orthogonalized axes. *D* is the distance (in Å) from the plane to the origin. The rms deviation (Å × 10<sup>3</sup>) of the italic atoms from the plane is *δ*.

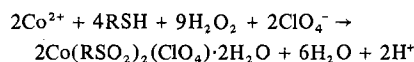
The S-O bond lengths of 1.457 (3) and 1.473 (3) Å are within the range observed in octahedral cobalt(III) sulfite complexes<sup>48-51</sup> and are essentially identical with the S-O distances in [Co(en)<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)](ClO<sub>4</sub>)(NO<sub>3</sub>),<sup>6</sup> 1.456 (4) and 1.476 (4) Å.

The Co-S distance of 2.233 (1) Å is somewhat longer than the corresponding 2.191 (2) Å distance found in [Co(en)<sub>2</sub>(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)](ClO<sub>4</sub>)(NO<sub>3</sub>).<sup>6</sup> The Co(III)-S distance ranges from 2.259 to 2.285 Å in the distorted tris(4-morpholinecarbodithioate-*S,S'*) complex with Co(III).<sup>52</sup> The sum of the covalent radii for octahedral Co(III) (1.22 Å) and tetrahedral S (1.04 Å) is 2.26 Å, according to Pauling.<sup>53</sup>

In the cobalt-thiol system discussed in this work, several oxidation reactions occur in the presence of hydrogen peroxide. The cobaltous ion is oxidized to the +3 state, the thiol is oxidized to the sulfinate, and some thiol is oxidized to the disulfide, which forms a complex with Co(II). Probably a sulfenate intermediate also forms.

Transition-metal ions can catalyze the formation of disulfide from thiol in the presence of air or hydrogen peroxide.<sup>54</sup> For example, Fe(II) reacts with thiol to form a bis(thiolato)iron(II) complex, which is then oxidized to the Fe(III) complex by a free radical mechanism.<sup>55</sup> Such a mechanism seems to apply to Fe<sup>2+</sup>, Mn<sup>2+</sup>, and Co<sup>2+</sup> when the thiol is 3-hydroxy-2-mercaptopyridine, and yellow crystals of the disulfide are obtained.<sup>56</sup>

Oxidation to sulfenato and sulfinato complexes has been shown to occur in cobalt(III) cysteine and in [Co(en)<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)]<sup>2+</sup> complexes in the presence of hydrogen peroxide.<sup>6-10</sup> In its absence, only a reddish brown powder characterized as Co(RSSR)(ClO<sub>4</sub>)<sub>2</sub> by elemental analysis and its infrared spectrum is isolated. Thus the formation of the sulfinato complex requires the presence of hydrogen peroxide. The net reaction is



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**Registry No.** 2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>SH, 65149-73-7; [Co(2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 65150-30-3; [Co(2-pyCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)·2H<sub>2</sub>O, 65150-37-0.

**Supplementary Material Available:** A listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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## Stereochemistry of the Toluene Solvate of $\alpha,\beta,\gamma,\delta$ -Tetraphenylporphinatozinc(II)

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The crystal and molecular structure of the toluene solvate of  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatozinc(II) has been determined by x-ray diffraction techniques. The compound crystallizes in the triclinic system, space group  $P\bar{1}$ . The unit cell has  $a = 11.349$  (2) Å,  $b = 11.404$  (2) Å,  $c = 10.502$  (2) Å,  $\alpha = 110.48$  (2)°,  $\beta = 103.87$  (2)°,  $\gamma = 107.65$  (2)°, and  $Z = 1$ . Measurement of diffracted intensities employed  $\omega$  scans with graphite-monochromated Mo  $K\alpha$  radiation on a Syntex  $P\bar{1}$  diffractometer. All independent reflections for  $(\sin \theta)/\lambda \leq 0.725$  Å<sup>-1</sup> (5436 unique observed data) were examined. These data were used for the determination of structure and full-matrix least-squares refinement. The final conventional and weighted discrepancy factors were 0.047 and 0.057. The molecule has required  $C_2$ - $\bar{1}$  symmetry. The average Zn-N bond distance is 2.036 (6) Å with the zinc atom precisely centered in the porphinato plane. The interplanar spacing between the porphyrin mean plane and a toluene plane is 3.34 Å.

Earlier studies<sup>2-6</sup> have established the structures of the  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato metal(II) derivatives of the first-row transition elements manganese(II) through copper(II). These studies have provided a quantitative picture of the structural changes, in a closely related series of complexes, resulting from the stepwise addition of d electrons. We

report herein the molecular stereochemistry of the final member of this series,  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatozinc(II), and in the following paper<sup>7</sup> that of the earliest known member<sup>8</sup> in the sequence,  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatochromium(II).

All of the previously studied derivatives, except MnTPP,<sup>2</sup> have the metal ion centered in the plane of the porphinato