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Amine Adducts of Thiocarbamate Complexes. Synthesis, Characterization, and Molecular Structure of Bis(cyclotetramethylenethiocarbamato)bis(pyrrolidine)cobalt(II)

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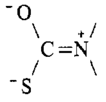
The crystal and molecular structure of the complex bis(cyclotetramethylenethiocarbamato)bis(pyrrolidine)cobalt(II), $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$, has been examined by single-crystal X-ray structural techniques. The complex crystallizes in the orthorhombic space group P_{ccn} (D_{2h}^{10}, No. 56) with cell dimensions of $a = 12.102$ (3) Å, $b = 15.013$ (3) Å, $c = 12.556$ (3) Å, and $Z = 4$. The intensities of 3734 reflections were measured on an automated Picker four-circle diffractometer of which 992 have been included in the refinement. Full-matrix least-squares analysis including hydrogen atoms gave final discrepancy factors of $R_1 = 0.046$ and $R_2 = 0.049$. The Co(II) ion is located at a center of twofold symmetry imposing C_2 symmetry on the molecule. The coordination geometry about the metal resembles a distorted octahedron with the thiocarbamate ligands chelated to the metal (Co-S = 2.584 (2), Co-O = 2.157 (4) Å) and the pyrrolidine ligands bonded in cis positions (Co-N(1) = 2.134 (5) Å). Solid-state spectral and magnetic properties of the complex are typical of distorted octahedral Co(II) systems and are consistent with the results of the molecular structure determination.

Introduction

The chemical and structural properties of thiocarbamate complexes have been shown within the past 5 years to differ markedly from the well-characterized dithiocarbamates. The dithiocarbamates, for example, form simple chelated bis and tris complexes with a variety of metal ions while the thiocarbamates in the absence of other ligands form sulfur-bridged polymeric species. Polymeric coordination geometries have been identified crystallographically for the complexes $[Ni(SOCN(C_3H_7)_2)_2]_6$[1] and $[M(SOCN(C_3H_7)_2)]_6$ (M = Cu, Ag)[2,3] and are postulated for the oligomeric complexes of Zn(II), Cd(II), and Hg(II).[4] No thiocarbamate complex has yet been found to have a simple chelated structure for the ligand. The bonding differences observed for the thiocarbamates relative to their dithiocarbamate analogs and other related sulfur-oxygen donor ligands seem to be related to the increased mercaptide character of the C-S bond in this ligand system and a decrease in the importance of resonance form III in the electronic description of the coordinated ligand.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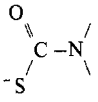
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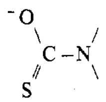
III

A distinctive feature of the chemistry of thiocarbamate complexes is the ease with which monomeric nitrogen base adducts are formed. Spectroscopic studies on the nickel complexes have shown that the polymeric structure of the parent complex is broken up with the formation of stable five- and six-coordinate adducts upon treatment with amines.[5] Similar studies carried out on the Zn(II) and Cd(II) complexes have indicated the exclusive formation of bis-amine adducts.[4] A structural study on the bis-piperidine adduct of the zinc(II) complex $Zn(SOCN(C_5H_{10}))_2$ revealed that upon adduct formation the thiocarbamate oxygens are displaced from the metal with the ligand bonded to the metal through the sulfur donors.[6] Structural features of this complex indicate that this mode of thiocarbamate coordination is also consistent with the mercaptide character of the sulfur.

While well-characterized dithiocarbamate complexes of Co(II) have not been reported, the thiocarbamates readily form polymeric complexes of the form $[Co(tic)_2]_n$. These oligomers add nitrogen base ligands in a manner similar to the Zn(II) systems previously studied, forming bis adducts of the form $Co(tic)_2(N)_2$. From general similarities of the coordination properties of Co(II) and Zn(II) with related sulfur-oxygen donor ligands the complexes $Co(tic)_2(N)_2$ might be expected to resemble their zinc analogs.[7] However, the results of a detailed study of the spectral and structural properties of bis(cyclotetramethylenethiocarbamato)bis(pyrrolidine)cobalt(II), $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$, show that this is not the case. The results of this study are presented herein.

