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Mercury(II) Halide Complexes with N,N-Dimethyl O-Ethylthiocarbamate. The Crystal Structure of $Hg(DMTC)Cl_2$

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The crystal structure of the title compound has been determined by X-ray crystallography using diffractometer data. The material crystallizes in the monoclinic space group $P2_1/a$ with four molecules in a cell of dimensions a *=10.73(1),* b *= 13.41(1),* c *= 7.71(1) Å, and β = 96.90(5)°. Refinement of the structure has led to a final value of the conventional R factor of 0.099. The crystals decompose under irradiation. The mercury(II) atom is trigonally bonded to two chlorine atoms (Hg–Cl bond distances of 2.47 and 2.38 Å) and to the sulfur atom from the ligand (DMTC = $(CH_3)_2N$-CS-OEt; Hg–S of 2.47 Å). In addition the metal atom of each DMTC·$HgCl_2$ unit makes two Hg···Cl contacts of 2.94 and 3.13 Å with chlorine atoms of two adjacent units to form an extended structure with mercury in effective five-coordination. The properties of the complexes $Hg(DMTC)X_2$ (X = Cl, Br, I) in solid and in benzene or acetone solutions have been studied by IR, ^1H NMR and osmometric methods.*

Introduction

The title ligand $(CH_3)_2N$-CS-OEt(DMTC) forms with palladium(II) and platinum(II) halides the 1:2 adducts $M(DMTC)_2X_2$ (M = Pd, Pt; X = Cl, Br, I) [1], whereas N-methyl O-ethylthiocarbamate (CH_3-NH-CS-OEt, MTC) gives, in addition to the 1:2 adducts, complexes where the central metal is bonded to three or four ligand molecules [2]. By reaction with mercury(II) halides MTC forms the adducts $Hg(MTC)_2X_2$ (X = Cl, Br, I) [3], where the mercury atom should have a distorted tetrahedral configuration by two halogen and two sulfur atoms, analogous to that observed in $Hg(TC)_2Cl_2$ (TC =

TABLE I. Analytical Data (the calculated values are in parentheses) and ^1H NMR Spectra (the chemical shifts are in ppm).

Compound	M.p. °C	C%	H%	N%	Hal%	Solvent	$N(CH_3)_2$	O-CH_2-*CH_3*	O-*CH_2*-CH_3
$Hg(DMTC)Cl_2$	72–3	14.8	2.8	3.5	17.5	Benzene	2.62–3.09	0.98	4.40
		(14.8)	(2.7)	(3.5)	(17.5)	$(CD_3)_2CO$	3.34–3.57	1.39	4.70
$Hg(DMTC)Br_2$	78–9	12.2	2.2	2.8	32.6	Benzene	2.56–3.05	0.97	4.36
		(12.2)	(2.2)	(2.8)	(32.4)	$(CD_3)_2CO$	3.36–3.57	1.39	4.67
$Hg(DMTC)I_2$	67–8	10.3	1.9	2.3	43.5	$(CD_3)_2CO$	3.38–3.52	1.37	4.61
		(10.2)	(1.9)	(2.4)	(43.2)				

TABLE II. Infra-red Bands around 1550 cm^{-1} and below 850 cm^{-1}.

$Hg(DMTC)Cl_2$	1580s	851s	813vw	720vw	665w	646m	527m	470m		403w	363vw	*280*mbr	240wbr	
$Hg(DMTC)Br_2$	1578s	857s	812vvw	720vw	669w	640w	527m	470m		408w			240wbr	*192*m
$Hg(DMTC)I_2$	1572s	857s	810vvw		670w	644mw	527m	470m	430vvw	410w	365vvw		240wbr	*156*w

H_2N-CS-OEt) by X-ray analysis [4]. The structural arrangement is instead doubtful for the 1:1 complexes $HgX_2 \cdot MTC$ (X = Cl, Br, I) [3]; in fact the chloro- and bromo- derivatives have been isolated each in two forms clearly identified by different far IR spectra. Both forms should have a polymeric arrangement, in which either hydrogen or halide bridges should be involved. By reaction of mercuric halides with the tertiary thiocarbamate DMTC only the 1:1 adducts have been isolated, confirming the importance of hydrogen bonds in stabilizing higher stoichiometries. This paper reports the preparation and characterization of the complexes $Hg(DMTC)X_2$ (X = Cl, Br, I), whose analytical and IR data are in Tables I and II. For $Hg(DMTC)Cl_2$ the crystal structure has been determined by X-ray diffraction.

