

COMPLEXES OF *N,N*-DIALKYL-DITHIOCARBAMATE ESTERS WITH MERCURY(II) DIHALIDES

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Reaction between mercury(II) dihalides (HgX_2) with *N,N*-dialkyldithiocarbamate esters [$\text{R}'(\text{R}_2\text{dtc})$] in organic solvents has resulted in the synthesis of complexes with the formula $\text{HgX}_2[\text{R}'(\text{R}_2\text{dtc})]$. On the basis of several physical measurements, including IR, Raman and PMR spectra, it is suggested that in these complexes mercury is three-co-ordinated by two halogens and one sulfur atom.

Introduction

In preceding papers¹⁻⁴ the preparation, properties and structure of *N,N,N'*, *N'*-tetra-alkylthiuram disulfide complexes with Zn(II), Cd(II) and Hg(II) dihalides were reported. The thiuram disulfides [$\text{R}_2\text{NC}(\text{S})\text{SS}(\text{S})\text{CNR}_2$] act as bidentate ligands, co-ordinating *via* the two terminal sulfur atoms. This study deals with the complexes of mercury(II) dihalides with *N,N*-dialkyldithiocarbamate esters [$\text{R}'(\text{R}_2\text{dtc})$, R' is the ester group]. As thiuram disulfide (which is not an ester in the proper sense of the word) can be written as $\text{R}'(\text{R}_2\text{dtc})$ with $\text{R}' = \text{R}_2\text{dtc}$, the relation of this study with the aforementioned papers will be evident. The esters reported here, however, possess only one terminal sulfur atom. For R an alkyl group is always substituted, R' is varied in size (steric effect) and in electronic properties (electronic effect). The structure of the complexes is mainly discussed on the basis of IR, Raman and PMR spectroscopic data.

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¹ H. C. Brinkhoff, J. A. Cras, J. J. Steggerda and J. Willemse, *Rec. Trav. Chim.*, **88**, 633 (1969).

² H. C. Brinkhoff, A. M. Grotens and J. J. Steggerda, *ibid.*, **89**, 11 (1970).

³ H. C. Brinkhoff, Thesis, Nijmegen 1970.

⁴ P. T. Beurskens, J. A. Cras, J. H. Noordik and A. M. Spruyt, *J. Mol. Cryst. Struct.* **1**, 93 (1971).

Results and discussion

When $R'(R_2\text{dtc})$ is reacted with $\text{HgX}_2 \dots X = \text{Cl, Br or I}$, complexes with the stoichiometric formula $\text{HgX}_2[R'(R_2\text{dtc})]$ are obtained, independent of the substituted group R' (Table I). Most of the complexes studied are with *N,N*-dimethyldithiocarbamate esters [$R'(\text{Me}_2\text{dtc})$] as several ethyl and *n*-butyl derivatives failed to give crystalline products. A disadvantage of the $R'(\text{Me}_2\text{dtc})$ complexes, however, is their low solubility in organic solvents. Therefore, molecular weight determinations and PMR recordings are restricted to very few complexes.

Table I

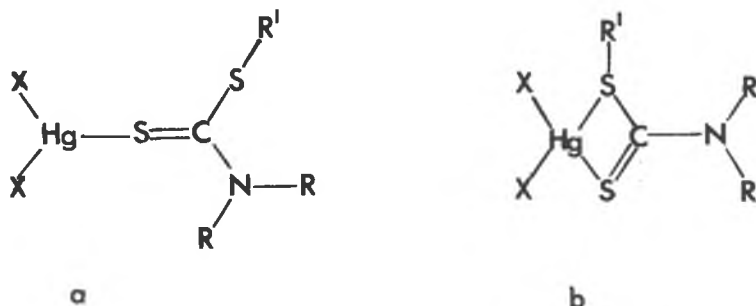
$\nu(\text{C}=\text{N})^*$ in $R'(R_2\text{dtc})$ and their complexes with HgX_2 .

R	$R'(\text{Me}_2\text{dtc})$	$\text{HgX}_2[R'(\text{Me}_2\text{dtc})]$		
		X		
		Cl	Br	I
$-\text{CH}_3$	1502	1541	1534	1529 cm^{-1}
$-\text{CH}_2-\text{CH}_3$	1494	1541	1536	1525
$-\text{CH}_2\text{-phenyl}$	1490	1533	1529	1518
$\text{CH}_2-\text{C}(\text{O})\text{-phenyl}$	1500	1536	1528	1526
$-\text{CH}_2\text{C}(\text{O})-\text{CH}_3$	1495			1525
$-\text{CH}_2\text{C}\equiv\text{N}$	1503			1536
	$R'(\text{Et}_2\text{dtc})$	$\text{HgX}_2[R'(\text{Et}_2\text{dtc})]$		
$-\text{CH}_3$	1493			1512
$-\text{CH}_2-\text{C}(\text{O})\text{-phenyl}$	1495	1523	1520	1516


* All these frequencies were calibrated on the band at 1602 cm^{-1} of polystyrene.

