Preparation, Properties, and Crystal Structure of Dichlorobis-(*O*-Ethyl thiocarbamate)mercury(II)

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The preparation, spectroscopic properties, and *X*-ray structure of the title compound have been determined. Crystals are monoclinic, space group $P2_1/n$, with unit cell dimensions: a = 10·994(12), b = 12·437(5), c = 10·568(6) Å, β = 101·59(7)° and Z = 4. The structure was solved by the heavy-atom method from 1624 reflections collected by counter, and refined by least-squares methods to R 0·045. It consists of monomeric molecules, with the mercury atom in a distorted tetrahedral configuration, associated in the crystal by a three-dimensional hydrogen-bond network. Some dimensions are: Hg–Cl 2·58(1) and 2·62(1), Hg–S 2·43(1) and 2·45(1) Å; Cl–Hg–Cl 96·2, S–Hg–S 129·9, and Cl–Hg–S 103·2 and 112·4°. The two thiocarbamate ligands are virtually planar, the angle between the normals to their planes being 46·2°.

ALTHOUGH a large number of addition compounds between mercury(II) chloride and thiocarbonyl ligands such as thiourea[1] and *NN'*-dialkyldithiocarbamate esters[2] have been studied, its compounds with thiocarbamate esters have not yet been investigated. In the course of our studies on the ability of ethyl thiocarbamate $R^1R^2N{\cdot}C(S)OEt$ (R^1, R^2 = H and/or Me or Et) to react with $HgCl_2$, we obtained several compounds of different stoicheiometry.[3] As part of our investigation of the influence of R^1 and R^2 on the general stability and stoicheiometry of these complexes, we have determined the structure of the compound L_2HgCl_2 (L = ethyl thiocarbamate).

EXPERIMENTAL

Preparation.—Ethyl thiocarbamate (0·02 mol), prepared as in ref. 4 and recrystallized from water, was dissolved in ethanol (5 ml). Mercury(II) chloride (0·01 mol) in ethanol (15 ml) was gradually added with stirring. After 10 h the solution was filtered to remove a slight quantity of an initial yellowish white precipitate. The crystals, which appeared after a few days, were washed with ethanol, recrystallized from acetone–light petroleum (1 : 1 v/v), and dried *in vacuo* (P_2O_5); m.p. 105—107 °C (Found: C, 14·95; H, 3·00; N, 5·70; Cl, 14·65. $C_6H_{14}Cl_2HgN_2O_2S_2$ requires C, 14·98; H, 2·87; N, 5·82; Cl, 14·70).

Vibrational Spectra.—I.r. spectra were measured on a Perkin-Elmer 337 spectrophotometer (KBr pellets) in the 4000—600 cm^{-1} region.

Crystal Data.—$C_6H_{14}Cl_2HgN_2O_2S_2$, M = 481·8, Monoclinic, a = 10·994(12), b = 12·437(5), c = 10·568(6) Å, β = 101·59(7)°, U = 1415·5 Å^3, D_m (by flotation) = 2·24 g cm^{-3}, Z = 4, D_c = 2·26 g cm^{-3}, $F(000)$ = 904. Space group $P2_1/n$ [a non-standard orientation of $P2_1/c$ from systematic absences: $h0l$ for $h + l$ odd, and $0k0$ for k odd with the following equivalent positions: $\pm(x, y, z)$; $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$]. Cu-$K_\alpha$ radiation, λ = 1·54178 Å; μ(Cu-K_α) = 269·6 cm^{-1}.

Intensity Data.—Data were collected for a crystal of dimensions *ca.* 0·26 × 0·18 × 0·07 mm^3, mounted about the *a* axis on a Siemens automatic four-circle diffractometer by use of Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter, and a Na(Tl)I scintillation counter. The θ—2θ scan technique was employed, with a five-value measuring procedure.[5] Of 1770 independent reflections to θ 55° measured, 146 having $|F_o| \leqslant 2\sigma$ were considered unobserved and omitted from the subsequent refinement. Lorentz, polarization, and absorption corrections were applied.[6] A Wilson plot enabled the data to be put on approximate absolute scale.

Although there was a possibility of radiation damage causing errors in the data, no evidence was found for crystal deterioration during data collection.

Determination of the Structure.—The crystal structure was solved by conventional heavy-atom techniques. Two cycles of structure-factor and Fourier calculations revealed all the non-hydrogen atom positions, and gave R 0·091. With the use of isotropic thermal parameters throughout, two cycles of block-diagonal least-squares refinement (unit weights) reduced R to 0·071.

