Molecular Structure and Electronic Spectra of Bis[β-mercapto-β′,β″-dimethylethylamino]cobaltate(II), $Co[SC(CH_3)_2CH_2NH_2]_2$

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Abstract: The crystal and molecular structures of $Co[SC(CH_3)_2CH_2NH_2]_2$ have been determined from single-crystal three-dimensional x-ray data collected by counter methods. The compound crystallizes as dark blue six-sided plates in space group $C222_1$ (D_2^5, No. 20) with $Z = 4$, $a = 5.592$ (5) Å, $b = 10.508$ (8) Å, $c = 21.85$ (1) Å, and $d_{obsd} = 1.39$ (1) g/cm^3. Least-squares refinement of 708 reflections having $F^2 \geq 3\sigma(F^2)$ gave a conventional R factor of 0.051. All atoms in the structure were located. The structure consists of discrete $Co[SC(CH_3)_2CH_2NH_2]_2$ molecules having C_2 overall symmetry an local C_{2v} symmetry for the bare CoS_2N_2 unit. The Co–S and Co–N bond lengths are 2.272 (2) and 2.057 (6) Å, respectively. A dihedral angle of 78.8 (2)° between the S–Co–S and N–Co–N planes indicates that the pseudotetrahedral CoS_2N_2 unit is slightly flattened. The observed Co···Co distance of 5.591 (6) Å effectively precludes significant metal–metal interactions. Single-crystal spectra have been measured over the 450–1900 nm region. The visible absorption spectra are markedly broadened and structured relative to those of strictly T_d Co(II) complexes. Absorptions at ~280 and ~370 nm (mull spectra) are assigned to the σ- and π-components of S → Co(II) charge transfer, respectively. The lowest energy electronic absorption of the free mercaptide ligand (λ_{max} 240 nm, ϵ ~2800) is blue-shifted to ~210 nm in $Co[SC(CH_3)_2CH_2NH_2]_2$ and to ~225 nm in the isostructural $Zn[SC(CH_3)_2CH_2NH_2]_2$ complex.

Two hypotheses have been advanced to account for the intense absorption at ~600 nm exhibited by blue Cu(II) proteins such as laccase and stellacyanin: (a) it is due to an especially intense ligand field excitation; (b) it arises from a charge transfer process involving Cu(II) and a sulfur atom from a neighboring cysteine residue. Recent electronic spectral[1] and Raman[2] studies of various blue Cu(II) proteins and electronic spectral studies of Co(II) doped stellacyanin, plastocyanin, and azurin[3] have supported the latter hypothesis. Absorptions of these Co(II) proteins at 300 and 355 nm were assigned as the σ- and π-components of a S(cysteine) → Co(II) charge transfer excitation, respectively. Intense low energy absorptions of the native blue copper proteins at ~600 and ~800 nm have been ascribed to analogous excitations of a S(cysteine)–Cu(II) chromophore. To better define the charge-transfer and related properties of such chromophores, we have chosen to synthesize and structurally characterize appropriate Co(II) and Cu(II) model mercaptide complexes. The present work deals primarily with one such model Co(II) complex.

Other workers have observed charge transfer and ligand field absorptions from aqueous complexes of Co(II) and ligands such as mercaptoacetate, cysteine, and cysteine methyl ester.[4,5] However, the structures of these aqueous species have not been well characterized, although evidence for the formation of Co(II) polynuclear ions has been presented.[6] With the exception[7] of the benzene thiolate Co(II) cluster $[Co_4(C_6H_5S)_{10}]^{2-}$, structural details of Co(II)–mercaptide bonding have not been identified. For $[Co_4(C_6H_5S)_{10}]^{2-}$ and comparable species, identification of the Co(II)–mercaptide charge transfer absorptions is expected to be difficult because of the complexity of these structures and/or the interference from strong ligand electronic absorptions. To minimize such spctral interference and to inhibit the formation of cluster species, we have prepared complexes of $^-SC(CH_3)_2CH_2NH_2$, a sterically hindered mercaptoamine related to the chelating drug penicillamine. We report here the molecular structure and electronic spectra of $Co[SC(CH_3)_2CH_2NH_2]_2$ which crystallizes as discrete pseudotetrahedral units.[8] The molecular structure of the isostructural $Zn[SC(CH_3)_2CH_2NH_2]_2$ will be described elsewhere.[9] Ultraviolet spectra of the free mercaptide ligand and of the Zn(II) complex are presented here; these facilitate our assignment of the charge-transfer spectra exhibited by the Co(II) complex.