Physical measurements. Electrical conductivity measurements in nitrobenzene all showed the complexes, as far as they are soluble, to be non-electrolytes. This is in accordance with the insolubility of these compounds in aqueous solution. Molecular weight determinations in benzene solution point to a monomeric structure of $\text{HgI}_2[\text{Me}(\text{Et}_2\text{dtc})]$. The mass spectrum of $\text{HgI}_2[\text{Me}(\text{Me}_2\text{dtc})]$ shows as fragment ion with highest mass that of the monomer (at 75° , using 70 eV-ionizing electrons) and thus gives additional evidence for the monomeric structure of the complexes. The com-


bined data suggest two possible structures which are illustrated in Fig. 1.*



IR and Raman spectra. Comparing the IR spectra ($4000\text{--}700\text{ cm}^{-1}$) of the free and coordinated dithiocarbamate ester, two significant differences are noted. Firstly the $\text{C}=\text{N}$ stretching band near 1500 cm^{-1} (characteristic for dithiocarbamates) shifts to a higher wavenumber on complex formation (Table I), indicating a higher $\text{C}=\text{N}$ bond order (π -bond order). It is noteworthy that as a function of halogen $\nu(\text{C}=\text{N})$ decreases in the sequence $\text{Cl} > \text{Br} > \text{I}$ according to the order of electronegativity. Secondly, remarkable changes are observed in the region of 950 cm^{-1} . For the *N,N*-dimethyldithiocarbamate esters a broad and intense band is present in this region. Upon complex formation this band is often split up into a number of bands while also intensity changes are observed. Moreover, this band(s) shifts to a slightly lower wavenumber. Since vibrational modes wherein $(\text{C}=\text{S})$ contributes to a considerable extent, are known to absorb in this region^{5,6}, these phenomena afford evidence for complex formation by means of the terminal sulfur atom. In fact, the latter could be expected on the basis of the similarity between the esters and thiuram disulfide.

In some of the esters R' contains a functional group e.g. if R' is $-\text{CH}_2-\text{C}(\text{O})-$  or $-\text{CH}_2-\text{CN}$. The reported functional groups, are, however, not linked* to the mercury atom as appeared from $\nu(\text{C}=\text{O})$ and $\nu(\text{C}\equiv\text{N})$ values.

* Structures wherein the nitrogen atom is coordinated to mercury must be rejected on the basis of the strong, positive mesomeric effect of the $-\text{NR}_2$ group. In this respect the $\nu(\text{C}=\text{N})$ data (Table I) are of conclusive evidence.




* As a preliminary result of a study of $\text{Pd}(\text{II})$ complexes with dithiocarbamate esters it is of interest that upon reaction of K_2PdCl_4 with $\text{Me}_2\text{N}-\text{CS}(\text{S})-\text{C}^*\text{H}_2-\text{C}(\text{O})-$  the ester is deprotonated by removing a proton from the α -carbon atom. In this case the ligand coordinates by means of the $\text{C}=\text{S}$ sulfur atom as well as by the $\text{C}=\text{O}$ oxygen atom.

⁵ M. L. Shankaranarayana and C. C. Patel, Spectrochim. Acta, **21**, 95 (1965).


⁶ H. C. Brinkhoff and A. M. Grotens, Rec. Trav. Chim., **90**, 252 (1971).

Table II

Raman spectral data.

R' \	HgX ₂ [R'(Me ₂ dtc)]			HgX ₂ [R'(Me ₂ dtc)]		
	X = Cl	Br	I	(Hg - S)	cm ⁻¹	
-CH ₃	280*	195	155	255	240	220
-CH ₂ -CH ₃	280*	195	155	235	230	225
-CH ₂ - 	290*	180	155	250	240	215
-CH ₂ -C(O)-			140			
- 	280*	195	155	230	225	215
		HgX ₂ [R'(Et ₂ dtc)]			HgX ₂ [R'(Et ₂ dtc)]	
-CH ₂ -C(O)-						
- 	280*	170	130	255	235	220

* These values correspond with those found in the IR spectra.

