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Structural Characterization and Resulting Implications for the Mechanism of Formation of Bis(2-mercaptoethylamine)ethylenediaminechromium(III) Perchlorate, $[(en)Cr(SCH_2CH_2NH_2)_2]ClO_4$

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Received November 10, 1975 AIC50814I

The crystal and molecular structure of the title compound has been determined from single-crystal, three-dimensional x-ray diffraction data collected by counter methods. This compound crystallizes from aqueous solution as opaque violet rectangular bipyramids with the following crystal data: orthorhombic space group F_{dd2}; cell constants $a = 17.205$ (6) Å, $b = 10.628$ (4) Å, $c = 16.018$ (6) Å; $Z = 8$; $\rho_{obsd} = 1.64$, $\rho_{calcd} = 1.67$ g/cm^3. The structure has been refined by full-matrix least squares using 243 independent reflections with $F^2 > 3\sigma(F^2)$ and a model which includes anisotropic thermal parameters for Cr, Cl, and S; the final unweighted R factor is 5.5%. The monomeric unit contains one chromium atom ligated by four nitrogen atoms and two sulfur atoms in approximate octahedral geometry. The sulfur atoms are in the trans configuration, there is a twofold axis bisecting the ethylenediamine ligand, the Cr–S bond length is 2.389 (5) Å, and the S–Cr–S bond angle is 174.1 (4)°. These results are briefly discussed in terms of possible mechanisms of formation of the $[(en)Cr(SCH_2CH_2NH_2)_2]^+$ cation and the nature of the ground-state trans effect induced by thiolato ligands in octahedral complexes.

Introduction

It has recently been reported[1,2] that facile electron transfer from chromium(II) to cobalt(III) occurs when low-valent sulfur serves as a bridge. Deutsch and Weschler[3] prepared (2-mercaptoethylamine)bis(ethylenediamine) chromium(III) perchlorate in order to investigate further the efficiency of electron transfer through thiolato sulfur. This preparation also yielded varying amounts of bis(2-mercaptoethylamine)ethylenediaminechromium(III) perchlorate. Since the visible absorption bands of this new species showed no observable splitting and were of relatively high intensity, the authors tentatively assumed the complex to be of the cis configuration.[4] However, the possibility of a trans configuration could not be rigorously excluded by this reasoning, and knowledge of the configuration is necessary in order to understand the mechanism of formation of this complex. Accordingly, this x-ray study was undertaken to establish firmly the structure of the title compound.

In addition, it should be noted that Elder et al.[5] have observed a significant thiolato-induced structural trans effect in cobalt(III) complexes but not in an analogous chromium(III) complex. The presence of a ground state trans effect may be used to explain certain kinetic phenomena; for example, the kinetic lability[6] of the trans ammonia in sulfito-*S*-pentaamminecobalt(III) can be accounted for by the large observed structural trans effect.[7] Thus, we also wished to determine whether this unusual structural phenomenon was present in the $[(en)Cr(SCH_2CH_2NH_2)_2]^+$ cation.

Experimental Section

Preparation and Crystallization of $[(en)Cr(SCH_2CH_2NH_2)_2]ClO_4$. The reduction of cystamine by chromium(II) in the presence of ethylenediamine to yield mixtures of $[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$ and $[(en)Cr(SCH_2CH_2NH_2)_2]^+$ has been previously described.[3] Ion-exchange chromatographic analysis (Dowex 50-X2, 200–400 mesh) of this product mixture readily separated the 1+ and 2+ products but showed no detectable fractionation of the 1+ band. Preparative separation and purification of $[(en)Cr(SCH_2CH_2NH_2)_2]ClO_4$ was achieved by fractional crystallization.[3] Crystals suitable for x-ray analysis were grown from dilute perchloric acid by slowly (ca. 12 h) cooling saturated solutions from 25 to 4 °C.

