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Crystal and Molecular Structure of $C_{13}H_{10}N_4S \cdot HgCl_2$, the Adduct of Anhydro-5-mercapto-2,3-diphenyltetrazolium Hydroxide and Mercury(II) Chloride

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The reaction between mercury(II) chloride and the meso-ionic compound, anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide (dehydrodithizone), gives a 1:1 adduct with the empirical formula $C_{13}H_{10}N_4S \cdot HgCl_2$. The adduct crystallizes in the monoclinic space group *C*2 with four formula units per cell of dimensions, $a = 25.717$ (10), $b = 6.476$ (6), and $c = 11.476$ (8) Å and $\beta = 102.79$ (3)°. The calculated and measured densities are 1.89 and 1.95 (5) g cm^{-3}, respectively. Intensity data were collected by counter methods with Mo Kα radiation at 22°. The structure was refined by full-matrix least-squares methods using 1134 independent reflections with $F^2 > 3\sigma F^2$ and anisotropic temperature factors for the heavy atoms to an unweighted *R* factor of 0.060. The structure consists of parallel chains of alternating mercury and sulfur atoms. The coordination polyhedron around the mercury atom is a distorted trigonal bipyramid with two apical sulfur atoms at distances of 3.28 (2) Å from the mercury atom. The equatorial plane contains the mercury atom, two chlorine atoms, and one sulfur atom. The Hg–Cl distances are 2.34 (1) and 2.57 (1) Å, and the Hg–S distance is 2.40–(1) Å.

Introduction

The oxidation of dithizone with a variety of oxidizing agents gives at least five oxidation products[1,2] one of which is an orange-red crystalline compound, dehydrodithizone. The structure of this oxidation product was incorrectly postulated at first but later[2] the compound was correctly predicted to be the meso-ionic sydnone, anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide. This prediction was subsequently confirmed by a single-crystal X-ray structure determination.[3] Dehydrodithizone should have some interesting metal complexing properties that arise from the extensive electron delocalization in the tetrazole ring system and the exocyclic sulfur atom. In a preliminary survey of its reactions with metal ions it was found to react rapidly with mercury(II) chloride[4] and the product of the reaction which was isolated in the form of pale yellow crystals had the empirical formula $C_{13}H_{10}N_4S \cdot HgCl_2$. It was evident therefore that this compound was either a 1:1 adduct or an ionic substitution compound $[C_{13}H_{10}N_4S \cdot HgCl^+][Cl^-]$ in which the linear coordination geometry of $HgCl_2$ was retained. In view of the interest in the coordination chemistry of mercury(II), an ion which can assume a coordination number between two and six, and the recent interest in the properties of metal–tetrazole complexes, an X-ray structure determination of the pale yellow reaction product was undertaken.

Experimental Section

Preparation of the Adduct. Dehydrodithizone was synthesized by the oxidation of dithizone with hydrogen peroxide. A solution of hydrogen peroxide (2.5 ml of 30% H_2O_2) was diluted to 150 ml with water and added to a chloroform solution of dithizone (1.25 g in 100 ml) and the two-phase system was stirred vigorously for 1.5–2 hr. The pH of the aqueous phase was adjusted with 1 *M* NH_3 and 1 *M* HCl to a value between 8 and 8.5. The reaction consumes base and the pH of the aqueous phase was checked periodically. After about 2 hr the small orange crystals that were formed at the water-chloroform interface were separated by filtration, washed with water, and recrystallized from acetone. The purity of the compound was checked by examination of its infrared spectrum and by thin-layer chromatography. The structure of dehydrodithizone has been reported in an earlier paper.[3]

The adduct of dehydrodithizone with mercury(II) chloride was obtained by mixing equimolar amounts of mercury(II) chloride in water and dehydrodithizone in ethanol. Pale yellow needle-shaped crystals of the 1:1 adduct that were suitable for an X-ray analysis were obtained by crystallization from acetone.

