and Levy's function and error program), and Johnson's ORTEP. A local program, ENXDR, was used for data reduction.
(10) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, p 149.
(11) Supplementary material.
(12) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 597 (1972).
(13) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971).
(14) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1858 (1970).
(15) J. H. Enemark, M. S. Quimby, L. L. Reed, M. J. Steuch, and K. K. Walthers, *Inorg. Chem.*, **9**, 2397 (1970).
(16) J. R. Knox and C. K. Prout, *Acta Crystallog., Sect. B*, **25**, 2482 (1969).
(17) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).
(18) R. L. Gerling and E. L. Amma, *Inorg. Chem.*, **6**, 2009 (1967).
(19) G. E. Adams, G. S. McNaughton and B. D. Michael in "The Chemistry of Ionization and Excitation", G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, pp 281–293.
(20) L. E. Asher and E. Deutsch, *Inorg. Chem.*, **14**, 2799 (1975).

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

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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.

Table I. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^4$) for Nonhydrogen Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	1047.8 (3)	1293.6 (2)	1278.1 (2)	101.5 (5)	56.8 (2)	54.3 (2)	3.1 (3)	37.0 (3)	2.0 (2)
Cl(2)	729 (2)	1022 (1)	−614 (1)	134 (3)	64 (1)	62 (1)	−13 (2)	50 (2)	−6 (1)
Cl(3)	1680 (2)	825 (2)	3179 (2)	174 (4)	91 (2)	62 (2)	0 (2)	44 (2)	14 (1)
N(4)	3267 (6)	2776 (4)	2093 (4)	87 (9)	58 (4)	54 (5)	−10 (5)	44 (6)	−11 (4)
C(5)	2977 (8)	3408 (5)	2778 (6)	109 (12)	59 (6)	68 (6)	−3 (6)	54 (8)	−9 (5)
C(6)	4132 (8)	4118 (5)	3488 (6)	159 (14)	45 (5)	55 (6)	−2 (7)	50 (8)	−6 (4)
C(7)	5690 (9)	4167 (5)	3520 (6)	147 (13)	44 (5)	58 (6)	−20 (7)	25 (8)	−8 (5)
C(8)	6030 (7)	3512 (5)	2824 (6)	90 (11)	46 (5)	66 (6)	−17 (6)	37 (7)	3 (5)
C(9)	4778 (7)	2832 (5)	2121 (5)	89 (11)	44 (5)	45 (5)	1 (6)	24 (6)	−2 (4)
S(10)	4926 (2)	1959 (1)	1135 (2)	94 (3)	56 (1)	79 (2)	−16 (2)	54 (2)	−20 (1)
S(11)	−2580 (2)	1957 (1)	1552 (2)	93 (3)	54 (1)	73 (2)	15 (2)	50 (2)	13 (1)
C(12)	−2448 (7)	2852 (5)	572 (5)	104 (11)	36 (4)	38 (5)	−2 (6)	26 (7)	−9 (4)
C(13)	−3662 (8)	3572 (6)	−53 (6)	133 (12)	66 (6)	66 (6)	25 (8)	51 (8)	8 (5)
C(14)	−3333 (10)	4224 (6)	−748 (6)	202 (16)	50 (5)	64 (7)	40 (8)	44 (9)	11 (5)
C(15)	−1843 (10)	4148 (6)	−801 (6)	196 (15)	53 (5)	65 (7)	−9 (8)	58 (9)	5 (5)
C(16)	−720 (8)	3407 (6)	−160 (6)	120 (12)	67 (6)	69 (7)	−16 (7)	50 (8)	−3 (5)
N(17)	−998 (6)	2760 (4)	523 (5)	99 (9)	45 (4)	57 (5)	7 (5)	41 (6)	7 (4)

[a] See Figure 3 for the identities of the atoms. The estimated standard deviation is in the units of the least significant digit given for the corresponding parameter. The temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