Experimental Section

Synthesis of $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$. The thiocarbamate ligand was prepared as its pyrrolidinium salt from pyrrolidine and carbonyl sulfide in ether by procedures described elsewhere.[8] An 8.98-g (0.044-mol) sample of this salt was mixed thoroughly with 2.88 g (0.022 mol) of anhydrous cobalt(II) chloride and the resulting solid mixture was treated with 100 ml of dry ether containing 2.85 g (0.044 mol) of pyrrolidine. The mixture was shaken vigorously for about 10 min to give a dark blue solution. An additional 100 ml of ether was then added and the mixture was filtered. The filtrate was stirred for 1 hr, filtered again, and reduced in volume to about 60 ml. The filtrate remaining after another filtration was then allowed to evaporate slowly under a controlled flow of dry nitrogen. The crystals of the purple complex obtained by this procedure were washed with an acetone-ether solution (10:1) and dried *in vacuo*; mp 122–124°.

Spectral Measurements. Electronic absorption spectra of the complex were obtained in both solution and solid phases. Solid-state spectra were recorded on a Cary 14 from a Nujol mull, while solution spectra were recorded in spectral grade solvents.

Infrared spectra were obtained from KBr disks of the complex in the range 200–4000 cm^{-1}. The paramagnetic susceptibility was determined by the Faraday method.

Collection and Reduction of the X-Ray Data. A crystal of the complex $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ was mounted and prepared for the crystallographic study. Weissenberg and precession photographs of the *hk*0, *hk*1, *h*0*l*, *h*1*l*, 0*kl*, and 1*kl* zones indicated that the crystal belonged to the orthorhombic system. The observed extinction pat-

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tern of $hk0$, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$, and $0kl$, $l = 2n + 1$, is consistent with space group P_{ccn} (D_{2h}^{10}, No. 56)[9] with the crystal mounted along the c^* axis. The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 12 strong, independent reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 12.102$ (3) Å, $b = 15.013$ (3) Å, $c = 12.556$ (3) Å, and $V = 2281$ Å^3. An experimental density of 1.345 (5) g/cm^3 agrees well with a calculated density of 1.342 g/cm^3 for four molecules per unit cell. Thus either twofold or $\bar{1}$ symmetry is imposed on the molecule. The mosaic spread of the crystal was determined using the narrow-source, open-counter ω-scan technique.[10] The average width at half-height was found to be acceptable at 0.06°. An independent set of intensity data was collected by the θ-2θ scan technique using the Zr-filtered Mo Kα peak with allowances made for the Kα_1-Kα_2 separation at higher 2θ values. The data set was collected within the angular range $4.5° \leqslant 2\theta \leqslant 60°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/sec during the scan. The attenuators used were brass foil of thickness chosen to give an approximate attenuation factor of 2.5. During data collection the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 2% during the time required to collect the data. Data were processed in the usual way with values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. Since the crystal was approximately equidimensional and the linear absorption coefficient small ($\mu = 9.77$ cm^{-1}), no correction was made for absorption effects. The intensities of a total of 3734 reflections were measured of which 992 were observed to be greater than 2σ and have been included in the refinement.