Crystal Data. Preliminary oscillation and Weissenberg photographs obtained with nickel-filtered Cu Kα radiation indicated that the crystals of $C_{13}H_{10}N_4S \cdot HgCl_2$ were monoclinic and the systematic absences (*hkl*, $h + k = 2n + 1$) were consistent with one of the *C*-centered space groups *C*2, *Cm*, or *C*2/*m*. The crystal was not examined for piezoelectric properties. The *b*–*b** axis was coincident with the needle axis of the crystal. The lattice constants were determined from two cycles of least-squares refinement of the settings of seven reflections that had been accurately centered with Mo Kα_1 radiation ($\lambda = 0.70926$ Å) on a Picker four-circle FACS I automated diffractometer equipped with a graphite monochromator. The lattice constants and their estimated standard deviations at 22° are $a = 25.717$ (10), $b = 6.476$ (10), $c = 11.476$ (8) Å; $\beta = 102.79$ (3)°; $V = 1864$ Å^3; $d_{\text{obsd}} = 1.95 \pm 0.05$ g cm^{-3}, $d_{\text{calcd}} = 1.89$ g cm^{-3} for $Z = 4$ formula weights per unit cell. The crystal density was determined by the density gradient method with carbon tetrachloride and 1,2-dibromoethane.

Collection and Reduction of X-Ray Intensity Data. Intensity data were collected at 22° at a take-off angle of 1.2° with Mo Kα radiation; the θ–2θ scan technique was employed at a scan rate of 2° per minute. Stationary-crystal, stationary-counter backgrounds of 10 sec were taken at each end of the scan range. A needle-shaped crystal 0.30 mm long and of cross section 0.058 × 0.052 mm was used for the data collection. The needle axis was coincident with the Φ axis of the Picker FACS I diffractometer. The mosaicity of the crystal was examined by the ω-scan technique at a take-off angle of 0.5°. Several reflections that were examined showed no splitting and the width at a half-height of all the peaks was 0.16° or less. Seven reflections from the crystal were accurately centered through a narrow vertical slit at a take-off angle of 0.5°. An orientation matrix was calculated with these reflections and the diffraction data were collected. The same reflections were used for the least-squares refinement of the cell parameters. The scintillation counter had an aperture 4 mm wide and 4 mm high which was 31 cm from the crystal. No attenuators were used because none of the reflections exceeded 7000 counts/sec. The intensities of two standard reflections were monitored after every 75 reflections and were found to remain essentially constant, the deviations being predictable from counting statistics. It was concluded, therefore, that the crystal was stable in air and when exposed to X-rays for at least a period of 2 days during which time the intensity data were collected. In the data set that was collected in which $3° < 2\theta < 45°$, a total of 1430 independent intensities were recorded of which 1134 reflections which had $F_o^2 > 3\sigma F_o^2$ were used for the structure determination. The integrated intensity of a reflection was calculated from the equation $I = \mathrm{CT} - {}^1/_2(t_c/t_b)(B_1 + B_2)$ and the standard deviation of the intensity was $\sigma I = [\mathrm{CT} + {}^1/_4(t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$ where CT = total integrated count; B_1 = background count on low 2θ side

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[2] J. W. Ogilvie and A. H. Corwin, *J. Amer. Chem. Soc.*, 83, 5023 (1961).

[3] Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, 92, 1965 (1970).

[4] W. J. Kozarek and Q. Fernando, *J. Chem. Soc., Chem. Commun.*, 604 (1972).

Table I. Final Atomic Fractional Coordinates and Thermal Parameters

Atom	x	y	z	B, Å^2
Hg(1)	0.1950 (1)	0	−0.0487 (1)	[a]
Cl(1)	0.1541 (4)	0.0277 (72)	0.1362 (8)	[a]
Cl(2)	0.1291 (3)	−0.0017 (50)	−0.2261 (10)	[a]
S(1)	0.2864 (3)	0.0218 (83)	0.0580 (6)	[a]
C(1)	0.3199 (9)	0.0233 (132)	−0.0548 (21)	2.84 (70)
N(1)	0.2965 (9)	0.0293 (95)	−0.1754 (20)	3.40 (60)
N(2)	0.3370 (8)	0.0289 (81)	−0.2277 (19)	2.62 (56)
N(3)	0.3788 (9)	0.0365 (64)	−0.1479 (20)	3.23 (60)
N(4)	0.3718 (9)	0.0290 (88)	−0.0367 (21)	4.04 (66)
R(1)[c]	0.3260 (7)	0.0321 (46)	−0.4688 (17)	6.28 (51)
R(2)[c]	0.4872 (8)	−0.0334 (42)	−0.1804 (16)	6.59 (56)

Atom	$10^4\beta_{11}$[b]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Hg(1)	14.9 (2)	198 (3)	76 (1)	0	10 (1)	0
Cl(1)	18 (2)	450 (60)	114 (10)	24 (16)	1 (3)	127 (37)
Cl(2)	31 (2)	237 (4)	128 (10)	−5 (3)	38 (4)	51 (64)
S(1)	17 (1)	193 (54)	59 (7)	3 (2)	7 (3)	9 (40)