Observing the IR spectra in the region of 700-200 cm⁻¹ we were only able to assign $\nu(\text{Hg} - \text{Cl})$, as $\nu(\text{Hg} - \text{Br})$ and $\nu(\text{Hg} - \text{I})$ are usually known to absorb below 200 cm⁻¹. Raman spectra give more information as with $\nu(\text{Hg} - \text{Cl})$ also $\nu(\text{Hg} - \text{Br})$, $\nu(\text{Hg} - \text{I})$ and $\nu(\text{Hg} - \text{S})$ can be assigned (Table II). In spite of the fact that the local point symmetry of the complexes is C_{2v} or lower, we observed only one Hg-halogen stretching vibrational band. Apparently, the symmetric and asymmetric stretching absorption bands overlap each other. The latter and the tabulated $\nu(\text{Hg} - \text{Cl})$ values correspond well with those of the related thiuram disulfide complexes³ and point therefore to terminal bonded halogens. In the Raman spectra a band near 235 cm⁻¹ is always observed which is absent in the spectra of the dithiocarbamate esters and which cannot be ascribed to Hg-halogen vibrational modes. It appeared that the frequency decreases as a function of halogen in the order Cl > Br > I. The combined data afford evidence for the assignment of this band (which is too weak to be observed in the IR spectrum) to $\nu(\text{Hg} - \text{S})$, with sulfur being the terminal sulfur atom (C = S) of the dithiocarbamate ester. The finding of only one $\nu(\text{Hg} - \text{S})$ might suggest structure 1a rather than 1b. The latter seems to be supported by the fact that even when R' has an electron-withdrawing character (e.g. when R' is -CH₂-C(O)- or CH₂-CN) only one ligand is co-

ordinated to the mercury atom. As the coordinating capacity of the R'-S sulfur atom must then be thought negligible, structure 1a is probable. The non-coordination by the R'-S sulfur atom, previously indicated in rhodanine complexes⁷ gives support in this respect.

PMR spectra. Previous studies on R'(R₂dtc)^{8,9} indicated that hindered rotation around the C=N bond can be observed by PMR, showing two different proton resonances for the *N*-bonded alkyl groups. The infrared data (*vide infra*) undoubtedly indicate a higher C=N π -bond order upon complex formation. So the barrier to internal rotation around the C=N bond will increase upon coordination of the ester with HgX₂. The PMR spectra of Me(Et₂dtc) and HgI₂[Me(Et₂dtc)] are illustrated in Fig. 2.

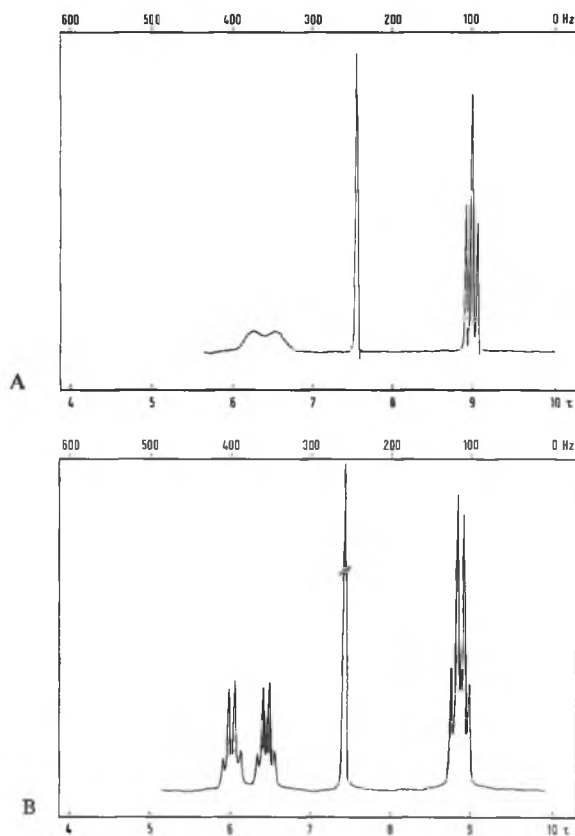


Fig. 2. PMR spectra of Me(Et₂dtc) (A) and HgI₂[Me(Et₂dtc)] (B), recorded in bromobenzene at 30°.

⁷ F. G. Moers and J. P. Langhout, *ibid.*, **89**, 1237 (1970).


⁸ C. E. Holloway and M. H. Gitlitz, *J. Can. Chem.*, **45**, 2659 (1967).

⁹ J. L. Richards, D. S. Tarbell and E. H. Hoffmeister, *Tetrah.*, **24**, 6485 (1968).

