# Bismuth(III) Halide Complexes with Thiocarbamic Esters

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*Bismuth trihalides form with N,N-dimethyl O-ethylthiocarbamate (DMTC) and N-methyl O-ethylthiocarbamate (MTC) the complexes $BiX_3 \cdot 2DMTC$ (X = Cl, Br), $BiX_3 \cdot DMTC$ (X = Br, I), $BiX_3 \cdot 2MTC$ (X = Cl, Br, I) and $BiI_3 \cdot MTC$. The ligands act as sulfur donors towards the bismuth atom. The behaviour of the complexes in deuterated benzene, chloroform, dimethyl sulfoxide and acetone is discussed on the basis of the $^1H$ NMR data.*

## Introduction

Bismuth trihalides are known to coordinate either thiocarbonyl or carbonyl donors giving complexes of various stoichiometries. $BiCl_3$ forms with thiourea a red 1:3 [1, 2] and a yellow 3:7 complex [2]; the crystal structures of both solids show differently coordinated Bi(III) moieties, where cationic and anionic bismuth complexes are present [2], as in $3BiCl_3 \cdot 4TSC$ (TSC = thiosemicarbazide) [3] and $BiCl_3 \cdot 3PhPTU$ (PhPTU = phenylpyridylthiourea) [4]. In the 1:2 $BiCl_3$–ethylenethiourea complex the coordination around the metal is octahedral by two terminal chlorine atoms, two sulfur atoms and two further chlorine atoms, bridging to give an infinite chain [3], whereas in $BiCl_3 \cdot 2L$, (L = 1-allyl-3-(2-pyridyl)thiourea [5] and 1,3-dimethyl-2(3H)-imidazolethione [6]), the two bridging chlorine atoms share the same bismuth atoms, giving binuclear complexes. With the last ligand $BiBr_3 \cdot L$ and $BiI_3 \cdot 3L$ have been also isolated [7]. Tetramethyl- and tetraethyldithiooxamide ($Me_4D$ and $Et_4D$) give respectively $BiX_3(Me_4D)_2$, (X = Cl, Br) and $BiX_3 \cdot Et_4D$ (X = Cl, Br, I), whose IR data are consistent with S,S-coordinated ligands [8].

With the oxygen donors, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and tetramethylurea (TMU) the complexes $BiCl_3 \cdot 2L$ (L = DMF, DMA, TMU) and $BiCl_3 \cdot 3L$ (L = DMA, TMU) have been reported [9], whereas benzophenone and its derivatives do not bond through the oxygen atom [10, 11].

Potentially polidentate molecules, containing ethereal or thioethereal groups, coordinate bismuth trihalides by various sites: 2-methyl-benzothiazole acts as a S,N bridging ligand [12], the analogous 2-methyl-benzoxazole acts as O-bonded [13], and in some thiadiazole derivatives the nitrogen atoms seem to be preferred in respect to the ethereal sulfur [14].

As part of a study of the complexing behaviour of bismuth(III) halides towards either carbamic or thiocarbamic esters, of general formula RR'N–CX–OEt (X = O, S), this paper reports the preparation and characterization of the N,N-dimethyl-O-ethylthiocarbamate (DMTC) and N-methyl O-ethylthiocarbamate (MTC) complexes of $BiX_3$ (X = Cl, Br, I).

## Experimental

$BiCl_3$ and $BiBr_3$ (Ventron) were dried *in vacuo* over $P_2O_5$ for several days; $BiI_3$ (C. Erba) was used as supplied. All the operations involving $BiCl_3$ and $BiBr_3$ were carried out in a dry-box under a nitrogen atmosphere. DMTC and MTC were prepared and purified as previously reported [15, 16]. Benzene was distilled under nitrogen from Na; n-hexane from Na/K.