[a] Atom refined anisotropically. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] R(1) and R(2) are the phenyl groups which are treated as rigid groups, and the fractional coordinates are those of the group centers.

of peak; B_2 = background count on high 2θ side of peak; t_c = time elapsed during scan; t_b = background counting time; and ρ = the conventional ignorance factor of 0.04. All data were corrected for Lorentz and polarization effects. The linear absorption coefficient for Mo Kα radiation was 92.7 cm^{-1}. Absorption corrections were applied to all the data by means of the program AGNOST.[5] The transmission factors varied from a maximum of 0.655 to a minimum of 0.557. No corrections were made for extinction since the F_o values of the strong reflections at low $(\sin\theta)/\lambda$ did not show any systematic deviations from the F_c values.

Structure Determination. The systematic absences $h + k = 2n + 1$ indicated that the space group was $C2$, Cm, or $C2/m$. An examination of the Patterson synthesis revealed the presence of a Harker plane, but there was no recognizable Harker line. Hence, the space group Cm was eliminated. The space group $C2/m$ requires that the molecule has mirror symmetry. Since this seemed unlikely, the refinement was carried out in the space group $C2$. The successful refinement in this space group clearly showed that there was no mirror plane. Furthermore, a statistical test of the distribution of intensities confirmed the choice of the noncentrosymmetric space group $C2$. The initial R value, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, was 0.27 with the positional parameters of the mercury atom. The chlorine and sulfur atoms were located from a Fourier synthesis and the R value was reduced to 0.17. The scattering factors employed were those given in International Tables.[6] The nonhydrogen atoms in the rest of the molecule were located from subsequent Fourier and difference Fourier syntheses. At this stage the data were corrected for absorption and the scattering curves of the mercury, chlorine, and sulfur atoms were corrected for anomalous dispersion with the $\Delta f'$ and $\Delta f''$ values taken from the International Tables.[6] When the refinement was continued it was found that the carbon atoms of the phenyl rings had large temperature factors and that the rings were slightly distorted. This behavior of the carbon atoms is not unexpected in a heavy atom structure. Although the location of the aromatic rings and their orientation can be determined readily, the individual carbon atoms could not be located with a sufficient degree of precision. For these reasons it was decided to continue the refinement with the phenyl rings treated as rigid groups[7] (C–C = 1.397 Å) and with a single isotropic temperature factor assigned to each group. In the final stages of the refinement anisotropic thermal parameters were introduced for the mercury, sulfur, and chlorine atoms and the hydrogen atoms in the phenyl groups were included as fixed contributions (C–H = 1.08 Å). After three cycles of refinement the R value converged to 0.060. In the final refinement cycle the largest shift in the positional parameters was 0.005 Å in the z coordinate of atom N(3). Anisotropic thermal parameter shifts for the heavy atoms were of the order of 0.5 esd and isotropic thermal parameter shifts for the remaining atoms were less than 0.1 esd. The least-squares refinements were carried out on $|F_o|$, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and the weighting factor w was calculated from the equation $w = 4F_o^2/\sigma^2(F_o)^2$.

Table II. Parameters Derived for the Carbon Atoms[a] in the Rigid Groups

Atom	x	y	z
	Group R(1)		
C(2)	0.3321	0.0200	−0.3453
C(3)	0.3114	0.1983	−0.4060
C(4)	0.3053	0.2104	−0.5294
C(5)	0.3199	0.0443	−0.5922
C(6)	0.3407	−0.1339	−0.5315
C(7)	0.3468	0.1461	0.4081
	Group R(2)		
C(8)	0.4345	−0.0229	−0.1694
C(9)	0.4649	−0.1973	−0.1300
C(10)	0.5177	−0.2079	−0.1410
C(11)	0.5400	−0.0439	−0.1914
C(12)	0.5097	0.1305	−0.2308
C(13)	0.4568	0.1411	−0.2199

	B, Å^2	Φ[b]	θ	ρ
R_1	6.28 (51)	−2.77 (2)	3.05 (3)	−1.49 (2)
R_2	6.59 (56)	0.09 (3)	2.72 (2)	−0.34 (3)

[a] The intra-ring C–C distance is 1.397 Å. [b] The angles Φ, θ, and ρ (in radians) align the internal coordinates within the ring with respect to the fixed external coordinate system.[7]