As regards a definite conclusion about the structure of the mercury complexes, the τ -values of the proton resonances of the ester group are of importance. A survey of the limited data is given in Table III. Upon complex formation of the ester with HgI_2 a downfield shift of 0.10 p.p.m. or less is noticed for the CH_3-S or CH_2-S proton resonances. If the CH_3-S (the coordinating capacity of this sulfur atom is relatively strong due to the positive inductive effect of the methyl group) or $-\text{CH}_2-\text{S}$ sulfur atoms were coordinated to the mercury atom a shift of the order of 0.6 p.p.m. would be expected¹⁰. Therefore, it is believed that mercury in these complexes is three-coordinated. The small downfield shift of $\tau\text{CH}_3-\text{S}$ as just

Table III
100 MHz PMR spectral data, recorded at 30°.

	$\tau(\text{CH}_x-\text{S}) \dots x = 2,3$	$\tau(\text{N}-\text{CH}_2)$		$\tau(\text{N}-\text{C}-\text{CH}_3)$		solvent
		I	II	I	(I+II) II	
$\text{Me}(\text{Et}_2\text{dtc})$	7.50 ^a	6.25 ^d	6.52 ^d	8.98 ^c		bromo- benzene ^e
$\text{HgI}_2[\text{Me}(\text{Et}_2\text{dtc})]$	7.40 ^a	6.00 ^b	6.42 ^b	8.80 ^c	8.87 ^c	bromo- benzene ^e
$\text{Phe}(\text{Et}_2\text{dtc})^g$	4.80 ^a	5.72 ^{b,d}	5.92 ^{b,d}	8.43 ^{c,d}	8.48 ^{c,d}	chloro- form ^f
$\text{HgI}_2[\text{Phe}(\text{Et}_2\text{dtc})]^g$	4.70 ^a	5.54 ^b	5.74 ^b	8.23 ^c	8.36 ^c	chloro- form ^f
		$\tau(\text{N}-\text{CH}_3)$				
		$\tau(-\text{CH}_2-\text{S})$				
		I	II			
$\text{Benzyl}(\text{Me}_2\text{dtc})$	5.50 ^a	6.85 ^{a,d}	7.17 ^{a,d}			bromo- benzene ^e
$\text{HgI}_2[\text{Benzyl}(\text{Me}_2\text{dtc})]$	5.49 ^a	6.72 ^a	7.03 ^a			bromo- benzene ^e

The intensity ratio I : II = 1 : 1. a = singlet, b = quartet, c = triplet, d = these signals are broadened by exchange due to rotation around the C=N band, e = TMS is used as internal reference, f = HMDS is used as external reference, g Phe = -C(O)-CH₂-.

¹⁰ N. Dunski and T. H. Crawford, J. Inorg. Nucl. Chem., 31, 2073 (1969).

reported might be ascribed to an enhanced contribution of resonance structure 3a. Furthermore, it is found that the average values of the *N*-alkyl proton resonances undergo a downfield shift upon complex formation. This must be interpreted in terms of a greater contribution of resonance structure 3b.

Summary and concluding remarks. Summarizing the results, it is believed that mercury in the complexes concerned is three-coordinated, as illustrated in Fig. 1a. Then mercury will have sp^2 -hybridized orbitals: so the metal, the two halogens and the terminal sulfur atom of the ester will be situated in one plane. Hence, the unoccupied p_z -orbital of mercury is available for dative π -bonding. In this respect it is noteworthy that $\nu(\text{Hg} - \text{S})$ increases with increasing $\nu(\text{C}=\text{N})$ (as the electronegativity of the halogens increases). Therefore, the shift of $\nu(\text{Hg} - \text{S})$ to a higher wavenumber might be related to a stronger π -bond between the sulfur and mercury atom. Crystallographic studies had already indicated a three-coordination of Hg in $\text{HgI}_3[\text{S}(\text{CH}_3)_3]$ ¹¹ and distorted tetrahedral arrangements around mercury (which can be considered as an intermediate between four- and three-coordination) in $\text{HgI}_4[\text{S}(\text{CH}_3)_3]_2$ and $\text{HgI}_2[\text{Me}_2\text{NC}(\text{S})\text{SS}(\text{S})\text{CNMe}_2]$ ^{12, 4}. These examples underline the probability of three-coordinated mercury in the complexes $\text{HgX}_2[\text{R}'(\text{R}_2\text{dtc})]$.

Another example of three-coordination is probably found in phenylmercury(II) *N,N*-dialkyldithiocarbamates, which compounds are monomeric in benzene solution. The NMR data support this assumption since at temperatures as low as -60° no splitting of the *N*-alkyl proton resonance could be observed in carbon bisulfide solution⁶.