Attempted Synthesis of $[(en)Co(SCH_2CH_2NH_2)_2]ClO_4$. In a procedure analogous to that used to prepare the title complex, cystamine was reduced by cobalt(II) in the presence of ethylenediamine. Ion-exchange chromatographic analysis of this product mixture showed no detectable (less than 1%) species of 1+ formal charge; the only observable cobalt(III) product was the previously described[5,8] $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ cation.

Table I. Summary of Crystal Data

Mol formula	$[Cr(SCH_2CH_2NH_2)_2(NH_2CH_2CH_2NH_2)]$-$ClO_4$
Mol wt	363.827
Linear abs coeff, μ:	12.78 cm^{-1}
Obsd density	1.64 g/cm^3
Calcd density	1.67 g/cm^3
Crystal dimensions	0.2 × 0.2 × 0.35 mm
Space group	F_{dd2} (C_{2v}^{19}), orthorhombic
Molecules/unit cell	8
Cell constants[a] a, b, c	17.205 (6), 10.628 (4), 16.018 (6) Å
Cell vol	2929.01 (19) Å^3

[a] Mo K$\bar{\alpha}$ radiation; λ 0.71069 Å. Ambient temperature of 23 °C.

Unit Cell and Diffraction Data. A series of zero- and first-level precession photographs indicated orthorhombic symmetry with the following systematically absent reflections: hkl, $h + k$, $k + l$, $l + h = 2n$; $0kl$, $k + l = 4n$; $h0l$, $l + h = 4n$; $hk0$, h, $k = 2n$; $h00$, $h = 4n$; $0k0$, $k = 4n$; $00l$, $l = 4n$. The only space group consistent with these absences is F_{dd2} (C_{2v}^{18}). The data crystal was a small square bipyramid with maximum dimensions of approximately 0.2 × 0.2 × 0.35 mm. The crystal was mounted on a thin glass fiber using Duco cement diluted with ethyl acetate, such that the 100 direction was approximately parallel to the Φ axis of the Syntex $P2_1$ diffractometer. The lattice parameters and orientation matrix were determined by a least-squares refinement of the angles of 11 machine-centered reflections whose 2θ values ranged from 15 to 25°. The x-ray source and diffractometer settings were identical with those used in subsequent collection of intensity data. The crystal gave ω-scan widths at half-height of around 0.15° for several low-angle reflections.

The density of several large crystals was determined by flotation in solutions of $CHCl_3$ and $CHBr_3$. The average measured density was 1.64 g/cm^3. The observed and calculated densities, unit cell parameters, and other crystal data are summarized in Table I.

Intensity data were collected using θ–2θ scans with graphite-monochromated Mo Kα radiation and a scintillation counter. The takeoff angle for the x-ray tube was 3° and the Bragg 2θ angle for the graphite monochromator crystal was 12.2°. The data were collected using a variable scan rate ranging from 1 to 29.3°/min. A scan width of 1.5° was sufficient to collect all of the peak intensity. Stationary-background counts were taken at the beginning and end of each scan with a total background time to scan time ratio of 0.25. Three standard reflections (602, 026, 062) were monitored every 50 reflections as a check on crystal and instrumental stability. No systematic fluctuation of intensity was observed during data collection.

A full form of data (all values of h, k, l) was measured out to $2\theta_{max} = 40°$. A total of 1716 reflections were collected. The data processing was carried out by our program ENXDR.[9] The parameter p, introduced to avoid overweighting the strong reflections, was set to 0.05. The corrected intensities were converted to values of F^2 by application

Table II. Positional[a] and Thermal[b] Parameters and Their Estimated Standard Deviations