Experimental Section

Preparation of $HSC(CH_3)_2CH_2NH_2 \cdot HCl$. This compound was synthesized using a published procedure[10] modified only by reducing the intermediate nitro precursor ($C_6H_5CH_2SC(CH_3)_2CH_2NO_2$) with Al(Hg) instead of with $LiAlH_4$. The resulting amine was cleaved in Na/NH_3 and crystallized as the HCl salt from ether/isopropyl alcohol. The product gave the anticipated NMR in D_2O and melted at 218 °C (sealed capillary, lit. 208 °C).[10]

Preparation of $Co[SC(CH_3)_2CH_2NH_2]_2$. The synthesis and isolation of this complex were carried out under a N_2 atmosphere in Schlenk apparatus of standard design. A deoxygenated solution of 0.566 g of ligand HCl (0.004 mol) and 0.476 g of $CoCl_2 \cdot 6H_2O$ (0.002 mol) in 150 cm^3 of distilled H_2O was treated with ~1 cm^3 of triethylamine. The resulting deep blue solution was filtered and allowed to stand at room temperature. Crystallization began after ~0.5 h and was completed after 2 days. Most of the crystalline product adhered to the glass walls. The crystals were isolated by decantation, washed with water and methanol, and dried in a N_2 stream. The complex crystallized as elongated six-sided plates which had a marked tendency to grow in stacks and which exhibited a blue-purple dichroism along the extinction directions shown in Figure 1. Aqueous solutions of the product were rapidly oxidized by air. Crystals coated with mineral oil were moderately air stable; however, they darkened after about 12 h. The crystals appeared to be stable indefinitely at 25 °C in a N_2 atmosphere.

Preparation of $Zn[SC(CH_3)_2CH_2NH_2]_2$. The synthesis of the Zn(II) complex paralleled that of the Co(II) analogue, except that anaerobic conditions were not required. A solution of 0.002 mol of ligand and 0.001 mol of $ZnSO_4 \cdot 7H_2O$ or $ZnCl_2 \cdot H_2O$ in 75 cm^3 of warm distilled water was made alkaline (pH 9–10) with Et_3N. The resulting cloudy mixture was filtered and allowed to stand at 25 °C for 1 day. The complex crystallized as colorless six-sided plates which exhibited a tendency to stack together. Crystallographic studies[9] of $Zn[SC(CH_3)_2CH_2NH_2]_2$ (currently R = 7%) have established its isostructural relationship to the Co(II) analogue.

Electronic-Spectral Measurements. Spectral measurements were made with a Cary Model 14 instrument. The use of nondispersed radiation for measurements in the 650–1900-nm spectral range did not cause serious photodecomposition of the samples. Polarization measurements were made with matched Glan-Thompson prisms that have a usable angular field of ~15°. Separate polarizers in the sample and reference beams were rotated in unison by a chain drive mechanism.

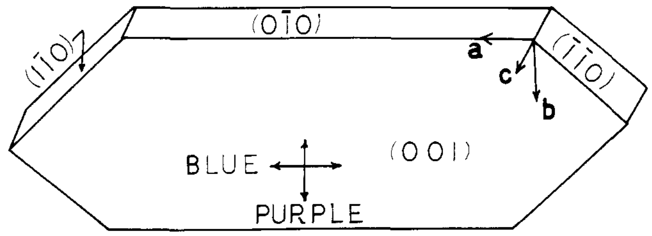

Figure 1. Sketch of a typical $Co[SC(CH_3)_2CH_2NH_2]_2$ crystal showing the crystallographic axes, extinction directions, and face indices.

Table I. Crystal Data for $Co[SC(CH_3)_2CH_2NH_2]_2$

FW 267.3		
Space group	$C222_1(D_2^5$, no. 20)	
$Z = 4$		
$a = 5.592$ (5) Å	$b = 10.508$ (8) Å	$c = 21.85$ (1) Å
$V = 1283.7$ Å^3		
$d_{obsd} = 1.39(1)$ g/cm^3	$d_{calcd} = 1.383$ g/cm^3	
$\mu = 16.7$ cm^{-1}	λ 0.71069 Å	

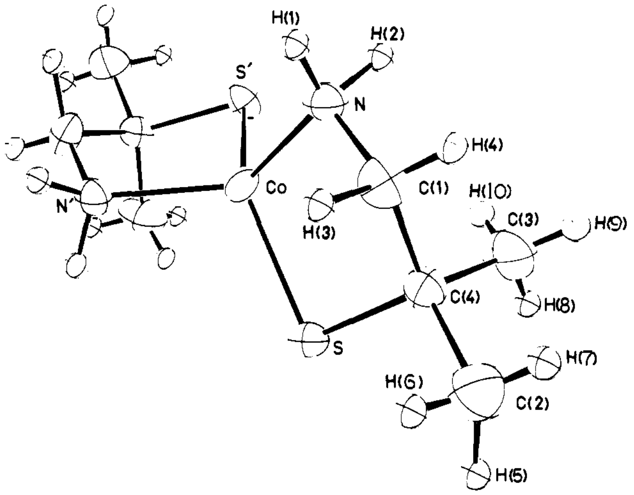

Figure 2. View of $Co[SC(CH_3)_2CH_2NH_2]_2$ showing the atom numbering scheme.