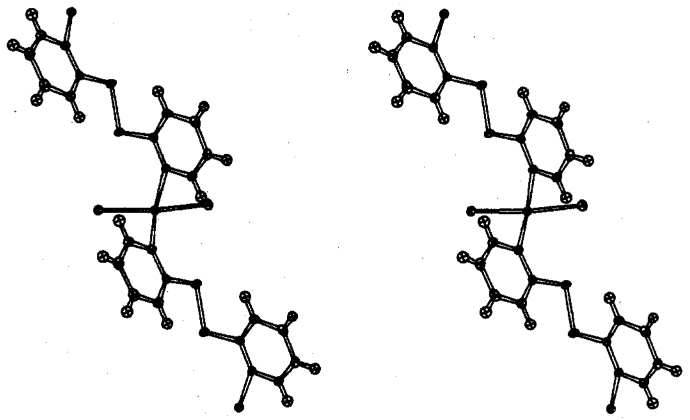

Figure 1. Stereoview of a section of the polymeric chain showing two complete disulfide ligands, three Hg(II) ions, and two Cl^- ions. Ellipsoids of 15% probability are shown.[23]

The temperature was maintained between 21 and 22 °C throughout. The θ–2θ scan mode was used with scan rate (ω) in 2θ of 1° min^{-1}. 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° at low 2θ to 2.3° at 45°. The intensities of three check reflections, which were remeasured after every 100 reflections during data collection, showed a small average decrease in intensity of 1%, for which the appropriate correction was applied.

Standard deviations were assigned to the individual reflections according to the formula

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

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrumental inaccuracies. The weights (w) used in least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 1847 symmetry-independent reflections measured, those for which $2\theta < 45°$, 1439 had intensities larger than 3 times their standard deviations, and only these were used in subsequent calculations. The intensities were corrected for Lorentz and polarization effects.[13] The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction. An absorption correction[14] (μ = 20.66 cm^{-1}) was applied which approximated the crystal shape by a 6 × 6 × 6 grid;[15] the calculated transmission coefficients ranged from 0.190 to 0.422.

The atomic scattering factors for Hg^0, Cl^-, S^0, N^0, C^0,[16] and H (bonded)[17] were used. The first three were modified to include the anomalous dispersion correction.[18]

Crystal Data

Dichloro[bis(2-pyridyl) disulfide]mercury(II), alternatively named dichloro(2,2'-dithiodipyridine)mercury(II), crystallizes as monoclinic plates in space group $P2_1/c$ with a = 8.959 (3) Å, b = 13.291 (7) Å, c = 12.918 (4) Å, β = 118.83 (2)°, V = 1347.5 (9) $Å^3$, mol wt 491.8, d_{obsd}(flotation) = 2.420 g cm^{-3}, d_{calcd} = 2.424 g cm^{-3}, Z = 4, and $F(000)$ = 912. 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 mercuric ion was learned from a three-dimensional Patterson function. The positions of all other nonhydrogen atoms were found by successive cycles of Fourier refinement using the fast-Fourier algorithm.[19] Hydrogen atom positions were calculated[20] assuming C–H distances[21] of 0.95 Å. Full-matrix least-squares refinement[22] with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms led to the final error indices $R_1 = \sum(|F_o - |F_c||)/\sum F_o = 0.020$ and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.022$. The "goodness of fit", $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 1.38. The number of observations used in least-squares is m (1439), and s (186) is the total number of parameters. The overdetermination ratio (m/s) is 7.7.

In the final cycles of least-squares refinement, all shifts in atomic parameters for nonhydrogen atoms were less than 0.8% of their esd's, and the largest shift in a thermal parameter was 1.3% of its esd. For the hydrogen atoms, these values were 3.3% and 1.1%, respectively. The largest peak on the final difference Fourier function, whose esd was calculated to be 0.1 e $Å^{-3}$, was 0.6 e $Å^{-3}$ in height and was located very close to the mercury atom. The final positional and thermal parameters, together with their standard deviations, are presented in Tables I and II.