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.2500 (0)	0.2500 (0)	0.2500 (0)	0.0015 (1)	0.0035 (4)	0.0017 (2)	−0.0010 (6)	0.0000 (0)	0.0000 (0)
Cl	0.0000 (0)	0.0000 (0)	0.4468 (6)	0.0038 (4)	0.0068 (8)	0.0033 (4)	−0.001 (1)	0.0000 (0)	0.0000 (0)
S1	0.1131 (3)	0.2852 (5)	0.2423 (5)	0.0019 (2)	0.0071 (6)	0.0025 (2)	−0.0011 (6)	0.0004 (6)	0.001 (1)

Atom	x	y	z	B, Å^2
O1	0.0128 (9)	0.109 (1)	0.496 (1)	5.6 (4)
O2	0.0636 (13)	−0.022 (2)	0.395 (1)	8.4 (6)
N1	0.268 (1)	0.375 (2)	0.350 (1)	2.9 (4)
N2	0.246 (1)	0.110 (1)	0.162 (1)	2.2 (4)
C1	0.220 (1)	0.197 (2)	0.428 (1)	3.0 (5)
C2	0.113 (1)	0.412 (2)	0.171 (2)	3.2 (5)
C3	0.181 (1)	0.405 (2)	0.111 (1)	2.6 (5)

Atom	x	y	z	B, Å^2
H1	0.1128 (0)	0.4951 (0)	0.1995 (0)	3.1714 (0)
H2	0.0618 (0)	0.4076 (0)	0.1345 (0)	3.1714 (0)
H3	0.1848 (0)	0.4815 (0)	0.0741 (0)	3.1563 (0)
H4	0.1761 (0)	0.3269 (0)	0.0727 (0)	3.1563 (0)
H5	0.2345 (0)	0.0378 (0)	0.1868 (0)	2.2226 (0)
H6	0.2047 (0)	0.1254 (0)	0.1280 (0)	2.2226 (0)
H7	0.3108 (0)	0.4221 (0)	0.3398 (0)	2.7169 (0)
H8	0.2295 (0)	0.4275 (0)	0.3549 (0)	2.7169 (0)
H9	0.1651 (0)	0.2310 (0)	0.4334 (0)	3.3499 (0)
H10	0.2283 (0)	0.1383 (0)	0.4804 (0)	3.3499 (0)

[a] The hydrogen positions were calculated and were not refined. [b] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

of Lorentz and polarization corrections. An absorption correction was not applied as the absorption coefficient was 12.78 cm^{-1} and the values of μt ranged only from 0.26 to 0.45. There were 243 reflections with $F^2 > 3\sigma(F^2)$ which were used in the final refinement.

Solution and Refinement of the Structure. The structure was solved by application of heavy-atom techniques. Full-matrix least-squares refinements on F were used in which the function minimized was $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors.[9] The weighting factor, w, is given by $w = 1/\sigma(F_o)^2$ where $\sigma(F_o)$ is calculated by

$$I = N_T - 2(N_{B1} + N_{B2})$$

$$\sigma(F_o)^2 = [N_T + J^2(N_{B1} + N_{B2}) + (pI)^2]^{1/2}/Lp$$

$$\sigma(F_o) = \sigma(F_o)^2/2F_o$$

where N_T, N_{B1}, and N_{B2} are the total peak and two background counts, J is the ratio of peak scan time to background scan time, and Lp is the Lorentz–polarization factor. The atomic scattering factors for neutral Cr, S, Cl, O, and H were taken from the values tabulated in ref 10.

Correction for anomalous dispersion effects of the chromium, chlorine, and sulfur atoms using both $\Delta f'$ and $\Delta f''$ were included in the calculation of the F's.[10]

The positions of the Cr, Cl, and S atoms were found from a three-dimensional Patterson map. Three cycles of isotropic least-squares refinement of these three atom positions followed by a difference Fourier synthesis on F located all nonhydrogen atoms. The hydrogen atom positions were calculated by assuming tetrahedral geometry and C–H bond lengths of 1.0 Å. In the final anisotropic refinement, the hydrogen atom contributions to the structure factors were calculated from these fixed positions and the temperature factors for all hydrogens were set to 6 Å^2. The final agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and R_2 (weighted R factor) $= [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.055 and 0.057, respectively. The final error in an observation of unit weight was 1.34. The final difference Fourier showed no peaks greater than 6% of the height of a C atom peak which were not due to residual noise around the heavy atom. Observed and calculated structure factors for the data set are available.[11] The positional and thermal parameters with their estimated standard deviations from the final least-squares refinement are given in Table II. Table III lists the rms amplitudes of vibration along the principal axes of the thermal allipsoids for all nonhydrogen atoms.