Solution and Refinement of the Structure. From a three-dimensional Patterson function it was determined that the position of the Co atom was at one of the twofold positions of the space group and was chosen to be position 4c. After two cycles of least-squares refinement of the scale factor, the cobalt z positional parameter and its isotropic thermal parameter descrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^{\,2})^{1/2}$ were 0.54 and 0.63, respectively. From the Fourier map based on this refinement the positions of the sulfur, oxygen, and pyrrolidine nitrogen atoms were determined. A refinement of these four atoms gave discrepancy indices of $R_1 = 0.317$ and $R_2 = 0.400$. A subsequent Fourier revealed the positions of the remaining nitrogen and carbon atoms. A refinement of all nonhydrogen atoms with isotropic thermal parameters gave discrepancy indices of $R_1 = 0.103$ and $R_2 = 0.110$. Two cycles of refinement with anisotropic thermal parameters assigned to all atoms gave indices of $R_1 = 0.069$ and $R_2 = 0.078$. A Fourier map based on the anisotropic refinement clearly indicated the positions of all 17 hydrogen atoms of the structure. Three cycles of refinement of both hydrogen and nonhydrogen atoms gave final discrepancy indices of $R_1 = 0.046$ and $R_2 = 0.049$. During all cycles of refinement the function minimized was $w(|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^{\,2}/\sigma^2(F_o^{\,2})$. The standard deviations $\sigma(F^2)$ were estimated from counting statistics described previously.[11] In all calculations the atomic scattering factors for the nonhydrogen atoms were those of Cromer and Waber,[12] while the hydrogen scattering factors were taken from the tabulation of Stewart, *et al.*[13] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Co and S atoms taken from the report by Cromer and Liberman.[14] At the completion of the refinement the standard deviation of an observation of unit weight was 1.06. The final positional and thermal parameters of the nonhydrogen atoms of the structure are given in Table I. Table II contains root-mean-square vibrational amplitudes of anisotropically refined atoms. Positional and thermal parameters for the hydrogen atoms are given in Table III. A table of the final F_o and $|F_c|$ values for the 992 reflections used in the refinement is available.[15]

Spectral and Magnetic Properties

The infrared spectrum of $\mathrm{Co(SOCN(C_4H_8))_2(NC_4H_9)_2}$ is consistent with that found for other thiocarbamate complexes.[16] Of particular interest is the 1500-1600-cm^{-1} region of the spectrum where the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching frequencies have been previously assigned.[4,16] A strong, relatively sharp band is located at 1565 cm^{-1} and another strong, somewhat broader band is centered at 1515 cm^{-1}. These bands, which compare favorably with those reported previously for thiocarbamate complexes, are assigned as $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ frequencies, respectively.[4,16,17] The alternative assignment of the band at 1565 cm^{-1} as an N-H deformation is not reasonable in view of the high band intensity and the fact that N-H deformation frequencies in secondary amines are weak and rarely observed.[18] Krankovits and coworkers[19] have recently proposed that the presence of a band near 1570 cm^{-1} in thiocarbamate complexes can be taken as an indication of uncoordinated oxygen. The present result clearly shows that this is not a reliable criterion and that at the present stage of development infrared studies cannot be used to determine the mode of coordination of thiocarbamate ligands.

The magnetic moment of $\mathrm{Co(SOCN(C_4H_8))_2(NC_4H_9)_2}$ was found to be 4.82 BM at 297.49°K and 4.57 BM at 100.5°K. The high-temperature value compares favorably with the magnetic moments of other cobalt(II) complexes, which normally fall in the range 4.7-5.2 BM.[20] The decrease in magnetic moment with decreasing temperature is consistent with the behavior expected for complexes with T ground terms.

The electronic spectrum of the complex was obtained within the energy range 5000-20,000 cm^{-1} using the mull technique. The spectrum consists of a broad band (width at half-height ~2,300 cm^{-1}) centered at 7700 cm^{-1} and a set of three closely spaced and more intense bands at 17,240, 18,180, and 19,230 cm^{-1}. Spin-allowed transitions for cobalt(II) in an octahedral field are $^4\mathrm{T_{1g}(F)} \rightarrow {}^4\mathrm{T_{2g}(F)}$ (ν_1), $^4\mathrm{T_{1g}(F)} \rightarrow {}^4\mathrm{A_{2g}(F)}$ (ν_2), and $^4\mathrm{T_{1g}(F)} \rightarrow {}^4\mathrm{T_{1g}(G)}$ (ν_3). The ν_2 transition is a two-electron transition and is not normally observed.[21] Thus, the low-energy band is assigned to the ν_1 transition and the group of three more intense bands are assigned as components of ν_3. The structured nature of ν_3 is not uncommon in the spectra of cobalt(II) complexes and is considered to arise either from spin-forbidden transitions to doublet terms or from low-symmetry ligand field components.[21] The latter factor is of particular significance in the present case in view of the highly distorted octahedral coordination geometry. When dissolved in the weakly polar solvents benzene and diethyl ether the purple complex gives either green (benzene) or amber (ether) solutions. The spectra of these solutions are similar showing a narrow symmetrical band at *ca.* 17,700 cm^{-1} and a broad unsymmetrical band of lower intensity with maxima at approximately 7400 and 9300 cm^{-1}. These results strongly suggest that in solution a structural change occurs for the complex. However, further