The crystals were oriented such that the light beam was normal to the (001) face and the vertical direction of the cell compartment was approximately parallel to the ($\bar{1}$10) face. Because the thin plates were pitted and not uniformly thick, accurate ε's for the spectral bands could not be obtained.

Standard cannula techniques were used to transfer solutions of the complex under N_2 to an air-tight spectral cell. The intensity of the visible absorption bands diminished as the complex proceeded to crystallize within the cell; no shifts in band positions were detected.

Dispersions of the Co(II) and Zn(II) complexes in either mineral oil or Fluorolube gease were used to obtain mull spectra. As expected, the infrared spectra of these complexes were nearly superimposable over the 4000–1300 cm^{-1} spectral range. Mulls of each complex (between KBr plates) that gave equally intense infrared absorptions were also investigated in the visible/near-UV region with the Cary 14 instrument. In this way, preliminary electronic-spectral comparisons could be made between comparably "concentrated" mulls of the Zn(II) and Co(II) complexes.

Collection of Diffraction Data. A six-sided plate of approximate dimensions 0.36 × 0.21 × 0.10 mm was mounted, under N_2, inside a glass capillary parallel to the long dimension (a). Preliminary Weissenberg photographs showed systematic absences for hkl ($h + k = 2n + 1$) and $00l$ ($l = 2n + 1$) along with mmm reciprocal lattice symmetry, fixing the orthorhombic space group as $C222_1$. Unit cell constants (Table I) were determined from a least-squares analysis of the θ, χ, and ϕ angles of 10 reflections centered using Mo Kα radiation and an Enraf-Nonius CAD-3 automated diffractometer. The density of the crystals was measured by the density gradient method[11] using CCl_4 and isoamyl alcohol; NH_4Cl ($d = 1.527$ g/cm^3), thiourea ($d = 1.405$ g/cm^3), and urea (1.323 g/cm^3) were used as standards.[12] The observed density of 1.39 (1) g/cm^3 agreed well with the value of 1.383 g/cm^3 calculated for $Z = 4$.

A total of 1127 reflections was collected at room temperature (22 ± 1 °C). Graphite monochromated Mo Kα radiation was detected with a scintillation counter and pulse height analyzer set to admit approximately 95% of the Kα peak. A θ–2θ scan was used to collect a unique data set in the range $2 \leq \theta \leq 30°$. The scan range (S) was set according to the function $S = 1.10 + 0.10 \tan \theta$. Background measurements were made at the beginning and end of each scan with the counter stationary; the total time for background counting was equal to the scan time. The scan rate was $\frac{1}{6}$°/s, and each reflection was scanned repeatedly to a maximum of five scans or until 8000 total counts were obtained. Intensities were placed on a common scale by dividing by the number of scans. The intensity of a standard reflection, measured at 50 reflection intervals, was consistent to ±2%. Lorentz and polarization factors were applied to the 1127 measured intensities. Of these, 708 with $F^2 \geq 3\sigma(F^2)$ were used in the structure solution and refinement; here, $\sigma(F^2) = (LP)^{-1}(N_t + (0.02N_n)^2)^{1/2}$ is the standard deviation estimated from counting statistics, N_t is the total count (scan plus background), N_n is the net count (scan minus background), and 0.02 is an estimate of instrumental instability. The linear absorption coefficient μ for Mo Kα radiation was 16.7 cm^{-1}, while maximum and minimum absorption factors for the data collected were calculated to be 1.28 and 1.67, respectively. Because this variation in absorption factors is relatively small, absorption corrections were not applied.

Solution and Refinement of the Structure.[13] Since $Z = 4$, the molecule must utilize some symmetry element of the crystal. Analysis of a normal sharpened Patterson map revealed the Co atom at special position b ($0,y,\frac{1}{4}$) and the unique S atom in a general position. A difference Fourier map based on the Co and S phases revealed the position of the N and four C atoms. All atoms were treated as neutral species, and, except for hydrogen,[14] scattering factors were obtained from the compilations of Cromer and Waber.[15] Initial refinement was based on F^2. Four cycles of refinement using isotropic temperature factors gave values of 0.12 and 0.19 for the functions $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF} = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, respectively; weights were set according to $w = 1/\sigma^2(F^2)$. All atoms were then allowed to vibrate anisotropically, and both real and imaginary parts of the anomalous dispersion corrections were applied to the Co and S atoms.[14] Two cycles of refinement reduced R_F and R_{wF^2} to 0.074 and 0.15, respectively. At this point, a difference electron density map was calculated, and the ten hydrogen atoms were located. They were included in the refinement with isotropic temperature factors equal to those of the atoms to which they were bonded. Inclusion of the H atoms reduced R_F and R_{wF} to 0.070 and 0.13.