Table III. Root-Mean-Square Amplitudes of Vibration of All Nonhydrogen Atoms along Principal Axes (10^3 Å)

Atom	Axis 1	Axis 2	Axis 3
Cr	128	162	150
Cl	239	206	195
S1	211	183	153
O1	267	267	267
O2	325	325	325
N1	192	192	192
N2	166	166	166
C1	194	194	194
C2	202	202	202
C3	183	183	183

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

Bond Lengths			
Cr-S1	2.389 (5)	N2-C3	1.503 (25)
Cr-N1	2.106 (19)	N1-C1	1.484 (25)
Cr-N2	2.056 (16)	C1-C1	1.525 (36)
S1-C2	1.774 (22)	Cl-C1	1.418 (20)
C2-C3	1.526 (29)	Cl-O2	1.319 (21)
Metal Coordination Angles			
S1-Cr-S1	174.08 (41)	N1-Cr-N1	80.73 (100)
S1-Cr-N1	94.87 (55)	N1-Cr-N2	170.74 (77)
S1-Cr-N1	89.65 (53)	N1-Cr-N2	93.63 (60)
S1-Cr-N2	92.40 (50)	N2-Cr-N2	92.87 (96)
S1-Cr-N2	83.50 (49)		
Ethylenediamine Angles			
N1-C1-C1	106.66 (146)		
2-Mercaptoethylamine Angles			
S1-C2-C3	111.24 (151)	N2-C3-C2	108.24 (169)
Perchlorate Angles			
O1-Cl-O1	112.17 (186)	O2-Cl-O2	107.41 (174)
O1-Cl-O2	110.34 (114)		

Table V. Comparison of Bond Lengths (Å)

		Bond length		
Bond	Ligand	Obsd[a]	Reported	Ref
C-N	$NH_2CH_2CH_2NH_2$	1.484 (25)	1.48	5, 12-15
C-C	$NH_2CH_2CH_2NH_2$	1.525 (36)	1.51	5, 12-15
C-S	$SCH_2CH_2NH_2$	1.774 (22)	1.818 (8)	5
C-C	$SCH_2CH_2NH_2$	1.526 (29)	1.467 (12)	5
C-N	$SCH_2CH_2NH_2$	1.503 (25)	1.483 (9)	5
C-C	$SCH_2CH_2NH_2$	1.526 (29)	1.511 (35)	16
C-C	$SCH_2CH_2NH_2$	1.526 (29)	1.51 (1)	17
C-C	$SCH_2CH_2NH_2$	1.526 (29)	1.510 (24)	18

[a] This study.

Description of the Structure and Discussion

The structure consists of discrete complex cations and perchlorate anions. Figure 1 shows a perspective drawing of a single chromium complex; it is six-coordinate, the three five-membered bidentate chelate rings providing approximate octahedral geometry. The two sulfur atoms are coordinated in the trans configuration, and a twofold axis bisects the ethylenediamine chelate. The torsional angles of the chelate rings along the C–C bond are 56.19° for ethylenediamine and 51.93° for 2-mercaptoethylamine. Other selected bond lengths and angles are presented in Table IV, and Table V shows that intraligand parameters correlate well with previously determined values. Since the sulfur atoms are trans to one another,