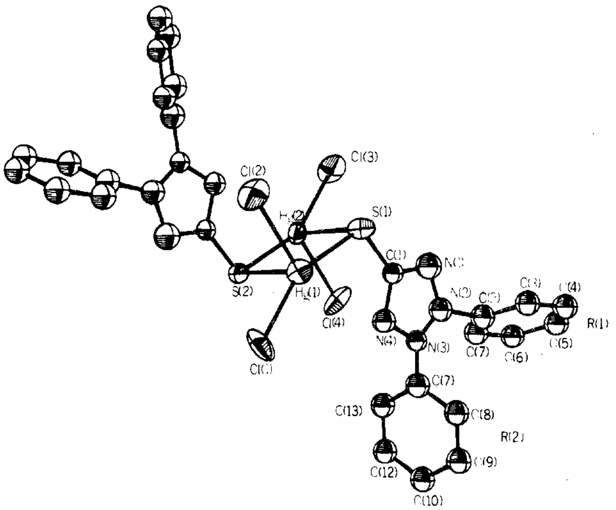

Figure 1. ORTEP diagram of two symmetry-related molecules of the adduct showing the numbering scheme.

Final atomic coordinates and temperature factors are given in Tables I and II with estimated standard deviations in the final digit in parentheses. The esd's were calculated from the inverse of the least-squares matrix. Bond distances and bond angles together with their estimated standard deviations are listed in Table III. A table of observed and calculated structure factors is available.[8]

Discussion

The reaction of mercury(II) chloride with dehydrodithizone gives a 1:1 adduct shown in Figure 1, in which only half of the structure is crystallographically independent; the remaining half is related by a twofold screw axis in the

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(5) AGNOST, a general program for absorption correction: P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, 18, 1035 (1965). Other programs used in this work included UAFACS, for data reduction, NUCLS, for least-squares refinement of individual atoms and rigid groups, Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE bond distance and bond angle program, and Johnson's ORTEP plotting program.

(6) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1965.

(7) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

(8) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2129.

Table III. Bond Distances and Bond Angles

Atoms	Distance, Å	Atoms	Angle, deg
Hg(1)-Cl(1)	2.34 (1)	Cl(1)-Hg(1)-Cl(2)	111.5 (4)
Hg(1)-Cl(2)	2.57 (1)	Cl(1)-Hg(1)-S(1)	151.8 (3)
Hg(1)-S(1)	2.40 (1)	Cl(2)-Hg(1)-S(1)	96.2 (3)
Hg(1)-S(2)	3.28 (2)	Hg(1)-S(1)-C(1)	102.4 (1)
S(1)-C(1)	1.71 (2)	S(2)-Hg(1)-S(3)	162.1 (3)
C(1)-N(1)	1.38 (2)	Hg(1)-S(1)-Hg(2)	96.7 (2)
N(1)-N(2)	1.31 (3)	S(1)-C(1)-N(1)	125 (2)
N(2)-N(3)	1.25 (3)	S(1)-C(1)-N(4)	123 (2)
N(3)-N(4)	1.33 (3)	C(1)-N(1)-N(2)	104 (2)
N(4)-C(1)	1.31 (3)	N(1)-N(2)-N(3)	108 (2)
N(2)-C(2)	1.33	N(2)-N(3)-N(4)	115 (2)
N(3)-C(8)	1.52 (3)	N(3)-N(4)-C(1)	102 (2)
		N(3)-N(2)-C(2)	128
		N(2)-N(3)-C(8)	123

direction of the Hg(1)-S(2) bond. The Hg(1)-S(1) distance is 2.40 Å and the Cl(1), Cl(2), Hg(1), and S(1) atoms are coplanar. The mercury atom, therefore, appears to have increased its coordination number from 2, in mercury(II) chloride, to 3, in the adduct. Moreover, if it can be assumed that the covalent radius of mercury in this adduct is 1.39 Å, which is intermediate between its tetrahedral covalent radius of 1.48 Å and digonal covalent radius of 1.30 Å,[9] the Hg(1)-S(1) distance agrees reasonably well with the sum of the covalent radii of the mercury (1.39 Å) and sulfur (1.04 Å) atoms. It is evident from the values of the angles around the mercury atom that there is considerable distortion in the trigonal adduct; the Hg(1)-Cl(1) and Hg(1)-Cl(2) distances (Table III) are also significantly different. It may be deduced, therefore, that the mercury atom does not use a set of equivalent sp^2 orbitals in adduct formation. It should be mentioned, however, that the long Hg(1)-Cl(2) bond (2.57 Å) may be partly attributable to the attraction of the Cl(2) atom toward the positive charge located in the tetrazole ring.[3]