Further refinement was based on F, and a weighting scheme was chosen by an analysis of variance to make $\Delta F/\sigma(F_o)$ independent of $|F_o|$. This led to the following assignments for $\sigma(F_o)$:$\sigma(F_o) = -0.080|F_o| + 2.76$ for $|F_o| \leq 29.5$; $\sigma(F_o) = 0.057|F_o| - 1.28$ for $|F_o| > 29.5$.

Three cycles of full-matrix least-squares refinement of all atomic coordinates and all non-hydrogen thermal parameters gave final values of 0.051 and 0.041 for R_F and $R_{wF} = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$, respectively. For the last cycle, all parameter changes were less than 0.5σ, where σ is the estimated standard deviation obtained from the inverse matrix. A final difference map showed a general background of approximately 0.3 e/Å^3 and revealed no significant features. Final atomic parameters and their estimated standard deviations are given in Tables II and III. A list of observed and calculated structure factors is available.[16]

Description of the Structure

A view of the complex, showing the numbering scheme, is given in Figure 2; the molecular packing is shown in Figure 3. Important interatomic distances and angles are presented in Table IV. The structure consists of discrete $Co[SC(CH_3)_2CH_2NH_2]_2$ units. Except for a possible hydrogen bonding interaction between H(1) and the mercaptide group of a neighboring complex (H···S″, 2.50 (9) Å, N···S″, 3.508 (5) Å, N—H···S″, 167 (6)°), the packing of the molecule reveals no unusual features. The observed Co···Co distance

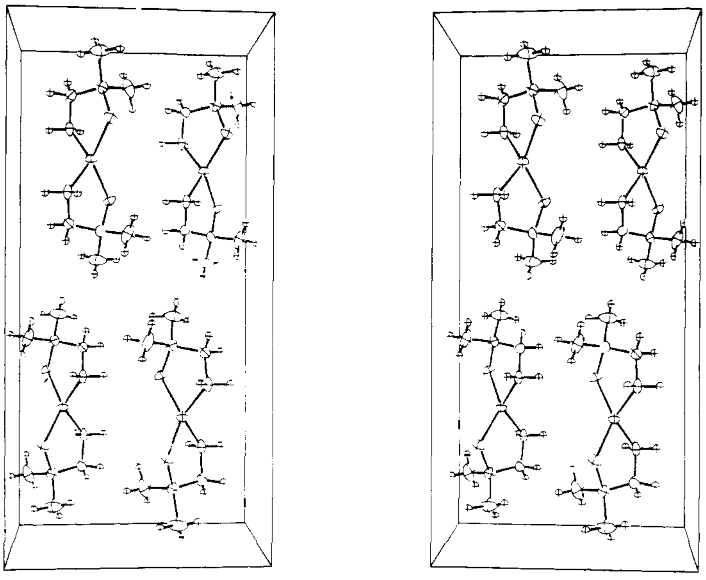

Figure 3. Stereographic view of the unit cell contents along $\bar{a}$; the b axis is horizontal and the c axis is vertical.

Table II. Fractional Atomic Coordinates (× 10^4) and Anisotropic Thermal Parameters[a] (× 10^4) for Non-Hydrogen Atoms [b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	1886 (1)	2500	172 (3)	47.9 (9)	10.2 (2)	0	3 (1)	0
S′	2670 (3)	1124 (2)	1807 (1)	153 (5)	64 (1)	13.1 (3)	17 (3)	1 (1)	2.8 (6)
N	1826 (9)	2796 (5)	3190 (3)	150 (15)	43 (5)	16 (1)	−6 (7)	0 (4)	1 (2)
C(1)	491 (10)	2748 (6)	3774 (3)	271 (27)	54 (5)	13 (1)	−8 (9)	5 (5)	−8 (2)
C(2)	−2464 (14)	1592 (9)	4426 (4)	276 (23)	123 (9)	17 (2)	−24 (14)	11 (6)	−1 (3)
C(3)	978 (12)	391 (8)	3969 (4)	223 (21)	74 (6)	29 (2)	30 (12)	0 (6)	16 (4)
C(4)	−809 (11)	1469 (6)	3872 (3)	169 (15)	58 (5)	12 (1)	8 (7)	0 (4)	2 (2)

[a] The anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses are the estimated standard deviations (obtained from the inverse matrix) in the least significant digits in this and in all other tables.