Experimental

The starting materials were commercial HgX_2 (X = Cl, Br, I) and DMTC, prepared as reported in ref. [1]. Benzene and n-hexane were distilled from Na.

Preparation of the Complexes

HgX_2 (X = Cl, Br, I) dissolved easily in a benzene solution of DMTC (molar ratio ≅ 1:3). By addition of n-hexane the product separated as an oil which crystallized slowly by washing with n-hexane. The chloro- and bromo- derivatives are white, the iodo complex is isolated as pale-yellow needles. All the complexes are soluble in acetone and CH_2Cl_2; Hg-$(DMTC)X_2$ (X = Cl, Br) dissolve in benzene, whereas the iodo derivative gives immediately a yellow solution from which a red solid separates, identified as HgI_2.

The IR spectra were recorded on a Perkin Elmer Mod. 580 Infrared Spectrometer (4000–400 cm^{-1}; Nujol and Voltalef 10S Mulls between KBr plates) and on a Beckman IR 11 Spectrophotometer (400–150 cm^{-1}, Nujol mulls between polythene plates).

Osmometric measurements in benzene and acetone were carried out by a Mechrolab Mod. 302 Vapor pressure Osmometer at 37 °C. The Van t' Hoff i values were calculated as $i = \Delta R_c/\Delta R_b$, where ΔR_c is the experimental osmometric value for a given concentration of complex (by F. W.) and ΔR_b is the value for an identical concentration of benzil as standard. Conductivities in acetone were measured at 25 °C with an LKB conductivity Bridge Mod. 3216B. The ^1H NMR spectra were recorded at 27 °C on a Bruker Spectrospin HFX-10 90 MHz Spectrometer. For benzene solutions the solvent signal was taken as internal shift reference; for d_6-acetone solutions benzene was used as internal standard, owing to the reaction of the complexes with TMS. The chemical shifts are given from TMS.

TABLE III. Crystal Data for $Hg(DMTC)Cl_2$.

$C_5H_{11}NOSCl_2Hg$	F.W. 405	
Crystal description	Transparent plates	
System	monoclinic	
Space group	$P2_1/a$	
Systematic absences	h 0 l	h odd
	0 k 0	k odd
General positions	$\pm(x, y, z; ½ + x, ½ - y, z)$	
Cell dimensions	a = 10.73(1) A	
	b = 13.41(1) A	
	c = 7.71(1) A	
	β = 96.90(5)°	
	V = 1101 A^3	
Density	2.44 g cm^{-1} for $Z = 4$	
μ(Mo-Kα)	166.9 cm^{-1}	

X-Ray Data

Well formed transparent plates of $Hg(DMTC)Cl_2$ were obtained by recrystallization from acetone/n-hexane. A small fragment was mounted on a Philips four-circle diffractometer and preliminary data established that the compound was monoclinic, belonging to space group $P2_1/a$. Unit cell parameters were obtained by a least-squares refinement of 25 carefully determined angular settings. Intensities were then measured, using Mo-Kα radiation, by the θ–2θ scan method in the range $2\theta < 50°$ with a scan rate of 2° min^{-1}. It was soon clear that the compound decomposed under irradiation, and after two days no reflection had a measurable intensity. The recorded intensities, corrected for Lorentz and polarization factors, were used as starting data.