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Table I. Final Atomic Positional and Anisotropic Thermal Parameters for $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.2500	0.2500	0.09709 (9)	0.0094 (1)	0.00420 (6)	0.00512 (8)	0.0003 (1)	0.0000	0.0000
S	0.1274 (2)	0.1694 (1)	0.2353 (1)	0.0110 (2)	0.0056 (1)	0.0067 (1)	0.0012 (1)	0.0010 (1)	0.0001 (1)
O	0.3018 (4)	0.1146 (3)	0.1256 (3)	0.0129 (5)	0.0052 (3)	0.0053 (3)	−0.0010 (3)	0.0012 (3)	0.0015 (2)
N(1)	0.1259 (4)	0.2326 (3)	−0.0219 (4)	0.0075 (5)	0.0053 (4)	0.0073 (4)	0.0007 (4)	0.0002 (4)	−0.0002 (3)
N(2)	0.2368 (4)	0.0167 (3)	0.2478 (4)	0.0080 (5)	0.0046 (3)	0.0071 (4)	0.0001 (4)	0.0004 (4)	0.0004 (3)
C(1)	0.2310 (5)	0.0958 (4)	0.1982 (5)	0.0086 (7)	0.0040 (3)	0.0059 (5)	−0.0003 (4)	−0.0014 (5)	0.0000 (3)
C(2)	0.3264 (6)	−0.0487 (4)	0.2197 (6)	0.0098 (7)	0.0052 (4)	0.0128 (7)	0.0021 (5)	0.0017 (6)	0.0008 (5)
C(3)	0.3050 (8)	−0.1227 (6)	0.2981 (8)	0.0205 (12)	0.0079 (6)	0.0187 (11)	0.0042 (7)	0.0062 (10)	0.0050 (7)
C(4)	0.2247 (7)	−0.0975 (5)	0.3749 (7)	0.0154 (12)	0.0079 (5)	0.0155 (9)	0.0017 (6)	0.0036 (8)	0.0062 (6)
C(5)	0.1658 (5)	−0.0129 (4)	0.3377 (5)	0.0080 (6)	0.0066 (4)	0.0086 (6)	−0.0005 (4)	0.0007 (5)	0.0019 (4)
C(6)	0.0157 (6)	0.2737 (5)	0.0024 (6)	0.0072 (7)	0.0082 (6)	0.0095 (6)	0.0012 (5)	0.0007 (5)	−0.0002 (4)
C(7)	−0.0683 (6)	0.2255 (5)	−0.0665 (7)	0.0086 (7)	0.0090 (7)	0.0143 (9)	0.0012 (5)	−0.0011 (7)	0.0013 (6)
C(8)	−0.0120 (7)	0.1428 (6)	−0.1054 (7)	0.0101 (8)	0.0099 (6)	0.0166 (9)	−0.0010 (6)	−0.0024 (8)	−0.0029 (7)
C(9)	0.1006 (6)	0.1398 (5)	−0.0520 (6)	0.0110 (8)	0.0069 (5)	0.0097 (7)	0.0007 (5)	−0.0020 (6)	−0.0020 (5)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Root-Mean Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Co	0.202 (2)	0.219 (1)	0.265 (2)
S	0.226 (3)	0.243 (2)	0.298 (3)
O	0.178 (7)	0.260 (6)	0.313 (6)
N(1)	0.224 (8)	0.244 (8)	0.256 (9)
N(2)	0.222 (7)	0.238 (9)	0.251 (8)
C(1)	0.205 (9)	0.214 (9)	0.264 (10)
C(2)	0.215 (10)	0.278 (10)	0.334 (10)
C(3)	0.247 (12)	0.323 (13)	0.476 (12)
C(4)	0.213 (11)	0.316 (12)	0.429 (11)
C(5)	0.220 (11)	0.254 (10)	0.302 (9)
C(6)	0.223 (11)	0.278 (9)	0.310 (11)
C(7)	0.243 (11)	0.316 (11)	0.349 (11)
C(8)	0.251 (11)	0.323 (11)	0.392 (11)
C(9)	0.238 (10)	0.273 (10)	0.326 (10)