Discussion

A molecule of bis(2-pyridyl) disulfide bridges between two $HgCl_2$ molecules which are equivalent by one lattice translation along a. By successive applications of this operation, a

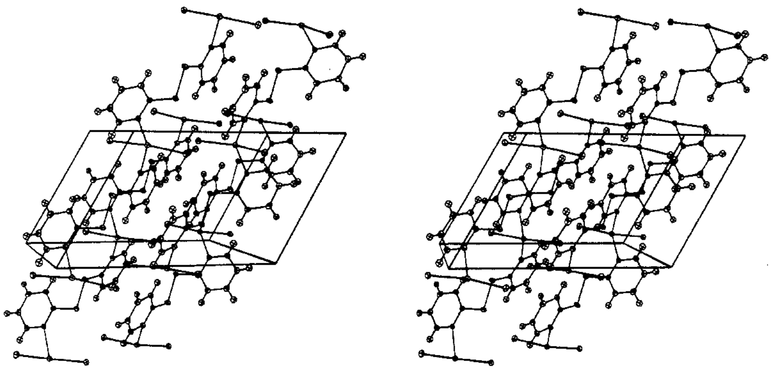

Figure 2. Stereoview illustrating the packing of the polymer in the crystal. Ellipsoids of 15% probability are used.[23] The view is approximately along the *c* axis with *a* vertical and *b* horizontal in the plane of the page.

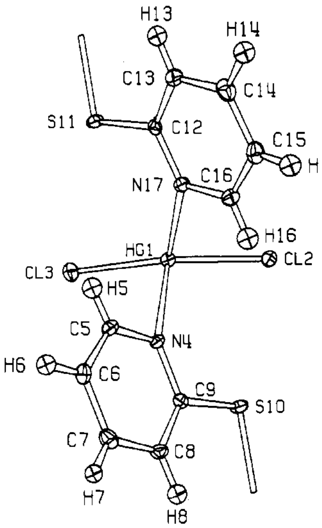

Figure 3. Fragment of the polymeric chain of dichloro[bis(2-pyridyl) disulfide]mercury(II) showing two half ligand molecules. Ellipsoids of 15% probability are used.[23]

Table II. Fractional Atomic Coordinates (×10³) and Thermal Parameters for Hydrogen Atoms[a]

Atom	*x*	*y*	*z*	*B*, Å²
H(5)	199 (7)	338 (4)	279 (5)	4.2 (14)
H(6)	394 (6)	452 (4)	398 (5)	3.5 (13)
H(7)	647 (6)	463 (4)	395 (4)	2.9 (12)
H(8)	711 (7)	344 (4)	284 (5)	3.9 (14)
H(13)	−468 (7)	360 (4)	−5 (5)	3.9 (13)
H(14)	−418 (7)	478 (4)	−121 (5)	4.2 (14)
H(15)	−156 (7)	457 (5)	−121 (5)	4.3 (14)
H(16)	30 (7)	333 (5)	−16 (5)	4.8 (15)

[a] See Figure 3 for the identities of the atoms.

polymeric chain with the repeat vector *a* is generated. See Figures 1 and 2.

Mercury(II) is coordinated by two chloride ions and two pyridyl nitrogen atoms (see Figure 3). The angles at Hg(II) presented in Table IIIB indicate an irregular coordination geometry. The N–$\mathrm{Hg^{II}}$–N angle of 81.1° is surprisingly small for a complex whose primary coordination number is 4. The Cl–$\mathrm{Hg^{II}}$–Cl angle is large, 154.8°, but not unusual for complexes of $HgCl_2$ with two organic ligand groups.