Table III. Hydrogen Fractional Atomic Coordinates (× 10^3) and Isotropic Temperature Factors (× 10^2)

Atom	x	y	z	B (Å^2)
H(1)	225 (16)	375 (9)	317 (4)	200
H(2)	288 (20)	240 (9)	321 (4)	200
H(3)	−78 (15)	355 (7)	374 (4)	210
H(4)	135 (15)	288 (8)	409 (4)	210
H(5)	−343 (21)	95 (10)	444 (5)	278
H(6)	−340 (18)	229 (9)	431 (4)	278
H(7)	−165 (16)	176 (9)	472 (3)	278
H(8)	39 (17)	−34 (9)	402 (4)	257
H(9)	204 (19)	55 (8)	432 (4)	257
H(10)	193 (15)	22 (9)	363 (3)	257

Table IV. Bond Lengths (Å) and Bond Angles (deg)

Co-S	2.272 (2)	N-Co-N′	124.6 (3)
Co-N	2.057 (6)	S-Co-S′	138.7 (1)
N-C(1)	1.479 (8)	N-Co-S′	109.0 (2)
C(1)-C(4)	1.544 (9)	N-Co-S	90.1 (2)
C(2)-C(4)	1.529 (10)	Co-S-C(4)	95.5 (2)
C(3)-C(4)	1.525 (10)	Co-N-C(1)	111.5 (3)
S-C(4)	1.849 (6)	S-C(4)-C(2)	108.2 (4)
Co···Co	5.951 (6)	S-C(4)-C(3)	109.6 (5)
N-H(1)	1.03 (9)	C(2)-C(4)-C(3)	110.5 (6)
N-H(2)	0.72 (10)	C(2)-C(4)-C(1)	108.7 (6)
C(1)-H(3)	1.10 (8)	C(3)-C(4)-C(1)	110.9 (5)
C(1)-H(4)	0.85 (8)	C(4)-C(1)-N	112.8 (5)
C(2)-H(5)	0.86 (11)	S-Co-S′/N-Co-N′	78.7 (2)
C(2)-H(6)	0.94 (10)		
C(2)-H(7)	0.81 (8)		
C(3)-H(8)	0.85 (10)		
C(3)-H(9)	0.98 (10)		
C(3)-H(10)	0.93 (8)		

(5.591 (6) Å), along with the absence of bridging groups, effectively precludes significant metal-metal interactions.

Crystallographic requirements fix the Co(II) site symmetry as C_2, although the bare CoS_2N_2 unit has C_{2v} symmetry. Each Co(II) atom is bonded to two sulfur and two nitrogen atoms. A dihedral angle of 78.8 (2)° between the S-Co-S′ and N-Co-N′ planes shows the S_2N_2 ligand arrangement to be a slightly compressed tetrahedron (dihedral angles of 90° and 0° are required for tetrahedral and square planar arrangements, respectively). A similar distortion from local tetrahedral symmetry in bis[dihydrobis(1-pyrazolyl)borato]cobalt(II) has been attributed[17] to the steric requirements of the bidentate ligands. However, this type of distortion was not observed[18] with bis(*N-tert*-butylpyrrole-2-carboxaldimino)cobalt(II) which also contains bidentate ligands. The dihedral angles of these latter two complexes were reported as 81.1° and 89.6 (4)°, respectively.

The Co-N(amine) bond length in the present structure (2.057 (6) Å) is approximately 0.08 Å longer than the Co(II)-N(aromatic) distances reported for several pyrrole,[18] pyrazole,[17] and imidazole[19] complexes, suggesting weaker bonding in the present structure. Within the error of measurement, it is equal to that reported[18] (2.066 (8) Å) for the Co-N(azomethine) bond in bis(*N-tert*-butylpyrrole-2-car-

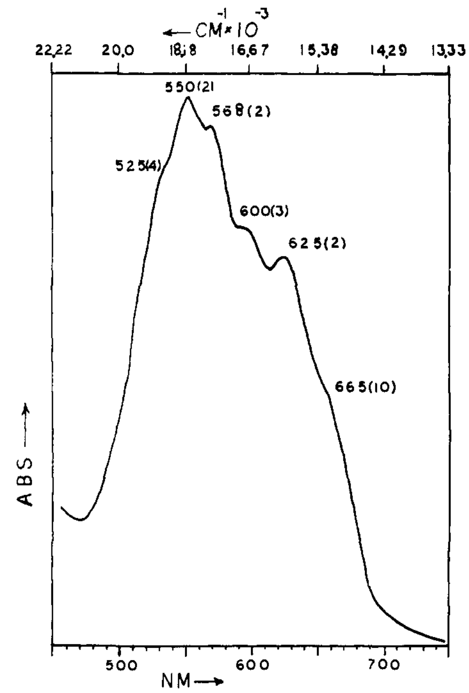

Figure 4. Single-crystal electronic spectrum of $Co[SC(CH_3)_2CH_2NH_2]_2$ taken with unpolarized radiation at 80 K over the 450-750-nm region. The light beam was normal to the (001) face.