Refinement was continued by use of a full-matrix least-squares program which minimized the function $\Sigma w(K|F_o| - |F_c|)^2$. The weighting scheme used was $w^{-1} = \Sigma a_i|F_o|^i$, the parameters a_i being varied during the course of refinement so as to maintain mean values of $w(K|F_o| - |F_c|)^2$ approximately constant over equally populated region of $|F_o|$. Anisotropic thermal parameters were introduced for all non-hydrogen atoms, together with an anomalous dispersion correction for the mercury, chlorine, and sulphur atoms ($\Delta f'$, $\Delta f''$ from ref. 7).

After four full-matrix cycles R was 0·045. At this stage, an analysis of the distribution of $w|\Delta F|^2$ did not suggest any more appropriate weighting scheme and a difference-Fourier synthesis showed no significant features.

Scattering factor curves for neutral atoms were taken from ref. 7. Final observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21172 (3 pp., 1 microfiche).‡ Final atomic parameters for the crystallographically independent atoms, together with their estimated standard deviations, are listed in Table 1, and anisotropic thermal parameters in Table 2.

We were pleasantly surprised that the hydrogen atoms could be located in the presence of the mercury atom from

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‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] P. D. Brotherton and A. H. White, *J.C.S. Dalton*, 1973, 2696; 2698, and refs. therein.

[2] H. C. Brinkhoff and Y. M. A. Dautzenberg, *Rec. Trav. chim.*, 1972, **91**, 117.

[3] L. Sindellari and F. D'Angeli, Abstracts, A.I.C.I. Congress, Taormina, 1972, *A*33.

[4] B. Holmberg, *J. prakt. Chem.*, 1905, **71**, 273.

[5] W. Hoppe, *Angew. Chem.*, 1965, **77**, 484.

[6] G. Kopfmann and R. Huber, *Acta Cryst.*, 1968, **A24**, 348; 1969, **A25**, 143.

[7] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; D. T. Cromer, *ibid.*, p. 17.

a difference-Fourier synthesis, although the data were not of sufficient quality to allow refinement of the hydrogen parameters.

Final bond lengths and angles are shown in Figure 1 (a) and (b), together with the atom numbering system used in the crystallographic analysis.

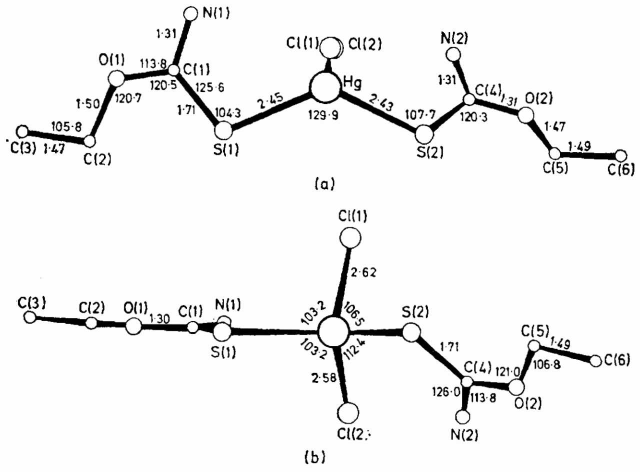

FIGURE 1 (a) Projection of the molecule on the mean plane defined by Hg, S(1), C(1), N(1), and O(1), and (b) perspective drawing of the molecule, showing bond lengths (Å) and angles (°). σ 0·1 Å [0·02 for C(2)–C(3) and C(5)–C(6)] and *ca.* 0·8° (0·2° for angles involving Hg); angle Cl(1)–Hg–Cl(2) 96·2°

TABLE 1

Final fractional co-ordinates, with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms ($\times 10^4$)

	x/a	y/b	z/c
Hg	2439(0)	1035(0)	2006(0)
Cl(1)	3013(2)	1318(2)	−260(2)
Cl(2)	2138(3)	−1023(2)	1802(3)
S(1)	4444(3)	1217(2)	3508(3)
S(2)	500(2)	1981(2)	1950(3)
O(1)	6569(6)	275(6)	3472(6)
O(2)	−1837(6)	1373(6)	1442(7)
N(1)	5101(9)	−229(7)	1864(10)
N(2)	−544(9)	23(7)	1504(9)
C(1)	5412(9)	364(8)	2908(9)
C(2)	7106(11)	971(10)	4602(11)
C(3)	8437(10)	701(11)	4936(12)
C(4)	−676(10)	1061(7)	1606(9)
C(5)	−2169(10)	2517(9)	1304(12)
C(6)	−3547(11)	2572(11)	1005(15)