Table III. Refined Hydrogen Atom Positions in $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$

	x	y	z	B, Å^2
HN(1)	0.147 (5)	0.262 (4)	−0.052 (5)	6.4 (1)
H1C(2)	0.402 (5)	−0.019 (4)	0.235 (5)	5.8 (1)
H2C(2)	0.313 (5)	−0.060 (4)	0.150 (5)	8.7 (2)
H1C(3)	0.385 (6)	−0.155 (5)	0.317 (5)	10.2 (2)
H2C(3)	0.244 (5)	−0.144 (4)	0.236 (5)	11.2 (2)
H1C(4)	0.193 (6)	−0.129 (5)	0.413 (6)	8.6 (2)
H2C(4)	0.301 (5)	−0.075 (5)	0.419 (6)	7.3 (1)
H1C(5)	0.171 (5)	0.031 (4)	0.395 (5)	7.8 (1)
H2C(5)	0.082 (5)	−0.039 (4)	0.306 (5)	6.34 (1)
H1C(6)	−0.008 (6)	0.265 (5)	0.090 (6)	5.5 (1)
H2C(6)	0.008 (6)	0.336 (5)	−0.002 (6)	6.3 (1)
H1C(7)	−0.132 (5)	0.216 (4)	−0.044 (5)	8.4 (1)
H2C(7)	−0.074 (5)	0.274 (5)	−0.136 (6)	8.2 (2)
H1C(8)	0.003 (6)	0.155 (5)	−0.190 (5)	11.2 (2)
H2C(8)	−0.052 (6)	0.100 (5)	−0.095 (6)	8.3 (1)
H1C(9)	0.119 (7)	0.125 (6)	−0.082 (7)	10.1 (2)
H2C(9)	0.042 (7)	0.093 (6)	0.016 (7)	6.2 (2)

Table IV. Principal Interatomic Distances and Angles for $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$

Distances, Å			
Co-S	2.584 (2)	C(4)-C(5)	1.529 (9)
Co-O	2.157 (4)	N(1)-C(6)	1.502 (7)
Co-N(1)	2.134 (5)	N(1)-C(9)	1.476 (8)
S-C(1)	1.735 (6)	C(6)-C(7)	1.518 (9)
O-C(1)	1.283 (7)	C(7)-C(8)	1.498 (9)
C(1)-N(2)	1.342 (7)	C(8)-C(9)	1.519 (10)
N(2)-C(2)	1.506 (7)	S- - -S′	3.830 (4)
N(2)-C(5)	1.486 (7)	S- - -O	2.651 (5)
C(2)-C(3)	1.506 (9)	N(1)-NH	0.83 (3)
C(3)-C(4)	1.421 (10)	C-H (av)	0.99 (3)

Angles, Deg			
S-Co-O	67.3 (1)	O-C(1)-N(2)	119.3 (6)
S′-Co-O	99.4 (1)	S-C(1)-N(2)	118.4 (5)
O-Co-N(1)	101.8 (2)	C(1)-N(2)-C(5)	125.9 (5)
O-Co-N(1)′	91.6 (2)	C(1)-N(2)-C(2)	120.4 (5)
O-Co-O′	160.9 (2)	C(2)-N(2)-C(5)	113.5 (5)
S-Co-S′	95.7 (1)	N(2)-C(2)-C(3)	101.8 (5)
S-Co-N(1)	90.5 (1)	C(2)-C(3)-C(4)	111.4 (6)
S-Co-N(1)	158.7 (1)	C(3)-C(4)-C(5)	109.5 (6)
N(1)-Co-N(1)′	91.1 (3)	C(4)-C(5)-N(2)	102.2 (5)
Co-S-C(1)	72.7 (2)	C(6)-N(1)-C(9)	104.7 (5)
Co-O-C(1)	97.6 (2)	N(1)-C(6)-C(7)	106.5 (5)
Co-N(1)-C(6)	115.6 (2)	C(6)-C(7)-C(8)	106.0 (5)
Co-N(1)-C(9)	116.2 (2)	C(7)-C(8)-C(9)	106.8 (5)
O-C(1)-S	122.2 (5)	C(8)-C(9)-N(1)	105.7 (5)