A closer examination of the environment around the mercury atom shows that there are two sulfur atoms S(2) and S(3) (only one of which is shown in Figure 1) at a distance of 3.28 Å from the mercury atom. Since this distance is less than the sum of the van der Waals radii of the mercury (1.50 Å) and sulfur (1.85 Å) atoms,[9] the two sulfur atoms S(2) and S(3) are weakly bonded to the mercury atom. Hence, the coordination polyhedron around the mercury atom is a distorted trigonal bipyramid in which the apices are occupied by the two sulfur atoms S(2) and S(3), the S(2)-Hg(1)-S(3) angle being 162.1°, and the equatorial plane consists of the Cl(1), Cl(2), Hg(1), and S(1) atoms (Figure 2). The mercury atom is therefore five coordinate in this structure. Because d-s mixing is energetically favorable for the d^{10} system in the third transition series, it is necessary to invoke some type of hybridization of the d_{z^2} and s orbitals to form the five-coordinate mercury adduct. The distortion of the trigonal bipyramid can arise from the partial negative charges on the sulfur atoms of the dehydrodithizone ligands as well as the difference in the electronegativity of the sulfur and the chlorine donors.

Owing to the presence of the long Hg(1)-S(2) and Hg(1)-S(3) type of bonds in the structure, the adduct can be considered to be a polymer consisting of a ladder-like arrangement of infinite parallel chains of alternating mercury and sulfur atoms, the two chains in the ladder being 2.40 Å apart. One of the rectangular units, Hg(1)-S(1)-Hg(2)-S(2), that form the ladder is shown in Figure 1, and the manner in which the ladder is extended is seen in Figure 3. Since the S(2)-Hg(1)-S(3) angle in the ladder is 162.1 and not 180°, the ladder is slightly folded. The environment around the sulfur atoms must also be trigonal bipyramidal if it can be assumed that one of the empty d orbitals is in the equatorial plane containing the atoms Cl(1), S(1), and Hg(1). Each sulfur atom forms two types of bridges: a Hg-S-Hg bridge in which both Hg-S distances are 3.28 Å and the Hg-S-Hg angle is 162.1°, and an Hg(1)-S(1)-Hg(2) bridge in which the Hg(1)-S(1) distance is 2.40 Å, the Hg(2)-S(1) distance is 3.28 Å, and the Hg(1)-S(1)-Hg(2) angle is 96.7°.

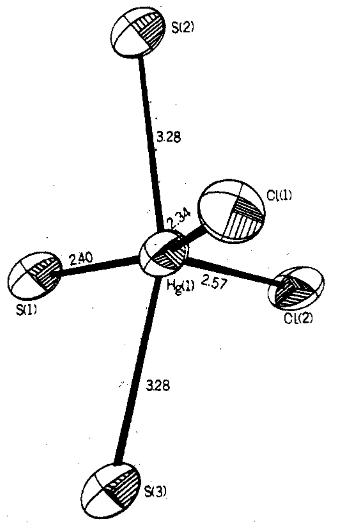

Figure 2. ORTEP diagram of the trigonal-bipyramidal coordination around the mercury atom.

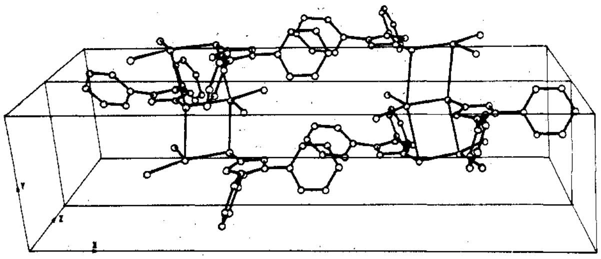

Figure 3. ORTEP diagram of the contents of half the unit cell showing the folded ladder-like arrangement of the chains of alternating sulfur and mercury atoms.

It is noteworthy that the dehydrodithizone molecule is essentially unchanged when the exocyclic sulfur atom is coordinated to mercury. The C-S bond distance retains its partial double bond character that it had in the free dehydrodithizone molecule but the dihedral angle between the phenyl groups has increased from 45° in the uncomplexed dehydrodithizone[3] to 66° and is probably caused by crystal packing forces.

Registry No. $C_{13}H_{10}N_4S \cdot HgCl_2$, 39291-58-2.

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[9] D. Gardenic, *Quart. Rev., Chem. Soc.*, 19, 303 (1965).