(*b*) Hydrogen atoms ($\times 10^3$); these co-ordinates were determined from difference-Fourier syntheses, but not refined

H(1)[N(1)]	553	−60	140
H(2)[N(1)]	407	−43	157
H(1)[N(2)]	−130	−27	127
H(2)[N(2)]	17	−43	140
H(1)[C(2)]	687	190	427
H(2)[C(2)]	633	77	540
H(1)[C(5)]	−153	267	227
H(2)[C(5)]	−150	303	83
H(1)[C(3)]	867	127	570
H(2)[C(3)]	883	100	417
H(3)[C(3)]	843	−17	527
H(1)[C(6)]	−383	327	87
H(2)[C(6)]	−390	220	187
H(3)[C(6)]	−390	213	17

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	383(4)	510(4)	396(4)	23(2)	98(2)	−1(2)
Cl(1)	506(15)	424(13)	389(14)	7(11)	161(11)	0(10)
Cl(2)	508(15)	401(15)	480(16)	25(11)	105(12)	3(10)
S(1)	437(15)	604(17)	466(16)	49(13)	58(12)	−245(12)
S(2)	419(14)	411(15)	728(19)	−16(12)	149(13)	−132(13)
O(1)	411(42)	426(37)	438(38)	−16(31)	48(32)	−59(31)
O(2)	432(43)	468(40)	435(41)	−9(33)	128(31)	−108(33)
N(1)	586(60)	764(67)	596(61)	214(53)	25(48)	−332(55)
N(2)	582(57)	461(61)	535(57)	−56(43)	163(45)	−71(41)
C(1)	318(56)	434(58)	384(55)	6(44)	34(43)	6(47)
C(2)	418(64)	646(74)	324(60)	−72(51)	−129(47)	−47(47)
C(3)	404(64)	821(83)	549(69)	16(61)	10(51)	−182(66)
C(4)	418(64)	434(66)	266(53)	21(45)	59(43)	−6(39)
C(5)	481(63)	413(63)	666(72)	2(50)	135(54)	69(54)
C(6)	431(68)	720(87)	1137(112)	123(62)	86(70)	313(81)

* Values of U_{ij} in the temperature factor $\exp[-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \ldots)]$ so that, for instance, U_{11} is the mean-square amplitude of vibration parallel to a^*.

TABLE 3

Least-square planes, with, in square brackets, deviations (Å) of the most relevant atoms. The equation of a plane in direct space is given by $Px + Qy + Rz = S$

	P	Q	R	S
Plane (1): S(1), C(1), N(1), O(1)	4·000	9·269	−6·557	0·603
[S(1) 0·0, C(1) 0·0, N(1) 0·0, O(1) 0·0, Hg 0·02, S(2) 0·15, C(2) 0·12, C(3) 0·18]				
Plane (2): S(2), C(4), N(2), O(2)	−1·928	−1·366	10·501	1·679
[S(2) 0·0, C(4) −0·01, N(2) 0·0, O(2) 0·0, Hg −0·18, S(1) 0·98, C(5) −0·23, C(6) −0·29]				
Plane (3): S(1), C(1)—(3), N(1), O(1)	3·654	9·177	−6·788	0·353
[S(1) 0·01, C(1) −0·02, N(1) 0·03, O(1) −0·06, C(2) 0·01, C(3) 0·02, Hg 0·13, S(2) 0·32]				
Plane (4): S(2), C(4)—(6), N(2), O(2)	−2·514	−0·759	10·544	1·774
[S(2) 0·0, C(4) 0·01, N(2) −0·05, O(2) 0·10, C(5) −0·05, C(6) −0·02, Hg −0·35, S(1) 0·71]				
Plane (5): Hg, Cl(1), Cl(2)	9·927	−1·680	2·305	2·710
[S(1) 2·31, S(2) −2·10, O(1) 4·57, O(2) −4·43, N(1) 2·82, N(2) −2·91, C(1) 3·27, C(4) −3·19]				
Plane (6): Hg, S(1), S(2)	4·438	8·685	−6·977	0·582
[Cl(1) 2·08, Cl(2) −1·78, O(1) 0·15, O(2) −1·21, N(1) 0·18, N(2) −1·85, C(1) 0·11, C(4) −1·08]				

Angles (°) between planes

(1)–(2)	46·2	(3)–(4)	46·2
(1)–(3)	2·5	(3)–(5)	87·8
(1)–(5)	90·0	(3)–(6)	4·7
(1)–(6)	4·0	(4)–(5)	78·7
(2)–(4)	4·2	(4)–(6)	44·8
(2)–(5)	75·2	(5)–(6)	88·3
(2)–(6)	43·5		

Equations of some relevant planes in the molecule are reported in Table 3, selected intra- and inter-molecular distances are listed in Table 4. The solution and refinement of the structure were carried out by use of '*X*-Ray '70,' [8] integrated with the ABSORP program of Dr. G. Kopfmann of the Max Plank Institute of München. Calculations were made on the Consorzio Interuniversitario dell'Italia Nordorientale, Casalecchio (Bologna), CDC 6600 computer.