The $\mathrm{Hg^{II}}$–Cl distances averaging 2.335 Å are close to those commonly found in organic complexes of $HgCl_2$. As examples, comparable corresponding distances are found in dichlorobis(phenoxathiin)mercury(II),[24] 2.325 (8) Å, dichlorobis(pyridine *N*-oxide)mercury(II),[25] 2.328 (16) Å, dichlorobis(triphenylarsine oxide)mercury(II),[26] 2.33 Å, dichlorobis(2-imidazolidinone)mercury(II),[27] 2.309 (4) Å, and

Table III. Molecular Dimensions and Esd's[a]

A. Bond Lengths, Å			
Hg(1)-Cl(2)	2.348 (2)	C(7)-C(8)	1.387 (9)
Hg(1)-Cl(3)	2.323 (2)	C(8)-C(9)	1.384 (9)
Hg(1)-N(4)	2.632 (5)		
Hg(1)-N(17)	2.527 (5)	C(12)-C(13)	1.380 (9)
Hg(1)-Cl(2)′	3.380 (2)	C(13)-C(14)	1.377 (10)
		C(14)-C(15)	1.373 (11)
S(10)-S(11)″	2.030 (2)	C(15)-C(16)	1.366 (10)
S(10)-C(9)	1.774 (6)		
S(11)-C(12)	1.783 (6)	C(5)-H(5)	0.90 (6)
		C(6)-H(6)	0.91 (6)
N(4)-C(5)	1.333 (9)	C(7)-H(7)	0.90 (5)
N(4)-C(9)	1.339 (7)	C(8)-H(8)	0.97 (6)
N(17)-C(12)	1.336 (7)		
N(17)-C(16)	1.339 (9)	C(13)-H(13)	0.91 (6)
		C(14)-H(14)	1.02 (6)
C(5)-C(6)	1.374 (9)	C(15)-H(15)	0.89 (6)
C(6)-C(7)	1.378 (9)	C(16)-H(16)	0.92 (6)
B. Bond Angles, Deg			
Cl(2)-Hg(1)-Cl(3)	154.8 (1)	N(17)-C(12)-C(13)	123.1 (6)
Cl(2)-Hg(1)-N(4)	102.8 (1)	C(12)-C(13)-C(14)	117.5 (7)
Cl(2)-Hg(1)-N(17)	90.9 (1)	C(13)-C(14)-C(15)	120.4 (7)
Cl(3)-Hg(1)-N(4)	91.5 (1)	C(14)-C(15)-C(16)	118.2 (7)
Cl(3)-Hg(1)-N(17)	112.1 (1)	C(15)-C(16)-N(17)	123.1 (6)
N(4)-Hg(1)-N(17)	81.1 (2)	C(16)-N(17)-C(12)	117.8 (6)
N(4)-Hg(1)-Cl(2)′	162.9 (1)		
N(17)-Hg(1)-Cl(2)′	116.0 (1)	H(5)-C(5)-N(4)	120 (4)
		H(5)-C(5)-C(6)	116 (4)
Hg(1)-N(4)-C(5)	112.7 (4)	H(6)-C(6)-C(5)	122 (3)
Hg(1)-N(4)-C(9)	127.7 (4)	H(6)-C(6)-C(7)	119 (3)
Hg(1)-N(17)-C(12)	126.4 (4)	H(7)-C(7)-C(6)	122 (3)
Hg(1)-N(17)-C(16)	114.8 (4)	H(7)-C(7)-C(8)	119 (3)
		H(8)-C(8)-C(7)	126 (3)
S(10)-S(11)″-C(12)″	104.6 (2)	H(8)-C(8)-C(9)	116 (3)
S(11)″-S(10)-C(9)	105.3 (2)		
S(10)-C(9)-N(4)	111.6 (4)	H(13)-C(13)-C(12)	122 (4)
S(10)-C(9)-C(8)	125.5 (5)	H(13)-C(13)-C(14)	120 (4)
S(11)-C(12)-N(17)	111.8 (4)	H(14)-C(14)-C(13)	120 (3)
S(11)-C(12)-C(13)	125.1 (5)	H(14)-C(14)-C(15)	119 (3)
		H(15)-C(15)-C(14)	123 (4)
N(4)-C(5)-C(6)	123.4 (6)	H(15)-C(15)-C(16)	119 (4)
C(5)-C(6)-C(7)	118.6 (6)	H(16)-C(16)-C(15)	121 (4)
C(6)-C(7)-C(8)	119.1 (6)	H(16)-C(16)-N(17)	116 (4)
C(7)-C(8)-C(9)	118.2 (6)		
C(8)-C(9)-N(4)	122.9 (6)		
C(9)-N(4)-C(5)	117.7 (5)		
C. Selected Torsion Angles, Deg			
C(9)-S(10)-S(11)″-C(12)″	93.7	N(17)-C(12)-S(11)-S(10)″	164.2
C(8)-C(9)-S(10)-S(11)″	12.7	Hg(1)-N(4)-C(9)-S(10)	18.1
C(13)-C(12)-S(11)-S(10)″	16.9	Hg(1)-N(17)-C(12)-S(11)	14.0
N(4)-C(9)-S(10)-S(11)″	168.6		