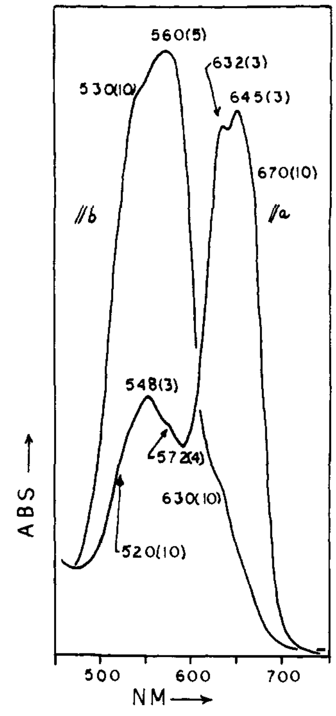

Figure 5. Polarized single-crystal spectra of $Co[SC(CH_3)_2CH_2NH_2]_2$ taken at 300 K over the 450-750-nm region with the light beam normal to (001) and the electric vector parallel to either the crystallographic *a* or *b* axes.

boxaldimino)cobalt(II). The Co-S bond distance (2.272 (2) Å) is comparable to that reported[7] (2.25 (1) Å) for the terminal $C_6H_5S^-$ ligation in $[Co_4(C_6H_5S)_{10}]^{2-}$, the only other structurally characterized tetrahedral Co(II)-S complex of which we are aware. The structure of the ligand itself shows no unusual features and is similar to that reported for $HSCH_2CH_2NH_2 \cdot HCl$.[20]

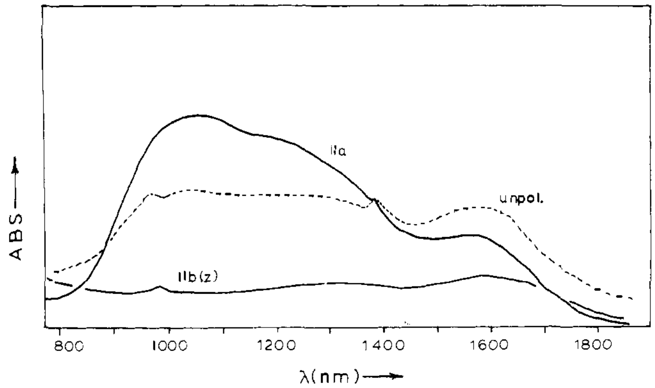

Figure 6. Polarized single-crystal spectra of $Co[SC(CH_3)_2CH_2NH_2]_2$ taken at 300 K over the 750-1900-nm region with the light beam normal to (001) and electric vector parallel to either the crystallographic *a* or *b* axes. Reference unpolarized spectra measured at 80 K with the light beam normal to (001) are drawn with a dashed line (- - -).

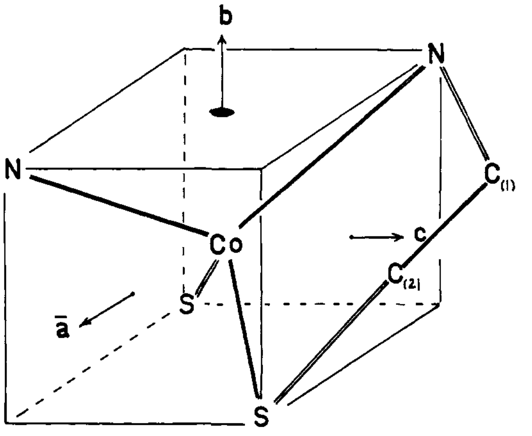

Figure 7. The relationship between the molecular and crystallographic axes for $Co[SC(CH_3)_2CH_2NH_2]_2$.

Electronic Spectral Studies

Visible-Near-IR Region. Single-crystal visible spectra in the 450-750 nm region are presented in Figure 4 (80 K, unpolarized) and in Figure 5 (300 K, polarized). Single-crystal polarized infrared spectra in the 750-1900 nm region are shown in Figure 6, while Figure 7 gives the relationship between the molecular and crystal axes. The appearance of the unpolarized spectra changed little over the 80-300 K temperature range. Although cooling produced a modest sharpening of the absorption bands, neither fine structure nor changes in relative band intensities were observed. Polarization measurements were restricted by the size and plate-like habit of the crystals to the a and b directions. Consequently, we were unable to determine whether the polarized spectra agreed with the strict C_2 overall symmetry (nonequivalent spectra for *a* and *c* polarized radiation) or with the C_{2v} local symmetry of the CoS_2N_2 unit (equivalent spectra for *a* and *c* polarized radiation).

All of the single-crystal spectra showed broad structured band systems in the visible and infrared regions; these are characteristic of pseudotetrahedral Co(II) complexes.[21,22] The solution spectra of the complex (Figure 8) showed considerably less structure. Since neither the structure of the solution species nor the extinction coefficients of their absorption bands are known at this time, the solution results must be regarded as preliminary. They are included only to indicate that the solution and solid state spectra differ substantially.