The structure was solved by interpretation of Patterson and difference electron density maps, and refined by least-squares calculations to R 16.5% when it was evident that further efforts to obtain a better convergence would be prevented by the poor quality of the data. Accordingly the crystals, which in the meantime had assumed a powdery appearance, were freshly re-prepared and a new crystal fragment, of approximate dimensions 0.12 × 0.10 × 0.03 mm, was selected for the X-ray work. The fragment was coated with lacquer to prevent deterioration on exposure to air, and mounted on a glass fiber. Unit cell parameters were rapidly re-determined and the new values (Table III), which agree well with the old values, were used to record a new set of data. This time the reflexion sphere was limited to $2\theta < 40°$ in order to reduce the number of high-angle reflexions (most of which had very low intensities), and the recording speed was increased to 4° min^{-1} in order to reduce the total time of irradiation. In this way a set of 955 unique reflections was recorded

TABLE IV. Positional Parameters ($\times 10^4$) and Temperature Factors ($\times 10^3$).

Atom	x	y	z	U
Hg	9419(2)	5159(2)	7362(4)	*
Cl(1)	10096(13)	3705(10)	5752(20)	*
Cl(2)	10835(14)	6120(13)	9300(20)	*
S	7122(12)	5414(12)	6961(23)	*
O	6334(36)	5002(25)	3706(55)	69
N	6715(38)	3683(28)	5280(58)	52
C(1)	6716(42)	4632(32)	5166(67)	38
C(2)	6356(62)	6005(46)	3188(86)	85
C(3)	6019(57)	6173(42)	1325(82)	66
C(4)	6375(48)	3117(37)	3645(72)	50
C(5)	7019(63)	3134(45)	6894(80)	77
H(21)	7176	6263	3502	70
H(22)	5781	6345	3825	70
H(31)	6036	6753	2036	70
H(32)	5464	6277	284	70
H(33)	6839	6042	1035	70
H(41)	6329	2480	4175	70
H(42)	6970	3096	2827	70
H(43)	5575	3291	3060	70
H(51)	7215	3589	7831	70
H(52)	7722	2715	6799	70
H(53)	6320	2738	7109	70

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	41	82	70	−4	−5	−10
Cl(1)	69	58	52	13	21	−1
Cl(2)	68	116	45	−28	−4	−2
S	18	90	88	14	5	−10

*Anisotropic thermal parameters in the form:
$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$

TABLE V. Distances (Å) and Angles (Deg).

(a) Bond Distances

Hg–Cl(1)	2.47(1)	O–C(2)	1.40(7)
Hg–Cl(2)	2.38(2)	C(2)–C(3)	1.46(9)
Hg–S	2.47(1)	C(1)–N	1.28(6)
S–C(1)	1.75(6)	N–C(4)	1.48(7)
C(1)–O	1.25(7)	N–C(5)	1.45(8)

(b) Contact distances*

Hg···C(1^{i})	2.94
Hg···C(2^{ii})	3.13

(c) Angles*

Cl(1)–Hg–C(2)	122.7(7)	Hg–S–C(1)	100(2)
Cl(1)–Hg–S	113.3(6)	S–C(1)–O	120(4)
Cl(2)–Hg–S	123.8(7)	S–C(1)–N	123(5)
Cl(1)–Hg–Cl(1^{i})	84.7(4)	O–C(1)–N	117(5)
Cl(2)–Hg–Cl(1^{i})	94.0(5)	C(1)–O–C(2)	128(5)
S–Hg–Cl(1^{i})	95.6(5)	O–C(2)–C(3)	115(6)
Cl(1)–Hg–Cl(2^{ii})	92.3(5)	C(1)–N–C(4)	117(5)
Cl(2)–Hg–Cl(2^{ii})	83.9(5)	C(1)–N–C(5)	124(5)
S–Hg–Cl(2^{ii})	89.7(5)	C(4)–N–C(5)	119(5)

*None	x	y	z
i	2 − x	1 − y	1 − z
ii	2 − x	1 − y	2 − z

in about 8 hr. During this time the intensities of two reference reflections, measured at intervals of 100 reflections, gradually declined to 70% of their starting values.