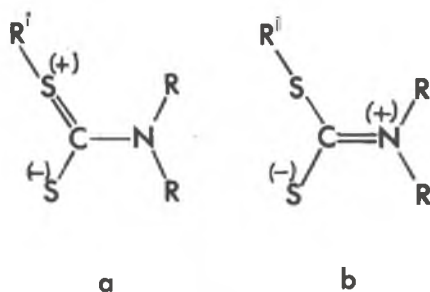


Fig. 3.

¹¹ R. H. Fenn, *Acta Cryst.*, **20**, 20 (1966).

¹² R. H. Fenn, *ibid.*, **20**, 24 (1966).

Experimental part


Electrolytic conductivities were measured with the Metrohm Konduktoskop E 365. Molecular weights were determined using a Hewlett Packard 302 B osmometer. The mass spectrum was recorded on a Varian Atlas SM1B. Infrared spectra in the region of 4000-700 cm^{-1} were measured using a Perkin-Elmer 257 spectrometer. The recording of the spectra in the region of 700-200 cm^{-1} was carried out with a Hitachi EPI-L model. A Cary-81 spectrometer was employed for measuring Raman spectra* with a He-Ne laser. Finally, NMR spectral data were obtained with a Varian HA-100 spectrometer.

The esters were prepared in accordance with the literature^{13, 14}. The general procedure for making the HgCl_2 and HgBr_2 complexes was to add a solution of HgX_2 (1 mole) in ethanol to a solution of the ester (1 mole) in the same solvent. The crystals often separated rapidly. Sometimes addition of petroleum ether was necessary to start crystallization.

When HgI_2 was used a different procedure had to be followed: To a solution of the ester (1 mole) in ether, acetone, chloroform or carbon disulfide an equivalent amount of HgI_2 was added. The mercury diiodide then dissolved by complex formation with the ester. Precipitation of the complex could, if necessary, be facilitated by addition of petroleum ether. The analyses (C, H, N, halogen) of the complexes were in agreement with the theoretical values. Therefore it is sufficient to give the solution from which the compounds are crystallized and the melting points. In illustration of such an analysis we report that of $\text{HgCl}_2[\text{Me}(\text{Me}_2\text{dtc})]$.

Found : C 11.84; H 2.24; N 3.48; Cl 17.32.
Calc. for $\text{HgCl}_2[\text{Me}(\text{Me}_2\text{dtc})]$: C 11.81; H 2.23; N 3.44; Cl 17.43%.

$\text{HgCl}_2[\text{Me}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 121-125°;
 $\text{HgBr}_2[\text{Me}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 114-116°;
 $\text{HgI}_2[\text{Me}(\text{Me}_2\text{dtc})]$, acetone + petroleum ether, m.p. 106-108°;
 $\text{HgCl}_2[\text{Et}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 111-115°;
 $\text{HgI}_2[\text{Et}(\text{Me}_2\text{dtc})]$, acetone + petroleum ether, m.p. 83-87°;
 $\text{HgCl}_2[\text{Benzyl}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 126-128°;
 $\text{HgBr}_2[\text{Benzyl}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 112-116°;
 $\text{HgI}_2[\text{Benzyl}(\text{Me}_2\text{dtc})]$, acetone + petroleum ether, m.p. 104-106°.

Phe =  -C(O)-CH₂-

$\text{HgCl}_2[\text{Phe}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 134-138°;
 $\text{HgBr}_2[\text{Phe}(\text{Me}_2\text{dtc})]$, ethanol, m.p. 130-134°;
 $\text{HgI}_2[\text{Phe}(\text{Me}_2\text{dtc})]$, carbon disulfide, m.p. 107-110°;
 $\text{HgI}_2[\text{acetyl}(\text{Me}_2\text{dtc})]$, ethanol;
 $\text{HgI}_2[\text{NC}-\text{CH}_2(\text{Me}_2\text{dtc})]$, chloroform;
 $\text{HgI}_2[\text{Me}(\text{Et}_2\text{dtc})]$, acetone + petroleum ether, m.p. 97-99°;
 $\text{HgCl}_2[\text{Phe}(\text{Et}_2\text{dtc})]$, ethanol, m.p. 120-122°;
 $\text{HgBr}_2[\text{Phe}(\text{Et}_2\text{dtc})]$, ethanol, m.p. 150-152°;
 $\text{HgI}_2[\text{Phe}(\text{Et}_2\text{dtc})]$, acetone, m.p. 134-135°.

* We gratefully acknowledge the use of this spectrometer from the Department of Organic Chemistry of the University of Leiden.

¹³ C. W. Pluygers, Thesis, Utrecht, 1959.

¹⁴ G. D. Thorn and R. A. Ludwig, 'Dithiocarbamates and related compounds', Elsevier, Amsterdam, 1962.

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