### *Preparation of the Complexes*

The 1:2 adducts of the bismuth halides with both ligands were generally prepared by dissolving the salt in a benzene solution of the ligand (molar ratio $BiX_3$: L varying from 1:4 to 1:7) and by adding n-hexane until precipitation; the 1:1 adducts were obtained from benzene solutions containing a slight excess of ligand, either by cooling or by adding n-hexane. Below is a typical procedure:

#### *$BiBr_3 \cdot 2MTC$ and $BiBr_3 \cdot MTC$*

By adding MTC (≃4 mmol) to a suspension of $BiBr_3$ (1 mmol) in 2 ml of benzene, and orange-yellow solution A and an oily residue B were obtained. The solution A was decanted and treated with n-hexane: an orange oil separated, which slowly

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solidified giving crystals of the 1:2 complex. The residue B was extracted in benzene by gentle heating; crystals of the 1:1 adducts were isolated by addition of n-hexane. The complexes were washed with n-hexane and dried *in vacuo*.

By reaction of $BiI_3$ and DMTC in benzene and subsequent addition of n-hexane, only the 1:1 complex was isolated, also using molar ratios up to 1:10. Attempts to prepare the 1:1 $BiCl_3$ complexes with both ligands by operating at 1:1 molar ratios, gave mixtures of 1:1 and 1:2 adducts.

The complexes $BiX_3 \cdot 2DMTC$ (X = Cl, Br) are soluble in $CHCl_3$, $CH_2Cl_2$ and benzene; $BiX_3 \cdot 2MTC$ and the 1:1 adducts are generally less soluble in those solvents, where the iodo-derivatives decompose releasing ligand molecules and separating a black solid, identified as $BiI_3$. All the complexes dissolve in acetone and dimethyl sulfoxide (DMSO) with a total releasing of the ligands (see $^1H$ NMR data).

*Measurements*

The IR spectra were recorded on a Perkin Elmer Mod. 580 Spectrophotometer (Nujol mulls between CsI discs) in the 4000–350 $cm^{-1}$ region; by a Beckman IR 11 Spectrophotometer (Nujol mulls between polythene plates) in the 400–150 $cm^{-1}$ region. The $^1H$ NMR spectra were registered on a Varian FT 80A NMR Spectrometer.

## Results and Discussion

Differing from the bismuth halides, the prepared complexes (Table I) are stable in the solid state enough to be characterized in air, whereas they decompose in wet solvents. Bismuth chloride and bromide prefer generally to coordinate two DMTC and MTC molecules; $BiI_3$ gives with DMTC the 1:1 adduct only, also if a large excess of ligand is used.

The IR data of all the complexes are consistent with coordination through the sulfur atom. Free DMTC shows a strong band at 1530 $cm^{-1}$ assigned as $\nu$(C–N); a shift to higher frequencies (1570–1580 $cm^{-1}$) has been previously observed in the 1:2 complexes of platinum(II) and palladium(II) halides [15] and in the 1:1 complexes of mercury(II) halides [17]. The crystal structures of a number of those complexes, for instance $[Hg(DMTC)Cl_2]_n$ [17] and *trans*-$Pd(DMTC)_2Cl_2$ [18], confirmed that DMTC acts as sulfur donor. The IR data of the bismuth halide complexes (Table I) present a similar trend. The $\nu$(C–N) of the 1:1 DMTC adducts depends on the halide; in fact it is at 1567 $cm^{-1}$ and 1580 $cm^{-1}$ for the iodo- and bromo-derivative respectively, whereas it is observed at 1595 $cm^{-1}$ for the chloro-derivative, which has been isolated impure for a variable amount of the 1:2 adduct. The $\nu$(C–S), at 865 $cm^{-1}$ in free DMTC, shifts to lower frequencies (5–15 $cm^{-1}$) on coordination (Table I and ref. [15, 17]).

TABLE I. Analytical Data (the calculated values are in parentheses) and Infrared Bands ($cm^{-1}$).