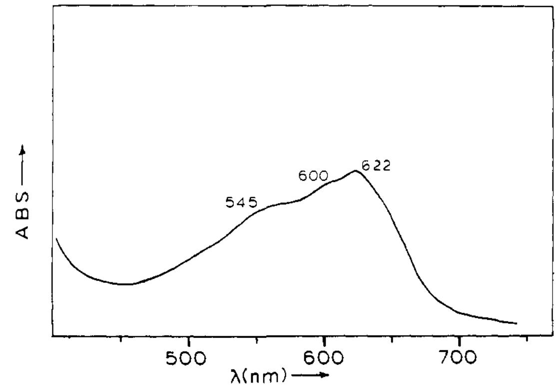

Figure 8. The solution spectrum of $Co[SC(CH_3)_2CH_2NH_2]_2$ taken at 298 K over the 400–750-nm region.

With strictly tetrahedral Co(II) ions, the two commonly observed quartet-quartet transitions are $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$; the $^4A_2 \rightarrow {}^4T_2(F)$ transition usually is obscured by infrared vibrations. Our studies were restricted to the spectral regions appropriate for observing the $^4A_2 \rightarrow {}^4T_1(F)$ near-infrared and $^4A_2 \rightarrow {}^4T_1(P)$ visible absorptions. A maximum of three low symmetry orbital components is allowed in C_2 symmetry for electronic transitions to these parent states.[22] The complexity of the visible absorption spectra (Figures 4 and 5) shows that a strictly tetrahedral model cannot be used to interpret these spectra. Attempts to interpret the electronic spectra of other pseudotetrahedral Co(II) complexes have been discussed in detail elsewhere.[22,23] In addition to the effects of the low symmetry ligand field, factors such as the spin-orbit coupling of Co(II), Jahn-Teller splitting of excited states, and mixing of neighboring doublet states with components of the $^4T_1(P)$ state[24] must be considered. This last effect, present to some degree even in strictly T_d Co(II) systems, may be heightened in the title complex by its low symmetry, the spin-orbit effects of the sulfur-containing ligand, and a fairly strong ligand field. An estimate of the ligand field may be obtained if the centers of gravity of the near-infrared and visible absorptions are assumed to approximate the energies of the "parent" $^4A_2 \rightarrow {}^4T_1(F)$, $^4T_1(P)$ transitions.[25] Estimates of $\nu_2 \cong 8600$ and $\nu_3 \cong 17\,600$ cm^{-1} were obtained in this fashion and used to calculate values of 5000 and 740 cm^{-1} for D and B, respectively. The states responsible for the visible bands are presumably neighboring quartet and doublet spin-orbital components that are well mixed by the large, low symmetry ligand field. We see no way to reliably interpret our spectral results further until the nature of these states can be probed by detailed ligand field calculations.

To probe the Co(II) site symmetry in the enzyme alkaline carbonic anhydrase, other workers have compared the MCD and optical spectra of the enzyme to those of model Co(II) complexes.[26,27] Here, we note that the single-crystal optical spectra of the pseudotetrahedral title complex approximate the absorptions of this t enzyme (bands at 518, 555, 618, and 642 nm). Although the interpretation of this result is not yet clear, it does suggest that additional emphasis be placed on pseudotetrahedral Co(II) chromophores.

UV Region. Aqueous solutions of $HSC(CH_3)_2CH_2NH_2 \cdot HCl$ at pH 11-12 exhibited a shoulder (λ_{max} 240 nm, $\beta \cong 2800$) on the tail of a more intense higher energy band (λ_{max} not observed). At this high pH, the ligand is largely ionized; absorption at 240 nm is characteristic of deprotonated mercaptans.[28] Mull spectra of $Zn[SC(CH_3)_2CH_2NH_2]_2$ consisted of a single absorption at ~225 nm which we assign to the blue-shifted mercaptide absorption of bound $^-SC(CH_3)_2CH_2NH_2$. The stabilization of the mercaptide lone pairs upon complexation may be expected to shift the ligand localized n → π* absorptions to higher energy. Mull spectra of $Co[SC(CH_3)_2CH_2NH_2]_2$ included bands at ~370 and ~280 nm. The band at 280 nm was more intense and appeared as the shoulder of a higher energy band ($\lambda_{max} \leq 210$ nm). Extrapolating from the behavior of the free mercaptide ligand and its Zn(II) complex, we attribute this high energy band in part to a localized mercaptide transition which has been blue-shifted in the Co(II) complex. Finally, we suggest that the absorptions at ~280 and 370 nm arise from the σ- and π-components of S → Co(II) ligand metal charge transfer, respectively. The separation between these absorptions, ~8000 cm^{-1}, may be compared with the values of 3600-4900 cm^{-1} reported[3] for the seemingly analogous UV absorptions of several Co(II)-doped blue copper proteins. Our studies support the S → Co(II) LMCT assignment that has been proposed by other workers for the absorptions of Co(II)-doped stellacyanin, plastocyanin, and azurin at ~300 and ~355 nm. However, the splitting of the mercaptide σ and π orbitals and energies of the S → Co(II) LMCT absorptions will depend on both the chemical nature and symmetry of the Co(II) ligand donor set. Therefore, $Co[SC(CH_3)_2CH_2NH_2]_2$ cannot exactly mimic the chromophores of the above Co(II) proteins.