[a] The esd is in the units of the least significant digit given for the corresponding value. The coordinates of the primed atoms are related to those given in Table I by −*x*, −*y*, −*z*; doubly primed atoms, by 1 + *x*, *y*, *z* or −1 + *x*, *y*, *z*.

Table IV. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

	Plane 1		Plane 2		Plane 3		Plane 4	
	N(4)	*−1*	N(17)	*−2*	N(4)	*0*	Cl(2)	*0*
	C(5)	*8*	C(12)	*4*	Hg(1)	*0*	Hg(1)	*0*
	C(6)	*−7*	C(13)	*−2*	N(17)	*0*	Cl(3)	*0*
	C(7)	*1*	C(14)	*−3*	C(9)	−683	N(4)	2158
	C(8)	*4*	C(15)	*5*	S(10)	−2026	S(10)	3404
	C(9)	*−4*	C(16)	*−1*	S(11)	2079	S(11)	−2770
	Hg(1)	591	Hg(1)	−448	C(12)	753	N(17)	−1020
	S(10)	−54	S(10)	290	Cl(2)[b]	−16		
	S(11)	176	S(11)	51				
$q_{b \times (a \times b)}$	179		862		−5304		9065	
q_b	−6639		6283		13		2574	
$q_{a \times b}$	7476		7732		8477		3348	
D	−0.648		2.659		1.153		1.056	
δ	5		3		0		0	

[a] Italicized deviations 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 (× 10^4), q, are with respect to orthogonalized axes. The rms deviation (Å × 10^3) of the italicized atoms from the plane is δ. D is the distance (in Å) from the plane to the origin. See Figure 3 to identify the planes. [b] The coordinates of the Cl(2) atom in plane 3 are related to those given in Table I by inversion at the origin.

chlorotrichloromethyl(1,10-phenanthroline)mercury(II),[28] 2.31 Å. These distances are close to those found in linear $HgCl_2$ molecules in the gas phase,[29] 2.28 Å, and the corresponding distance in crystalline $HgCl_2$,[30] 2.25 Å.

In comparsion to the sum of the approximate (tetrahedral) covalent radii[31] for Hg and Cl, 1.48 + 0.99 = 2.47 Å, and Hg and N, 1.48 + 0.70 = 2.18 Å, the average coordination distances observed in this complex, 2.335 and 2.580 Å, respectively, indicate that the Hg^{II}–N interaction is particularly long and decidedly secondary. These results are consistent with the 2.34-Å Hg^{II}–Cl bonds and 2.60-Å Hg^{II}–N bonds observed in bis(pyridine)dichloromercury(II).[32] The vapor pressure of pyridine over that complex led Grdenić[32] to conclude that pyridine is held only as molecules of crystallization, and not as ligands, in the crystal structure. At such long Hg^{II}–N distances, the pyridyl groups are relatively unperturbed by coordination; this, presumably, contributed to the conclusion,[10] on the basis of spectral measurements, that the pyridyl groups do not coordinate to Hg(II) and therefore, in part, that the disulfide group must.