| Compound | Colour | M.p. °C | C% | H% | N% | $\nu$(C–N)[a] | $\nu$(C–S)[a] |
|---|---|---|---|---|---|---|---|
| $BiCl_3 \cdot 2DMTC$[b] | pale yellow | 89–91 | 20.6 (20.6) | 4.1 (3.8) | 4.7 (4.8) | 1565 | 853 |
| $BiBr_3 \cdot 2DMTC$ | golden yellow | 93–4 | 16.9 (16.8) | 3.1 (3.1) | 3.9 (3.9) | 1568 | 855 |
| $BiBr_3 \cdot DMTC$ | greenish yellow | 125–7 | 10.6 (10.3) | 1.9 (1.9) | 2.4 (2.4) | 1580 | 851 |
| $BiI_3 \cdot DMTC$[c] | red-brown | 108–10 | 8.5 (8.3) | 1.6 (1.5) | 1.9 (1.9) | 1567 | 850 |
| | | | | | | $\nu$(N–H)[d] | $\nu$(C–N) + $\delta$(N–H) |
| $BiCl_3 \cdot 2MTC$[e] | golden yellow | 90–2 | 17.2 (17.3) | 3.1 (3.3) | 5.0 (5.1) | 3230 | 1578sh, 1572s, 1515sh |
| $BiBr_3 \cdot 2MTC$ | golden yellow | 103–5 | 14.0 (14.0) | 2.7 (2.6) | 4.1 (4.1) | 3260 | 1582sh, 1572s, 1520sh |
| $BiI_3 \cdot 2MTC$[f] | bright red | 84–5 | 11.6 (11.6) | 2.3 (2.2) | 3.3 (3.4) | 3300 | 1579s, 1560shs |
| $BiI_3 \cdot MTC$ | red-violet | 113–4 | 6.9 (6.8) | 1.6 (1.3) | 1.9 (2.0) | 3310 | 1572s |

[a]Strong bands. [b]Cl%, 18.2(18.3). [c]I%, 51.9(52.7). [d]Medium bands. [e]Cl%, 19.3(19.2). [f]I%, 45.5(46.0).

The IR spectrum of free MTC presents a broad $\nu$(N–H) band at 3280 $cm^{-1}$ and a strong absorption at 1535 $cm^{-1}$, assigned as mainly $\nu$(C–N) with a small $\nu$(N–H) contribution, in accordance with analogous thioamides [19, 20]; the weak band at 3070 $cm^{-1}$ is a $\nu$(C–N) overtone. The $\nu$(N–H) in $BiX_3 \cdot 2MTC$ (Table I) depends on the halogen, as previously found in $HgX_2 \cdot 2MTC$ (X = Cl, 3210 $cm^{-1}$; Br, 3230 $cm^{-1}$; I, 3260 $cm^{-1}$) [21]; the trend in both series indicates a decreasing of the hydrogen bond strength in the order Cl > Br > I. Hydrogen bonds do not involve halide ions; in fact in complexes of the type $[M(MTC)_4]X_2$ (M = Pd, Pt; X = Cl, Br) [16, 22] and $[M(TC)_4]X_2$ (M = Pd, Pt; X = Cl, Br; TC = ethylthiocarbamate) [23], where the halide ions are held by a network of hydrogens, the $\nu$(N–H) appear as broad bands centered at about 2950 $cm^{-1}$. The three bismuth adducts present a very weak absorption at around 3120–3150 $cm^{-1}$, which is probably an overtone of the strong $\nu$(C–N) band (1570–1580 $cm^{-1}$, Table I). The band assignable as $\nu$(C–S) is at 713 $cm^{-1}$ in $BiX_3 \cdot 2MTC$ (X = Cl, Br), at 708 $cm^{-1}$ in $BiI_3 \cdot 2MTC$ and at 712 $cm^{-1}$ in $BiI_3 \cdot MTC$.

The far IR absorptions, tentatively assigned as $\nu$(Bi–X), are respectively, for $BiCl_3 \cdot 2DMTC$: 250sh, 273s $cm^{-1}$; $BiCl_3 \cdot 2MTC$: 280sh, 264s; $BiBr_3 \cdot 2DMTC$: 180m, 165ms; $BiBr_3 \cdot 2MTC$: 175sh, 164ms; $BiBr_3 \cdot DMTC$: 226ms, 180sbr. The values are generally in accordance with those reported in the literature for bismuth halide complexes with oxygen, nitrogen and sulfur donors [8, 9, 24–26]. In the palladium and platinum complexes previously studied the metal–sulfur bands were weak and broad; in the bismuth complexes one or two weak absorptions, at 300 and 275 $cm^{-1}$, are generally present, which should be assigned as $\nu$(Bi–S) [26].