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Supplementary Material Available: Structure factor tables for $Co[SC(CH_3)_2CH_2NH_2]_2$ (4 pages). Ordering information is given on any current masthead page.

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The Trans-Influence and Axial Interactions in Low Spin, Tetragonal Cobalt(II) Complexes Containing Macrocyclic and/or Cyano Ligands. Pulse Radiolytic Studies in Fluid Solution, Electron Paramagnetic Resonance Spectra at 77 K, and Single-Crystal X-Ray Structures[1]

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Abstract: Investigations of the weak interactions between low spin cobalt(II) species and their axial ligands have been performed. X-ray structural studies of six-coordinate $Co(N_4)(OH_2)_2^{2+}$ and $Co(N_4)(ClO_4)_2$ complexes, where (N_4) is an equatorially coordinated tetradentate macrocyclic ligand, reveal that the axial Co–ligand bond lengths are 0.3–0.5 Å longer per bond than are the equatorial Co–ligand bond lengths. By means of the pulse radiolytic reductions of the corresponding cobalt(III) complexes, low spin cobalt(II) species of the types $Co^{II}(N_4)L_2$ ($L = NH_3, NO_2^-, CN^-$) and $Co^{II}(CN)_5X$ ($X = Cl, CN$) have been generated, and the rates of ligand exchange with water in the reduced species have been determined by a kinetic conductivity method. All the cobalt(II) species have been found to be very labile in two (axial) coordination positions, with an appreciable range of rate constants ($k \geqslant 10^3\ s^{-1}$) which depend on both the equatorial and the axial ligands. Electron paramagnetic resonance spectra have provided evidence for interactions with either one or two axial ligands (at 77 K) but on the whole have not provided definitive criteria regarding the coordination number of low spin cobalt(II) species in fluid solution. At least some of the ambiguity may arise because the unpaired electron is in an antibonding orbital. Comparison of the results of this and other studies suggests a strong trans influence in the axial ligand interactions of low spin cobalt(II) complexes. A simple three-center bonding model has been used to describe the weak axial interactions. This model also provides a convenient basis for interpreting the absorption spectrum of a $Co^{II}(N_4)CN$ transient generated in the pulse radiolysis studies. It is inferred that the synergistic trans-influence deduced for low spin cobalt(II) species may be a significant factor in inner sphere electron transfer reactions.

Although the aqueous solution chemistry of low spin cobalt(II) complexes is relevant to the chemistry of such natural systems as the corrinoids[3] and to various issues of concern in the fixation of dioxygen,[4] relatively little is known of the chemical behavior of such systems. Synthetic low spin cobalt(II) systems include the pentacyanocobaltate(II) ion, oxime complexes, Schiff-base complexes, and macrocyclic complexes. The dearth of information regarding the solution chemistry of these cobalt(II) complexes is attributable in part to the difficulties in handling relatively oxygen sensitive species, and in part to the lability of the d^7 electronic configuration.[6-12] In contrast, a substantial literature is developing concerning the structural chemistry of these systems.[13-17] In the solid state the low spin cobalt(II) complexes containing synthetic ligands are tetragonally distorted five-[13] or six-coordinate[14-17] species. Despite the limited correlative solution chemistry, there has been appreciable concern with the nature of the species in solution. Inferences regarding the nature of the low spin cobalt(II) species in solution have been most often based on the 77 K EPR spectra of frozen solutions,[3,4,18-24] and on solid state structural studies.[13-15,25] While both the structural and EPR studies provide evidence for five-[4,13,18,21-23,25,26] and six-coordinate[14,15-17,19,20,22,23] species, a substantial body of opinion seems to have developed that the species in solution are five coordinate.[4,18,21] Some of the low spin cobalt(II) species claimed to be five coordinate[5,21] in aqueous solution are in fact six coordinate diaquo species in the solid state.[15] Since it seemed surprising that the number of axial ligands should decrease as the activity of the ligand is increased, and since the color difference which has come to be associated with five- and six-coordinate cyano and phenylisocyanide complexes[13,22] has not been established as a general property of low spin cobalt(II), we have undertaken to compare solid state, EPR, and solution studies of several low spin cobalt(II) complexes. Since all the solid state structural studies of low spin cobalt(II) complexes reveal tetragonal distortion, we investigated axial ligand lability as the solution property most sensitive to variations in structural and spectroscopic parameters of these complexes. The solvated electron reduction of various cobalt(III) complexes provides a very convenient means of in situ preparation of cobalt(II) complexes with a variety of axial ligands. We have employed the recently reported kinetic conductivity method coupled to pulse radiolysis[11,12] to examine the axial lability of such cobalt(II) complexes.

Experimental Section

A. Preparation of Complexes. Methods of preparation and characterization of the cobalt(III) complexes employed in this study may

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