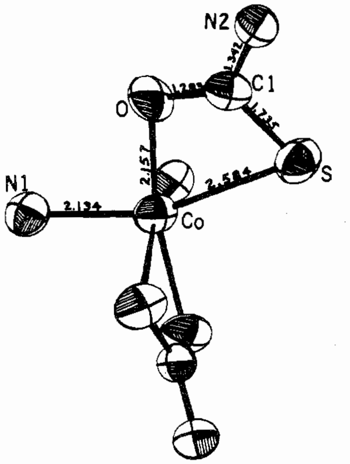

Figure 1. View of the inner coordination geometry of the $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ molecule. Ring carbon atoms have been omitted for clarity.

work is necessary to distinguish among the various structural modifications possible for the complex.

Discussion of the Structure

The thiocarbamate ligands are chelated to the Co ion forming a monomeric complex with a distorted octahedral coordination geometry. Perspective views of the molecule are shown in Figures 1 and 2 with a view of the contents of the unit cell in Figure 3. Intramolecular bond distances and angles are presented in Table IV. The thiocarbamate oxygen atoms are oriented in trans positions about the metal with the sulfur atoms bonded in cis positions with a large S-S′ separation of 3.830 (4) Å. The pyrrolidine nitrogens complete the octahedron, bonding in the remaining cis positions.

It is significant that both the thiocarbamate donor atoms remain coordinated to the metal in $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$. The complex represents the first thiocarbamate system found to have a simple chelated structure for the ligand and is additionally an unusual example of an octahedral

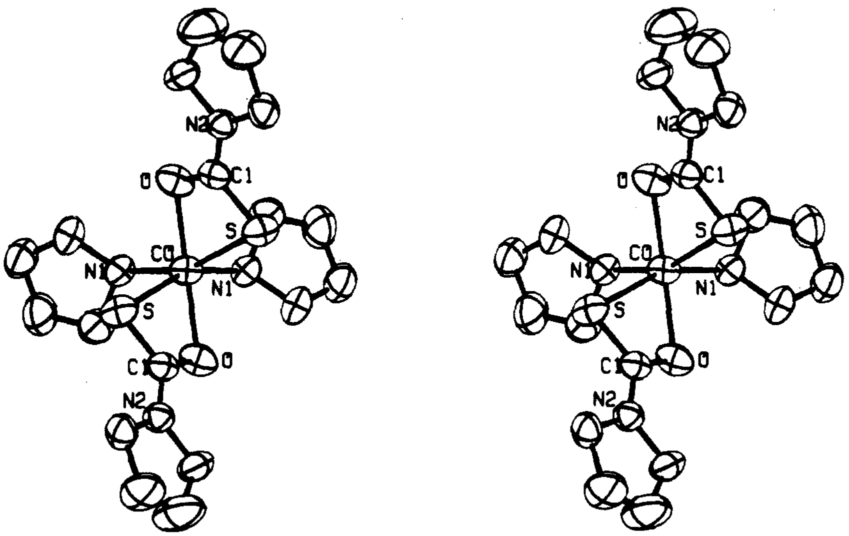

Figure 2. Stereoscopic view of the $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ molecule.