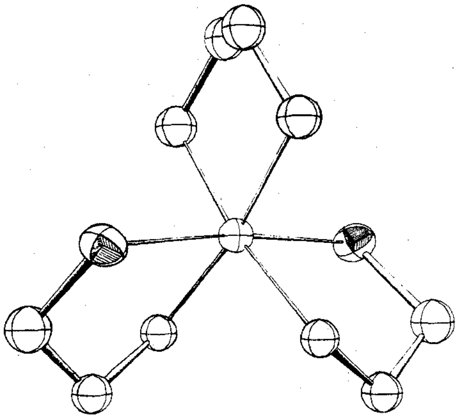
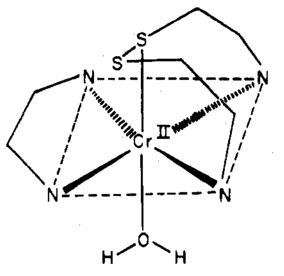


Figure 1. Perspective view of *trans*-bis(2-mercaptoethylamine)-ethylenediaminechromium(III). Thermal ellipsoids are drawn at the 40% contour level.

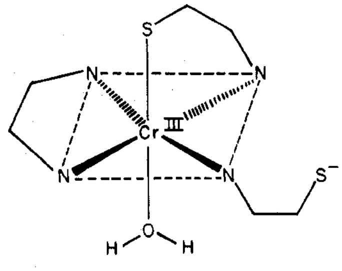
there is only one type of Cr–N bond and a thiolato-induced ground state trans effect cannot be directly evaluated by comparing Cr–N bond lengths that are cis and trans to a coordinated sulfur.[5,7] However, data obtained by Elder er al.[5] on another thiolatochromium(III) complex of 1+ formal charge provide an interesting comparison in this context. The average Cr–N bond length observed herein for $[(en)Cr(SCH_2CH_2NH_2)_2]^+$ is in good agreement with the average cis Cr–N bond length observed by Elder for $[(en)_2Cr(SCH_2COO)]^+$ (2.081 (25) vs. 2.090 (13) Å) whereas the Cr–S bond length observed herein is significantly longer than that observed by Elder (2.389 (5) vs. 2.337 (2) Å). It is tempting to speculate that this Cr–S bond elongation is due to a mutual trans effect, each sulfur atom both effecting and being affected by a ground-state trans effect. This phenomenon would be difficult to rationalize within the framework of existing trans effect theories and its evaluation will require additional experimental evidence.

The relatively high values for the isotropic thermal parameters for the perchlorate anion are indicative of the disorder and/or librational motion characteristic of this anion. However, since this portion of the structure is not directly related to the problems under investigation, no attempts were made to resolve this disorder.

The preparative reaction which leads to the title compound is complicated and not amenable to detailed kinetic analysis.[3] However, the following qualitative observations allow some implications to be drawn concerning the mechanism of this reaction. (1) The reduction of cystamine by aqueous ethylenediaminechromium(II) mixtures yields both $[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$ and $[(en)Cr(SCH_2CH_2NH_2)_2]^+$ in relative amounts which depend upon reactant ratios. (2) The analogous reduction with ethylenediamine–cobalt(II) mixtures yields only the $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ ion (vide infra). (3) The only detectable $[(en)Cr(SCH_2CH_2NH_2)_2]^+$ isomer has the trans configuration (vide infra). (4) Pulse radiolysis studies have shown that the reduction of organic disulfides (RSSR) by hydrated electrons leads to the relatively stable radical ion dimers $RSSR^-$;[19] recent work has also shown that $RSSR^-$ species (both free and coordinated) very likely play an important role in the chromium(II) reduction of organic disulfides.[20] Specifically, point (2) implies that the essential chemistry leading to *trans*-$[(en)Cr(SCH_2CH_2NH_2)_2]^+$ involves the chromium center, and point (3) implies that this chromium center is tetragonally stereospecific. From these observations and implications, a reasonable scheme for the formation of *trans*-$[(en)Cr(SCH_2CH_2NH_2)_2]^+$ may be constructed about an intermediate, I, which is comprised of one chromium(II), one ethylenediamine, and one $RSSR^-$ radical ion dimer (there are several plausible routes for the formation of I). Since chromium(II) complexes are subject to strong Jahn–Teller distortions, the proposed formulation of I puts the weak $RSSR^-$ and OH_2 ligands in axial positions and the strong $R'NH_2$ ligands in equatorial positions. This intermediate then presumably decays by internal electron transfer to give II, a chromium(III) complex containing one