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TABLE 4

Non-bonded distances (Å)

(*a*) Intramolecular $\leqslant 3\cdot5$ Å			
Hg ··· N(1)	3·35	Cl(2) ··· N(1)	3·39
Hg ··· N(2)	3·45	Cl(2) ··· N(2)	3·18
Hg ··· C(1)	3·32	S(1) ··· C(2)	2·94
Hg ··· C(4)	3·37	S(2) ··· C(5)	2·95
Cl(1) ··· N(1)	3·46		
(*b*) Intermolecular $\leqslant 4\cdot0$ Å			
Hg ··· Cl(2^{I})	3·87	S(2) ··· Cl(2^{I})	3·64
Cl(1) ··· N(1^{II})	3·23	S(1) ··· Cl(2^{I})	3·83
Cl(1) ··· N(2^{III})	3·23	Cl(2) ··· C(3^{V})	3·65
Cl(1) ··· O(2^{III})	3·71	Cl(2) ··· C(2^{V})	3·72
Cl(1) ··· C(2^{IV})	3·51	S(2) ··· N(1^{I})	3·79
Cl(1) ··· C(3^{IV})	3·74	O(1) ··· O(2^{VI})	3·32
Cl(2) ··· O(2^{III})	3·41	C(5) ··· O(1^{I})	3·49
Cl(2) ··· N(2^{III})	3·79	N(2) ··· N(2^{III})	3·62
Cl(2) ··· C(4^{III})	3·64		

Atoms derived by transformation of the asymmetric unit (x, y, z) are defined by superscript Roman numerals:

I $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
II $1 - x, \bar{y}, \bar{z}$
III $\bar{x}, \bar{y}, \bar{z}$
IV $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
V $1 - x, \bar{y}, 1 - z$
VI $1 + x, y, z$

RESULTS AND DISCUSSION

The structure is built up of monomeric molecules with the mercury atom in a distorted tetrahedral configuration, the molecules being associated in the crystal by a three-dimensional hydrogen-bond network (Figures 1 and 2).

The Hg–Cl distances are significantly larger than expected (2·47 Å) from the sum of their covalent radii[9,10] and values (2·32 and 2·33 Å) for $HgCl_2,2Ph_3AsO$,[11] an addition compound with a highly distorted tetrahedral configuration about mercury. We consider the lengthening of the Hg–Cl distances to be a consequence of NH ··· Cl hydrogen bonds (see later); in [HgCl(thiourea)$_2$]Cl,[12] where the crystal packing is dominated by such interactions, the distance is 2·57 Å.

As commonly observed for mercury compounds, the organic ligand binds to the metal *via* the sulphur atom, the Hg–S–C angles being *ca.* 106°. The Hg–S distances are shorter than expected (2·52 Å) from the sum of their covalent radii,[10] but within the range of previously reported Hg–S distances.[1,12–16]

The ethyl thiocarbamate groups are planar as can be seen from the S–C–N angles and the least-squares planes (Table 3). The root-mean-square displacements are all reasonable, the maximum deviation in each ligand being of the oxygen atom (−0·06 and 0·10 Å), as in similar complexes.[17] The mercury atom is out of the mean plane of the two ligands by only small amounts, the deviations being 0·13 and −0·35 Å, a feature which does not seem to be general with complexes of this type and has no immediate explanation. The angle between the ligand molecules is 46·2°. Corresponding dimensions on each of the ligands are similar. As expected, the S–C distances are significantly shorter than calculated[10] (1·81 Å), but similar to the value (1·72 Å) for free thiourea[18] and several of its derivatives and co-ordination complexes. This indicates the presence of some double-bond character; in fact, atoms C(1) and C(4) appear to be essentially sp^2 hybridized (Table 3). It should be remembered that, although C(1) and C(4) are sp^2 hybridized, the N(1)–C(1)–O(1) and N(2)–C(4)–O(2) angles (113·7—113·9°) are less than 120°, whereas the S(1)–C(1)–N(1) and S(2)–C(4)–N(2) (125·6—126·0°) are larger; this recalls the situation in similar compounds and could be explained by the formation of intra- and inter-molecular hydrogen bonds.