Refinement of atom parameters using these data converged to the final R of 9.9% when the maximum coordinate shift was less than one half of the corresponding e.s.d. Only the six non-hydrogen-non-carbon atoms were refined anisotropically in order to reduce the number of variables. The hydrogen atoms were assigned physically reasonable parameters and their contributions were included in structure factor calculations. The quantity minimized was $\Sigma w\Delta F^2$, where $w = 1.3168/(\sigma^2(F) + 0.008696\ F^2)$. A final difference Fourier synthesis showed some electron density residuals around the Hg positions, too near to mercury to have any reasonable chemical significance and probably due to series termination effects, even if some sort of disorder due to crystal decomposition cannot be excluded. An attempt to obtain a better $F_o - F_c$ agreement using in the refinement intensities corrected on the basis of the loss of intensity of the reference reflections gave no appreciable improvement.

Scattering factors for Hg were from Cromer and Waber [5], those for Cl, S, O, N, C from Cromer and Mann [6], and for hydrogen from International Tables for X-ray Crystallography [7]. The mercury scattering factor was corrected for anomalous dispersion with constant average values $\Delta f' = -2.74$ and $\Delta f'' = 9.28$ for the real and imaginary components. All calculations were done using the SHELX and the X-ray 72 program systems [8]. Final atomic positional and thermal parameters are listed in Table IV. Bond distances and angles and relevant contact distances are reported in Table V. Least squares planes are given in Table VI. Preliminary data show that $Hg(DMTC)Br_2$ is not isomorphous with the chloroderivative.

Description of the Structure

From Fig. 1, in which the conformation of the molecule is displayed together with the numbering scheme, and Fig. 2, in which the unit cell content is projected along the c axis of the cell, it can be seen that the 1:1 addition compound between $HgCl_2$ and the monodentate donor has an extended structure in which mercury achieves effective five-coordination in the approximately trigonal bipyramidal geometry.

TABLE VI. Least Squares Planes and Distances (A) of Atoms from the Planes. Equation of the plane is Ax + By + Cz = D, referred to monoclinic coordinates.

Plane I: Cl(1), Cl(2), S
$2.25x + 8.18y - 6.04z = 1.83$ A
[Hg* 0.06]

Plane II: S, C(1), O, N
$10.48x + 0.01y - 2.53z = 5.71$ A
[S −0.001, C(1) 0.02, O −0.01, N −0.01, C(2)* 0.15, C(3)* 0.26, C(4)* 0.05, C(5)* −0.10]

Plane III: C(1), N, C(4), C(5)
$10.60x - 0.28y - 2.10z = 5.90$ A
[C(1) 0.00, N 0.00, C(4) 0.00, C(5) 0.00, O(1)* −0.11]

Plane IV: O, C(2), C(3)
$10.57x - 1.28y - 2.03z = 5.30$ A
[N* 0.25, C(1)* 0.16]

Angles between the planes (°)

I–II	68.4	II–III	3.6
I–III	71.8	II–IV	6.7
I–IV	75.0	III–IV	4.3

*These atoms were not used in the plane calculations.

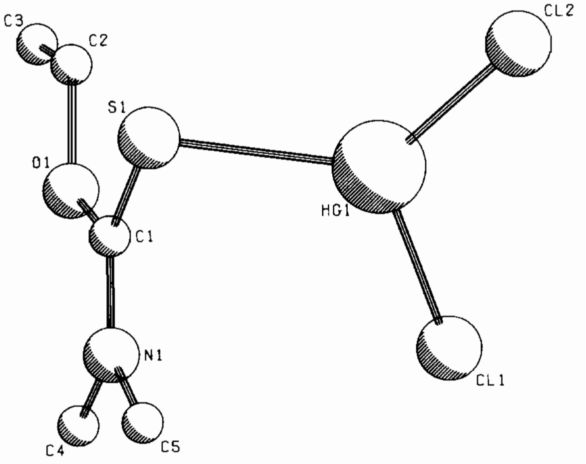


Fig. 1. Bonding and labelling scheme in the DMTC·$HgCl_2$ unit.

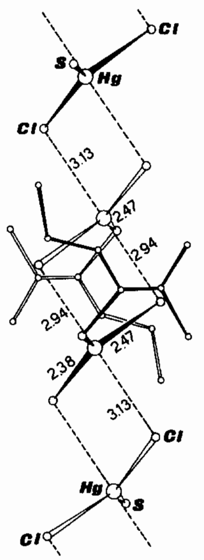


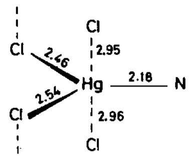
Fig. 2. Projection down *c* of the molecular arrangement.