Similar Hg^{II}–N distances are found in bis(chloropyridylmercury)tetracarbonyliron,[33] 2.51 Å, and in chlorotrichloromethyl(1,10-phenanthroline)mercury(II),[28] 2.57 and 2.61 Å. Distances ranging from 2.37 to 2.53 Å, involving ring nitrogens, are found in *cis*-dithiocyanatobis(1,10-phenanthroline)mercury(II).[34]

In addition to the two nitrogen atoms and two chloride ions coordinated to mercury(II), one additional approach at 3.380 (2) Å is made by a symmetry-related Cl(2). This distance is more than 1 Å longer than the two primary Hg^{II}–Cl bonds (see Table III), and it is the only additional Hg^{II}–Cl distance less than 4.0 Å. This Cl(2) ion lies very close to the Hg(1), N(4), N(17) plane (see plane 3 in Table IV); although the sum of the angles about Hg(1) in that plane is 360.0°, the individual angles range widely from 81.1 to 162.9° (see Table III).

A complex which might be expected to be similar to the one reported here, dichloro(2,4,6-trimethylpyridine)mercury(II),[35] is remarkably dissimilar. The stoichiometry is different: the shortest Hg^{II}–Cl distances average 2.50 Å; the coordination geometry is relatively close to trigonal bipyramidal with an equatorial Cl–Hg^{II}–Cl angle of 110.1°; and the Hg^{II}–N distance is very short, 2.18 Å. This example illustrates the sensitivity of Hg(II) coordination to relatively minor chemical differences.

The crystal structure of an organic disulfide complex of Hg(II) was determined once before.[36] There, as in this complex, coordination does not involve the disulfide group but involves other donor atoms of the disulfide molecule *N*,*N*,*N'*,*N'*-tetramethylthiuram disulfide. A comparison of coordination bond lengths involving these ligand donor atoms and the expected coordination bonding radii indicates that the thioketone groups of thiuram disulfide are better ligands to mercury(II) than the pyridyl groups of this work. Although the thiuram disulfide ligand forms a chelate ring, while the ligand in this work bridges cations, the C–S–S–C torsion angle remains near 90° in both complexes.

Two crystal structures of uncomplexed thiuram disulfide ligands, $R_2N–CS–S–S–CS–NR_2$, have been determined where the R groups are all methyl[37] or all ethyl.[38] In both cases, the S–S bond length is 2.00 Å and the C–S–S–C torsion angle is within a few degrees of 90°. The S–S bond is longer by 0.03 Å in the mercury(II) complex[36] of the first ligand even though the C–S–S–C angle is nearly unchanged by complexation. (It has been reported that the S–S bond length depends on the C–S–S–C torsion angle.[39]) The same change in ligand geometry is observed in dichloro[bis(2-pyridyl) disulfide]mercury(II) as compared to that of the ordered ring in the uncomplexed ligand:[40] the S–S bond has increased from 2.016 (2) to 2.030 (2) Å upon complexation while the C–S–S–C angle has remained nearly unchanged. It should be added that the S–S–C–X angles are less than 20°, or within 20° of 180°, where X is C, N, or S, in all five structures cited in this paragraph. Also, in each Hg(II) complex, the disulfide group is β to each of the two coordinating atoms, which are both unsaturated.

The geometry of the pyridine rings appears to be normal. The average C–C and C–N bonds are 1.38 and 1.34 Å, respectively, in agreement with similar averages found in the uncoordinated ligand,[40] 1.37 and 1.33 Å, and in other pyridyl groups.[41–44]

Reviews of the coordination geometry of mercury in its compounds and complexes by Grdenić[45] and Hursthouse[46,47] are available. Irregular coordination geometries abound.

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Registry No. $Hg(pySSpy)Cl_2$, 31-240-683.