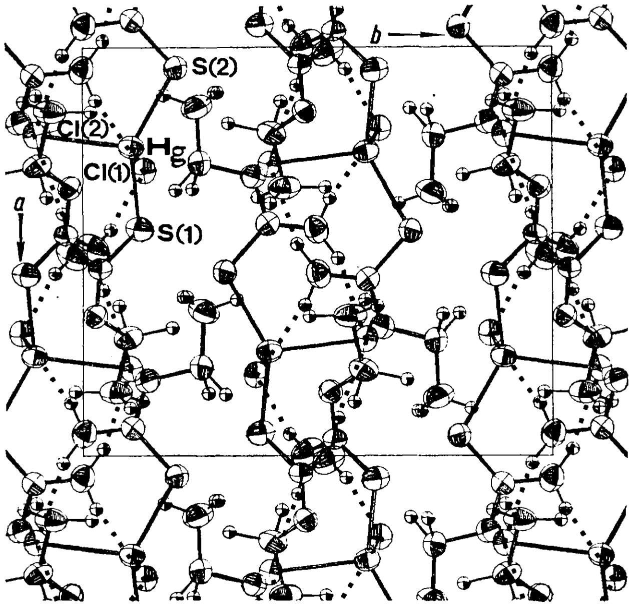

FIGURE 2 Arrangement of the molecules in the unit cell, viewed along the *c* axis; hydrogen bonds are denoted by dashed lines

The molecular arrangement of the complex is characterized by an extensive three-dimensional system of NH ··· Cl hydrogen bonds (Figure 2), while other packing contacts are normal van der Waals interactions (Table 4). The hydrogen bonds extend along the *a* axis and involve atoms N(1) [with Cl(2) and Cl(1^{II})] and N(2) [with Cl(2) and Cl(1^{III})]. That these are very probably true hydrogen bonds is indicated by consideration of the relevant distances and angles (Table 5). Thus, both chlorine atoms are acting as two hydrogen-bond acceptors, one inter- and the other intra-molecular.

The Hg–H(2)[N(1)] contact (2·66 Å) is the shortest Hg–H distance and this interaction may account for

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[18] M. R. Truter, *Acta Cryst.*, 1967, **22**, 556.

the co-ordinating ability of $R_2N{\cdot}C(\colon S){\cdot}OEt$ (R = H) and for the impossibility of obtaining an analogous complex when R = Me or Et.

A chlorine atom Cl(2^I) of a neighbouring molecule approaches the mercury atom (3·87 Å) at a distance greater than the usual van der Waals contacts (3·3 Å) [9], but in a direction just close to the perpendicular to an S,S,Cl face; the environment is thus verging on a trigonal-bipyramidal conversion.

TABLE 5

Distances (Å) and angles (°) involved in possible hydrogen bonds

D	A	D · · · A (Å)	H–D (Å)	H · · · A (Å)	∠A · · · H–D (°)	∠H–D · · · A (°)
N(1)	Cl(2)	3·39	1·14	2·31	157·8	14·9
N(1)	Cl(1^{II})	3·23	0·88	2·36	168·3	8·5
N(2)	Cl(2)	3·18	0·99	2·24	157·2	15·9
N(2)	Cl(1^{III})	3·23	0·90	2·36	163·9	11·7
N(1)	Cl(1) *	3·46	1·14	2·99	104·6	56·7

Roman numeral superscripts are defined in Table 4.

* Probably not a hydrogen bond.

I.r. spectra are consistent with co-ordination of the ligand to the metal *via* the sulphur atom. A shift to a higher wavenumber (20 cm^{-1}) of the band at 1600 (probably NH bending coupled with CN stretching) could be related to a higher C–N bond order.

In fact, the nature of the C–N as well as the C–S bond changes on co-ordination of the ethyl thiocarbamate through the sulphur atom. The bands due to C–S vibrations would therefore be shifted to a slightly lower wavenumber, as they are for thiourea and related complexes.[19] However, comparison of i.r. spectra (1500—600 cm^{-1}) of free and co-ordinated thiocarbamate esters, shows no significant differences. It is possible that, as reported by Tarantelli and Furlani,[20] the contributions to the frequency shift might cancel each other out, in the case of coupling between the CN and CS modes of vibrations. A shift of *ca.* 100 cm^{-1} downward in the NH stretching region (3500—3000 cm^{-1}) for the complex is probably due to intermolecular hydrogen-bond interactions.

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