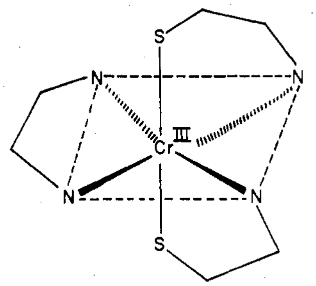


I



II

coordinated thiol and one free thiol. Closure of the sulfur chelate, which should be rapid in the basic reaction medium,[3] then yields the trans product



Acknowledgment. We wish to thank Tom Eccles and Marguerite Yevitz for their assistance in the structural analysis. E.D. gratefully acknowledges support from the National Science Foundation (Grant No. MPS74-01540 AO1). K.O.H. wishes to acknowledge the support of E. I. du Pont de Nemours and Co. and of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $[(en)Cr(SCH_2CH_2NH_2)_2]ClO_4$, 41777-29-1.

Supplementary Material Available: listing of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Polymeric Dichloro[bis(2-pyridyl) disulfide]mercury(II)

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Received November 11, 1975 AIC50815A

The crystal structure of dichloro[bis(2-pyridyl) disulfide]mercury(II), $Hg(C_{10}H_8N_2S_2)Cl_2$, 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 0.020 using 1439 intensities significant at the 3σ level. The colorless crystals form as monoclinic plates in the space group $P2_1/c$ with $a = 8.959$ (3) Å, $b = 13.291$ (7) Å, $c = 12.918$ (4) Å, and $\beta = 118.83$ (2)°, with four molecules per unit cell. The Hg(II) ion is coordinated by one pyridyl nitrogen atom from each of two different bis(2-pyridyl) disulfide molecules and by two chloride ions. The ligand bridges between Hg(II) ions which are equivalent by a lattice translation along a; in this way a polymeric sequence is generated. The disulfide group does not coordinate, and no chelate rings are formed. The coordination angles at Hg(II), Cl–Hg–Cl = 154.8° and N–Hg–N = 81.1°, and the four others which range from 90.9 to 112.1° are irregular. The Hg–Cl and Hg–N bonds average 2.336 and 2.580 Å, respectively. Although the C–S–S–C torsion angle (93.7°) is near 90°, its expected lowest energy value, the S–S bond length (2.030 (2) Å) is slightly longer than that found in the crystal structure of the uncomplexed ligand (2.016 (2) Å).

Introduction

The coordination of neutral organic disulfides to transition metal ions is a topic of current research interest, partly because of the roles that such complexes are likely to have in biochemical processes. A recent discussion of the crystallographic results in this area[1] indicated that complexes with only a few metal ions, Ni(II),[2-4] Cu(I),[5-7] Cu(II),[8] and Fe(III),[9] have been studied by diffraction methods.

A complex between Hg(II) and bis(2-pyridyl) disulfide was prepared and studied by spectroscopic methods.[10] The infrared spectrum was interpreted as indicative of a weak disulfide group interaction with Hg(II) and indicative of no pyridyl coordination at all. To confirm this result and to learn the geometry of disulfide coordination to Hg(II), a crystallographic study was undertaken. Unfortunately, the result disproves the spectral indications—the disulfide group does not coordinate, and the pyridyl groups do.