Supplementary Material Available: listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. M. Kadooka, L. G. Warner, and K. Seff, *Inorg. Chem.*, **15**, 812 (1976).
(2) P. E. Riley and K. Seff, *Inorg. Chem.*, **11**, 2993 (1972).
(3) L. G. Warner, T. Ottersen, and K. Seff, *Inorg. Chem.*, **13**, 2529 (1974).

(4) L. G. Warner, M. M. Kadooka, and K. Seff, *Inorg. Chem.*, **14**, 1773 (1975).
(5) T. Ottersen, L. G. Warner, and K. Seff, *Inorg. Chem.*, **13**, 1904 (1974).
(6) L. G. Warner, T. Ottersen, and K. Seff, *Inorg. Chem.*, **13**, 2819 (1974).
(7) M. M. Kadooka, L. G. Warner, and K. Seff, *J. Chem. Soc., Chem. Commun.*, 990 (1975).
(8) J. A. Thich, D. Mastropaolo, J. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **96**, 726 (1974).
(9) J. A. Bertrand and J. L. Breece, *Inorg. Chim. Acta*, **8**, 267 (1974).
(10) M. Keeton and A. B. P. Lever, *Inorg. Chem.*, **10**, 47 (1971).
(11) D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, **8**, 107 (1969).
(12) S. P. Sinha, *Spectrochim. Acta, Part A*, **24**, 927 (1968).
(13) T. Ottersen, LP-73 computer program, University of Hawaii, 1973.
(14) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).
(15) T. Dahl, ABSCO computer program, Chemistry Department, University of Oslo, modified by T. Ottersen, 1973.
(16) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
(17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(18) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(19) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "ALFF, Ames Laboratory Fast Fourier", Iowa State University, 1971.
(20) K. Seff, HFIND computer program, University of Hawaii, 1971.
(21) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(22) J. A. Ibers, NUCLS, full-matrix least-squares, Northwestern University, Evanston, Ill., based on ORFLS by W. R. Busing and H. A. Levy.
(23) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(24) R. S. McEwen and G. A. Sims, *J. Chem. Soc.*, 1897 (1969).
(25) G. Sawitzki and H. G. von Schnering, *Chem. Ber.*, **107**, 3266 (1974).
(26) C.-I. Brӓnden, *Acta Chem. Scand.*, **17**, 1363 (1963).
(27) R. J. Majeste and L. M. Trefonas, *Inorg. Chem.*, **11**, 1834 (1972).
(28) A. D. Redhouse, *J. Chem. Soc., Chem. Commun.*, 1119 (1972).
(29) W. Gordy and J. Sheridan, *J. Chem. Phys.*, **22**, 92 (1954).
(30) D. Grdenić, *Arh. Kem.*, **22**, 14 (1950).
(31) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 246.
(32) D. Grdenić and I. Krstanović, *Arh. Kem.*, **27**, 143 (1955).
(33) R. W. Baker and P. Pauling, *Chem. Commun.*, 573 (1970).
(34) A. L. Beauchamp, B. Saperas, and R. Rivest, *Can. J. Chem.*, **49**, 3579 (1971).
(35) S. Kulpe, *Z. Anorg. Allg. Chem.*, **349**, 314 (1967).
(36) P. T. Beurskens, J. A. Cras, J. H. Noordik, and A. M. Spruijt, *J. Cryst. Mol. Struct.*, **1**, 93 (1971).
(37) M. Maroy, *Acta Chem. Scand.*, **19**, 1509 (1965).
(38) I. L. Karle, J. A. Estlin, and K. Britts, *Acta Crystallogr.*, **22**, 273 (1967).
(39) A. Hordvik, *Acta Chem. Scand.*, **20**, 1885 (1966).
(40) N. V. Raghavan and K. Seff, *Acta Crystallogr., Sect. B*, in press, and references therein.
(41) K. Seff and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 1406 (1968).
(42) T. Ottersen and K. Seff, *Acta Crystallogr., Sect. B*, **30**, 955 (1974).
(43) T. Ashida, *Acta Crystallogr., Sect. B*, **26**, 454 (1970).
(44) J. E. Johnson and R. A. Jacobson, *Acta Crystallogr., Sect. B*, **29**, 1669 (1973).
(45) D. Grdenić, *Q. Rev., Chem. Soc.*, **19**, 303 (1965).
(46) M. B. Hursthouse, *Mol. Struct. Diffr. Methods*, **1**, 724 (1973).
(47) M. B. Hursthouse, *Mol. Struct. Diffr. Methods*, **2**, 422 (1974).