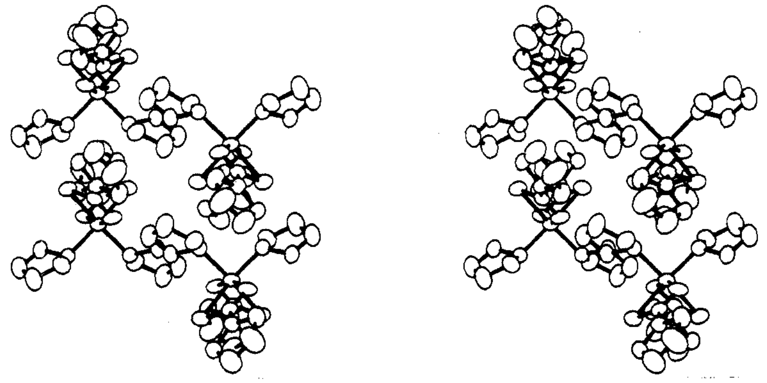

Figure 3. Stereoscopic view of the contents of the unit cell.

Co(II) complex containing Co-S bonding. Tetrahedral complexes of Co(II) with sulfur ligands are relatively common and have been well-characterized structurally. Studies on four-coordinate complexes of such ligands as thiourea,[22] diethyl thiophosphinate,[7] and *O*-ethyl *N*-phenylthiocarbamate[23] have been reported with Co-S distances found within the range 2.30-2.33 Å. Octahecral Co(II) complexes of sulfur donor ligands are more unusual with only the thiourea complex $Co(tu)_4Cl_2$ examined structurally.[24] The Co-S distances reported for this complex of 2.502 (6) and 2.553 (6) Å are more comparable to the value of 2.584 (2) Å found for $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ and may indicate a general increase of *ca.* 0.2-0.3 Å in Co-S distance in going from tetrahedral to octahedral coordination geometries for Co(II) complexes of sulfur ligands.

In contrast to the weak nature of the Co-S bond in $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ the Zn-S bond in $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ was found to be unusually strong.[6] The oxygen atoms in the zinc structure were uncoordinated and hydrogen bonded to the piperidine amine protons. The Co-O distance of 2.157 (4) Å in the present structure is long compared to Co-O distances of 2.00-2.03 Å found for terminal oxygen donors in six-coordinate acetylacetonate structures[25] and values of 2.034 to 2.131 Å found in the cyclopropyleneurea complex $[Co(pu)_5]_2{}^{4+}$.[26] With both Co-S and Co-O distances relatively long in $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ it is clear that the chelated thiocarbamate ligand is weakly bonded to the metal due to the combined effects of the low affinity of octahedral Co(II) for sulfur donor ligands and the poor donor ability of the thiocarbamate oxygen. This seems also to be true of the cobalt(II) thiocarbamate ester complexes where the ligand is easily displaced from the metal by poorly coordinating solvents.[23]

While the thiocarbamate ligand is weakly bonded to the Co, the pyrrolidine ligand has an unusually short Co-N(1) distance of 2.134 (5) Å. Amine nitrogen distances of 2.154 (6) Å for cyclohexylamine and values of from 2.17 to 2.20 Å for pyridine have been reported for six-coordinate amine adducts of cobalt(II) acetylacetonate ligands.[25] The weak coordination of the thiocarbamate and strong coordination of the amine in $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$ are consistent with the class a nature of the metal ion.

Bond distances and angles within the thiocarbamate ligand in the present structure suggest that of the ligand resonance forms considered in the Introduction structure III plays a more significant role than in previous complexes. Structural work on other thiocarbamate complexes has generally indi-

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cated short C-O bond lengths (1.21-1.25 Å) and C-S (1.75-1.78 Å) and C-N (1.36-1.37 Å) bond lengths longer than values found in dithiocarbamate structures.[6] Present values of 1.283 (7) Å for the C-O distance, 1.735 (6) Å for the C-S distance, and 1.342 (7) Å for the thiocarbamate C-N distance indicate a more delocalized π system for the SOCN group. The multiple character of the thiocarbamate C-N bond is reflected in the geometry of the pyrrolidine ring. An interior C(2)-N(2)-C(5) angle of 113.5 (5)° for the thiocarbamate pyrrolidine is significantly larger than the value of 104.7 (5)° for the amine ligand. Enlargement of this angle further seems to result in considerable anisotropy for atoms C(8) and C(9) of the ring.