Preparation Section

Mercuric chloride and bis(2-pyridyl) disulfide were obtained from Mallinckrodt Chemical Works and Aldrich Chemical Co., respectively. All other chemicals were of reagent grade quality. The laser-Raman (excitation at 5145 Å), infrared, and ultraviolet spectra were obtained using Cary 82, Beckman IR-10, and Cary 14 spectrometers, respectively. Elemental analyses were performed by Galbraith Laboratories.

Preparation of Dichloro[bis(2-pyridyl) disulfide]mercury(II), $Hg(pySSpy)Cl_2$.[10] A 0.81-g (0.0030-mol) sample of mercuric chloride was dissolved in 35 ml of hot ethanol. To this solution was added 35 ml of hot ethanol solution containing 0.0030 mol of the ligand, bis(2-pyridyl) disulfide. The volume of the resulting solution was subsequently reduced to 60 ml. Fine, white, featherlike crystals formed as the solution was allowed to cool at room temperature. Recrystallization from hot ethanol gave large colorless plates. Anal. Calcd for $HgC_{10}H_8N_2S_2Cl_2$: Hg, 40.77; C, 24.42; H, 1.64; S, 13.04; Cl, 14.42. Found: Hg, 41.03; C, 24.36; H, 1.62; S, 13.05; Cl, 14.25.

Spectroscopic Section

The infrared spectrum of dichloro[bis(2-pyridyl) disulfide]mercury(II) differs little from that of the uncomplexed ligand. The spectrum of the complex exhibits four ν(C=C) and ν(C=N) bands at 1575, 1555, 1440, and 1405 cm^{-1}, with a ring breathing mode at 989 cm^{-1}. The free ligand has the corresponding bands at 1568, 1552, 1440, 1407, and 980 cm^{-1}, respectively. Such small shifts to higher energy are indicative[11,12] of weak pyridine coordination. In the electronic spectrum, shifts of the pyridine absorption bands to longer wavelength relative to the free ligand (272 → 287 and 228 → 234 mμ) are observed, indicating again, as in the corresponding Co(II) complex, dichloro[bis(2-pyridyl) disulfide]cobalt(II),[1] that pyridyl groups coordinate.

The suggestion that long weak Hg^{II}–S bonds occur in the complex[10] is not supported by the Raman spectrum. A ν(SS) band of medium intensity occurs at 548 cm^{-1}, which is nearly the same (only 1 cm^{-1} higher) in energy as the corresponding band of the free ligand. This indicates that the chemical environments of the disulfide group in the complex and in the free ligand are quite similar. One may expect that coordination by Hg(II) would have modified ν(SS) and that such coordination does not exist in the complex. The results presented in this work (see Discussion) are in accord with that expectation.

In the corresponding Co(II) complex, dichloro[bis(2-pyridyl) disulfide]cobalt(II),[1] an intense ν(SS) band was observed at 522 cm^{-1}, shifted 25 cm^{-1} to lower energy in the complex as compared to that in the free ligand. The disulfide group does not coordinate to the metal ion in that complex, so that such complexation is not responsible for the shift. However, large changes are observed in the S–S–C–C torsion angles (and in the S–S–C–N torsion angles which are approximately supplemental to S–S–C–C) upon complexation, and it is to this that the shift in the ν(SS) band is attributed.[1] The C–S–S–C torsion angle is nearly unchanged. One may expect that the constancy of the ν(SS) band in the Hg(II) complex as compared to that of the free ligand indicates that the torsion angles involving the disulfide group are not appreciably different in the two structures. The results presented in this work (see Discussion) are in accord with that expectation.

Diffraction Section

A single crystal of $Hg(C_{10}H_8N_2S_2)Cl_2$ of extreme dimensions 0.08 × 0.14 × 0.30 mm was mounted approximately along its long axis, which did not coincide with the diffractometer ϕ axis.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ 0.70930 Å; Kα_2, λ 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 with 2θ values up to 22°. The program used was written by R. A. Sparks and is part of the diffractometer program library.