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Structure of the 14-Membered Macrocyclic Tetrathia Ether Complex of Copper(II). Evidence for Undistorted Geometries in Blue Copper Protein Models

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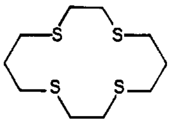
The crystal structure of $Cu(14\text{-ane-}S_4)(ClO_4)_2$ is reported where 14-ane-S_4 represents the saturated 14-membered cyclic tetrathia ether ligand, 1,4,8,11-tetrathiacyclotetradecane. The copper atom is centered in the plane of the four sulfur atoms with elongated bonds to two trans perchlorate groups completing the tetragonal coordination. Average bond lengths are Cu–S = 2.303 (1) Å and Cu–O = 2.652 (4) Å. The direct comparison of the crystal and solution spectra of $Cu(14\text{-ane-}S_4)(ClO_4)_2$ indicates that this complex maintains the same regular coordination geometry in the solution state. Moreover, the spectral and redox properties of the thia ether complex, similar to those exhibited by the blue copper proteins, indicate that coordinative distortion is not a primary factor in generating the distinctive properties which have been the hallmark of this class of proteins.

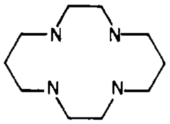
Introduction

Interest in macrocyclic complexes of transition metals has been stimulated both by their interesting kinetic and thermodynamic properties and by the apparent similarities of these species to systems of biological interest.[1] Most investigations reported to date have dealt with either the tetramine or polyether (crown ether) macrocycles. Recently, however, we have shown that the cyclic tetrathia ethers[2,3] represent an excellent series of ligands for the systematic investigation of the dependence of kinetic parameters on ligand ring size, presumably reflecting the influence of ligand structure upon bond formation and rupture processes.[4]

Of even greater interest is the very recent discovery that the copper(II) thia ether complexes exhibit unusual spectral and redox properties similar to those found in the blue copper proteins.[5-7] Since the blue copper protein phenomena have frequently been ascribed to the presence of tetrahedral or five-coordinate copper(II),[8-10] a rigorous determination of the structural features inherent in the copper(II) thia ether complexes was deemed a matter of the utmost importance.

In this paper we wish to report on the crystal structure of the diperchlorate salt of the most stable tetrathia ether–copper(II) complex involving the 14-membered macrocycle, 1,4,8,11-tetrathiacyclotetradecane (TTP or 14-ane-S_4). We will also compare this structure with that of the cyclic tetramine 1,4,8,11-tetraazacyclotetradecane (cyclam or 14-ane-N_4).


TTP
(14-ane-S_4)


cyclam
(14-ane-N_4)

Experimental Section

After recrystallization from a methanol–water mixture, a suitable crystal (0.11 × 19 × 23 mm) of $Cu(14\text{-ane-}S_4)(ClO_4)_2$ was mounted on a glass fiber with shellac. Initial x-ray examination by rotation and axial photographs on a Syntex $P2_1$ diffractometer yielded approximate lattice constants and showed the crystal to be of monoclinic symmetry. Least-squares refinement of 15 reflections with 2θ between 10 and 25°, which were centered with Mo Kα radiation (λ 0.71069 Å) diffracted from a highly oriented graphite monochromator in the parallel orientation with a takeoff angle of 4°, was used to determine precise lattice constants and orientation parameters. The crystal data are a = 7.904 (3) Å, b = 8.830 (4) Å, c = 16.840 (6) Å, β = 126.33