The crystallographic evidence makes it clear that the adduct is formed of $HgCl_2L$ groups in which there is relatively strong binding of the components, linked together by comparatively weak chlorine bridges, so that the general formulation $(HgCl_2L)_n$ can be given. The mercury atom is quasi coplanar with the three atoms forming the equatorial plane, being displaced by only 0.06 Å from this plane toward $Cl(1^i)$.

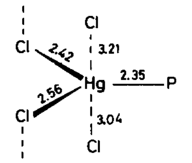
The Cl(1)–Hg–S bond angle (113°) is about 10° smaller than the Cl(2)–Hg–S and Cl(1)–Hg–Cl(2) angles, but even larger distortions from the idealized geometry are commonly observed in other Hg compounds, distortions which are probably due to the influence of the packing forces in the crystal.

Although the expected value from the sum of the covalent radii is 2.47 Å [9], a survey of the literature indicates that most Hg–Cl bond distances are in the range 2.28–2.33 Å, irrespective of the coordination number at mercury, and that longer Hg–Cl bond distances are always found in compounds where the chlorine atoms are bridging, or hydrogen bonded, or weakly bonded in polymeric structures, (*i.e.* wherever they are involved in some type of additional interaction). On this basis, the values found in this study seem to be reasonable if one takes into account that the shorter Hg–Cl(2) bond (2.38 Å) is associated with the weaker Cl(2)···Hg contact (3.13 Å), while the longer Hg–Cl(1) bond is associated with the relatively stronger Cl(1)···Hg contact (2.94 Å). Comparison among similar structures with mercury having an effective five-coordination (Table VII) shows that the observed asymmetry of the Hg–Cl bond lengths is systematic. The Hg–S distance (2.47 Å) appears somewhat longer than those usually reported for five-coordinated complexes and approaches the values of 2.45 and 2.43 Å found in $HgCl_2$(O-Ethylthiocarbamate$)_2$, where the sulphur donor ligand is very similar to DMTC and where mercury is four coordinated. Apart from the terminal

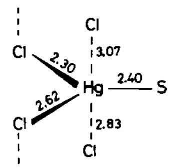
TABLE VII. Bond Lengths in Some Complexes Having Mercury in Effective Five-Coordination.



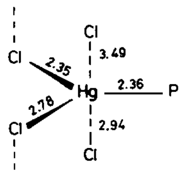
2,4,6-Trimethylpyridine. $HgCl_2$ [10]



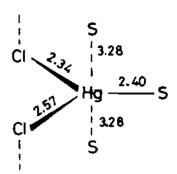
Triethylphosphine. $HgCl_2$ [11]



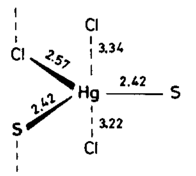
Tetrahydrothiophen. $HgCl_2$ [12]



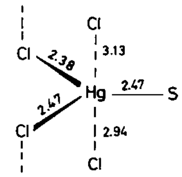
Trimethylphosphine. $HgCl_2$ [11]



Dehydrodithizone. $HgCl_2$ [13]



2 Thiourea. $HgCl_2$ [14]



DMTC. $HgCl_2$ [THIS WORK]

ethyl chain the six atoms of the organic ligand roughly lie in a plane inclined by about 70° with respect to the $HgCl_2$ plane. The N, C(1), C(4), and C(5) atoms are strictly coplanar and this plane is inclined by 3.6° to the S, C(1), O, N plane. Distances and angles in the ligand are normal.