The $^1H$ NMR data for DMTC and complexes in various deuterated solvents are reported in Table II; the DMTC spectra consist of a quadruplet (4.4–4.5 ppm) and a triplet (1.0–1.3 ppm) both due to the ethyl group protons, and of two singlets for the $N(CH_3)_2$ protons, owing to the hindered rotation about the C–N bond ([15, 17] and ref. therein). When the molecule coordinates through the sulfur atom, the double bond character of the C–N bond is enhanced; in the spectra of the complexes a larger separation of the $N(CH_3)_2$ singlets and a downfield shift of the $CH_2$ quadruplet is observed. The spectra of $BiX_3 \cdot 2DMTC$ (X = Cl, Br) and $BiBr_3 \cdot DMTC$ in $d_6$-benzene consist of sharp signals, whose position is indicative of coordinated DMTC, as in the adducts of palladium(II) and platinum(II) halides [15]; the complexes $[Hg(DMTC)X_2]_n$ (X = Cl, Br) show broad resonances, due to an equilibrium between complexed and free ligand [17]. When dissolved in $d_6$-benzene, $BiI_3 \cdot DMTC$ decomposes immediately to form solid $BiI_3$; the colourless solution contains free DMTC only, and no decomposition peak is observed in the $^1H$ NMR spectrum. This behaviour confirms the tendency of the iodo-derivatives to attain low coordination numbers and to easily release ligand molecules, as previously observed in the palladium and mercury complexes. In $d_6$-DMSO and $d_6$-acetone all the complexes release totally the ligand: the data for the bromo-derivatives (Table II) clearly indicate a cleavage of the bismuth–sulfur bond by these

TABLE II. $^1H$ NMR Spectra of DMTC and Complexes (t ≃ 27 °C; the chemical shifts are in ppm).

| Compound | Solvent | $N(CH_3)_2$ | $O-CH_2-CH_3$ | $O-CH_2-CH_3$ |
|---|---|---|---|---|
| DMTC | $d_6$-benzene | 2.45–2.97 | 4.43 | 1.03 |
| $BiCl_3 \cdot 2DMTC$ | $d_6$-benzene | 2.70–3.31 | 4.67 | 1.10 |
| $BiBr_3 \cdot 2DMTC$ | $d_6$-benzene | 2.69–3.31 | 4.65 | 1.12 |
| $BiBr_3 \cdot DMTC$ | $d_6$-benzene | 2.50–3.19 | 4.50 | 1.04 |
| $BiI_3 \cdot DMTC$[a] | $d_6$-benzene | 2.37–2.94 | 4.40 | 0.99 |
| $BiBr_3 \cdot 2DMTC$[b] | $d_6$-benzene + one drop $d_6$-DMSO | 2.56–3.06 | 4.42 | 1.03 |
| DMTC | $d_6$-DMSO | 3.10–3.29 | 4.54 | 1.25 |
| $BiBr_3 \cdot 2DMTC$[c] | $d_6$-DMSO | 3.12–3.28 | 4.42 | 1.26 |
| DMTC | $d_6$-acetone | 3.12–3.29 | 4.43 | 1.29 |
| $BiBr_3 \cdot DMTC$ | $d_6$-acetone | 3.15–3.34 | 4.46 | 1.31 |
| $BiBr_3 \cdot 2DMTC$ | $d_6$-acetone | 3.22–3.42 | 4.47 | 1.32 |
| DMTC | $CDCl_3$ | 3.11–3.36 | 4.50 | 1.34 |
| $BiCl_3 \cdot 2DMTC$ | $CDCl_3$ | 3.46–3.69 | 4.69 | 1.44 |
| $BiBr_3 \cdot 2DMTC$ | $CDCl_3$ | 3.50–3.69 | 4.66 | 1.44 |
| $BiBr_3 \cdot DMTC$ | $CDCl_3$ | 3.51–3.69 | 4.77 | 1.44 |

[a]The complex decomposes to $BiI_3$ (insoluble) giving a colourless solution. [b]By addition of one drop of $d_6$-DMSO to the yellow $d_6$-benzene solution a white precipitate is formed, which dissolves on shaking giving a colourless solution. [c]Colourless solution.