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Registry No. Co(SOCN(C_4H_8))$_2$(NC_4H_9)$_2$, 51286-76-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy of \$2.00 for microfiche, referring to code number INORG-74-1674.

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Crystal Structure of Potassium Pentachloroantimonate(III)

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The crystal structure of potassium pentachloroantimonate(III) (K_2SbCl_5, monoclinic, $P2_1/c$, a = 8.8686 (07) Å, b = 12.4577 (13) Å, c = 8.9280 (13) Å, β = 110.512 (11)°, Z = 4, Mo Kα radiation) has been determined by three-dimensional X-ray analysis. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least squares to a final conventional discrepancy factor of 0.055 for the 1546 observed reflections. The $SbCl_5^{2-}$ anion displays a distorted square-pyramidal configuration in which the axial antimony–chloride bond (2.385 (2) Å) is shorter than the mean basal antimony–chloride bond. Two of the four basal antimony–chloride bonds (2.622 (2), 2.625 (2) Å) are undistorted while the other two basal bonds (2.799 (2), 2.509 (2) Å) are distorted by interionic and packing forces.

Introduction

Structural investigations of antimony halide complexes have been actively pursued in this laboratory during recent years, beginning with the work of Lawton and Jacobson.[1] The structures of species containing antomony(III) are of particular interest because of questions concerning the stereochemical role of the lone pair of electrons.

Only a very few antimony(III) chloride structures have been reported in the literature. $SbCl_3$ exhibits a trigonal-pyramidal structure with antimony at the apex,[2] while in $(NH_4)_2SbCl_5$ the chlorine atoms are arranged in a square-pyramidal coordination geometry around the antimony.[3] In [C_5H_5NH][$Sb^{III}Cl_4$], the halogen configuration around the antimony can be described as tetragonally distorted octahedral with two of the equatorial atoms removed,[4] and $SbCl_6^{3-}$ forms perfect octahedra in $Co(NH_3)_6$ $SbCl_6$.[5]

Because of the seeming variety of structural geometries possible for antimony(III) and because the structure of $(NH_4)_2SbCl_5$ was determined only from film projection data, we decided to undertake a structure determination of K_2SbCl_5.

Experimental Section

Preparation. A sample of K_2SbCl_5 was kindly supplied by Dr. Donald Macalady, who prepared the compound in the following manner. Two solutions, one of $SbCl_3$ in 3 N HCl and one of KCl in 3 N HCl, were combined so that the molar ratio of potassium to antimony in the resulting solution was 5:7. This solution was allowed to stand, and crystals formed by slow evaporation. Microscopic examination revealed many different crystal morphologies. Thin plates appeared to be the basic unit of all these morphologies, however.

Crystal Data. A crystal was cut from one of these plates and mounted on the end of a glass fiber with Duco cement thinned with amyl acetate. Preliminary Weissenberg and precession photographs exhibited $2/m$ Laue symmetry, indicating a monoclinic space group. The following systematic absences were observed: $h0l$ when $l = 2n + 1$ and $0k0$ when $k = 2n + 1$. These absences are only consistent with the space group $P2_1/c$. The unit cell parameters at 25° are a = 8.8686 ± 0.0007, b = 12.4577 ± 0.0013, c = 8.9280 ± 0.0013 Å, and β = 110.512 ± 0.011°. These parameters and their standard deviations were obtained by a least-squares fit[6] to the 2θ values of 16 independent high-angle reflections whose centers were determined by left–right, top–bottom beam splitting on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.71069 Å). A calculated density of 2.711 g/cm^3 for four molecules per unit cell agrees quite well with an observed density of 2.72 ± 0.01 g/cm^3, determined by flotation techniques.

Collection and Reduction of X-Ray Intensity Data. For data collection, the crystal described above, measuring approximately 0.2 mm along each of the crystal axes, was mounted so that the c axis coincided with the ϕ axis of the diffractometer. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. The

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