Results and Discussion

The analytical data of the compounds prepared are reported in Table I. The IR spectra (Table II) are consistent with coordination through the sulfur atom; the stretching frequency of the C–N bond, at 1535 cm^{-1} in free DMTC, shifts to higher values in all the adducts, as observed in the sulfur bonded palladium and platinum derivatives [1]. The shift increases with the electronegativity of the halogen, as already found in the series $Hg(MTC)_2X_2$ (X = Cl, Br, I) [3] and $HgLX_2$ (X = Cl, Br, I; L = N,N-dialkyldithiocarbamate ester) [15]. In addition the ν(C–S), at 865 cm^{-1} in DMTC, moves slightly to lower wavenumbers in the complexes. In the far IR region the ν(Hg–X) appears as a broad band at 280 cm^{-1} (X = Cl), 192 cm^{-1} (X = Br) and 156 cm^{-1} (X = I), whereas the broad absorption around 240 cm^{-1} in the three complexes should be assigned as ν(Hg–S). The metal–halogen bands coincide with those reported for the 1:1 adducts with the dithiocarbamate esters [15]; the X-ray data for $HgCl_2 \cdot (CH_2)_4N\text{-}CS\text{-}SCH_3$ [16] suggests a dimeric structure held by chlorine bridges, with a distorted tetrahedral arrangement around each mercury atom bonded by one sulfur and three chlorine atoms.

The behaviour of the complexes in benzene and in acetone has been examined by osmometric and ^1H NMR (Table I) measurements. In benzene the van t'Hoff *i* values (at the molar concentration in parentheses) are for $Hg(DMTC)Cl_2$: 0.73(2.0 × 10^{-2}); 0.84(1.0 × 10^{-2}; 0.95(0.5 × 10^{-2}); 1.14 (0.25 × 10^{-2}); and for $Hg(DMTC)Br_2$: 0.78(2.7 × 10^{-2}); 0.93(1.38 × 10^{-2}); 1.11(0.69 × 10^{-2}); 1.30 (0.34 × 10^{-2}). When dissolved in benzene $Hg(DMTC)I_2$ separates HgI_2; the yellow solution contains probably the complex stabilized by an excess of ligand. The ^1H NMR data for the chloro- and bromo-complex in the same solvent (Table I) are indicative of ligand releasing. In fact free DMTC shows in benzene two singlets for the $N(CH_3)_2$ protons, at 2.45 and 2.97 ppm, owing to the hindered rotation about the C–N bond; the O–CH_2–CH_3 quadruplet is at 4.43 ppm, and the CH_3 triplet at 1.03 ppm ([1] and refs. therein). On complexing through the sulfur atom the double bond character of the C–N bond is enhanced, leading to a different magnetic environment for the protons of the methyl $N(CH_3)_2$ groups in *syn* and *anti* position with respect to the C–S group. At the same time the CH_2 signal shifts downfield in respect to the free ligand. For instance in *trans*-$Pt(DMTC)_2Cl_2$ the $N(CH_3)_2$ singlet separation is 0.96 ppm (0.52 in DMTC), and the CH_2 resonance is at 4.93 ppm. The ^1H NMR spectra of $Hg(DMTC)X_2$ (X = Cl, Br) in benzene present the two broad $N(CH_3)_2$ singlets 0.45 ppm apart and slightly downfield with respect to the free ligand; the CH_2 proton signal is not shifted. The ^1H NMR and osmometric data suggest that the long polymeric chain structure is broken in benzene, with concomitant release of ligand. Mercuric chloride and bromide are self-associated in benzene [17], giving dimeric species which can also form weak complexes with aromatic hydrocarbons [18]. From the above considerations, the data in benzene can be interpreted by the formation of dimeric species, similar to that given in ref. [16], partly dissociated to give mercuric chloride and free ligand.

The *i* values in acetone, where the three complexes behave as non-electrolytes, are for $Hg(DMTC)Cl_2$: 1.60(1.35×10^{-2}); 1.67(0.68×10^{-2}); 1.75(0.34×10^{-2}); and for $Hg(DMTC)Br_2$: 1.54(1.28×10^{-2}); 1.67 (0.64×10^{-2}); 1.86(0.32×10^{-2}). In addition the broad ^1H NMR signals indicate that in this solvent a large amount of free ligand is also present. In acetone $HgCl_2$ is slightly associated ($i \cong 0.9$ for a 1×10^{-2} *M* solution) and the complex $Hg(MTC)Cl_2$ behaves as a monomer [3]. It can be supposed that the polymer breaks in acetone giving the monomeric species, in equilibrium with the starting reagents.

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