TABLE III. $^1$H NMR Spectra of MTC and Complexes (t ≃ 27 °C; the chemical shifts are in ppm).

| Compound | Solvent | N–$CH_3$ | O–$CH_2$–$CH_3$ | O–$CH_2$–$CH_3$ | N–H |
|---|---|---|---|---|---|
| MTC | $d_6$-benzene | 2.17<br>2.59 (67%) | 4.40 | 1.00w<br>1.03s | 6.8w<br>5.4s |
| $BiCl_3$·2MTC | $d_6$-benzene | 2.55s<br>2.60w | 4.29s<br>4.40w | 0.87s<br>1.04w | 8.5s<br>5.1w |
| $BiBr_3$·2MTC | $d_6$-benzene | 2.52s<br>2.59w | 4.29s<br>4.42w | 0.94s<br>1.04w | 8.3<br>5.2 |
| $BiI_3$·2MTC[a] | $d_6$-benzene | 2.29br<br>2.54 (≃55%) | 4.30<br>4.40 | 0.91<br>1.01 | 6.2<br>5.1 |
| MTC | $CDCl_3$ | 2.87<br>3.08 (64%) | 4.56w<br>4.50s | 1.37w<br>1.30s | 7.1w<br>6.5s |
| $BiCl_3$·2MTC | $CDCl_3$ | 3.16 | 4.67[b] | 1.50[b] | 8.6s[b] |
| $BiBr_3$·2MTC | $CDCl_3$ | 3.21 | 4.72s<br>4.54vw | 1.52s<br>1.36vw | 8.3s<br>6.4vw |
| $BiI_3$·2MTC[a] | $CDCl_3$ | 2.97br<br>3.15 (62%) | 4.60w<br>4.52s | 1.45w<br>1.37s | 6.8w<br>6.1s |
| MTC | $d_6$-DMSO | 2.66<br>2.82 (75%) | 4.41w<br>4.36s | 1.24w<br>1.21s | 8.9 |
| $BiBr_3$·2MTC | $d_6$-DMSO | 2.68w<br>2.87s | 4.44w<br>4.40s | 1.29w<br>1.23s | 8.9 |

[a]The complex decomposes giving a black solid and an orange solution. [b]Very weak free ligand signals are also observed; the NH resonance is at 6.5 ppm (≃8%; 8 mg of complex in 0.5 ml of solvent).

solvents, both oxygen donors towards bismuth [24]. If one drop of $d_6$-DMSO is added to a $d_6$-benzene solution of $BiBr_3$·2DMTC, a colourless solution is obtained; the chemical shift values confirm that DMSO replaces all the ligand molecules as found for $M(DMTC)X_2$ solutions (M = Pd, Pt; X = Cl, Br) [27], where DMSO acts as sulfur donor. By gradually adding $d_6$-acetone to a $d_6$-benzene solution of $BiBr_3$·2DMTC, two series of resonances, due to coordinated and free DMTC, are observed; the total displacement of the ligand is attained for $d_6$-benzene/$d_6$-acetone mixtures about 1:1 in volume. The behaviour of the complexes in $CDCl_3$ is similar to that in benzene; in both solvents the separation of the $N(CH_3)_2$ singlets and the downfield shift of the $CH_2$ signals are less marked than for the palladium and platinum derivatives [15], suggesting that bismuth halides are weaker acceptors towards DMTC in respect of palladium and platinum halides.

At room temperature MTC is a mixture of the *syn* and *anti* isomers, whose relative amounts depend on the solvent ([16, 21, 22] and ref. therein) and can be estimated from the relative intensities of either the N–$CH_3$ doublets or the NH broad resonances (Table III). The $^1$H NMR spectra of $BiX_3$·2MTC (X = Cl, Br) in $d_6$-benzene (Table III and Fig. 1) consist of a series of strong signals due to coordinated MTC, along with a series of weak signals coinciding with the free MTC stronger isomer. The relative amounts of free and coordinated ligand are determined by the clearly separate NH resonances, at about 5.1 and 8.5 ppm respectively. The amount of free ligand is very low for the chloro derivative, whereas is present for about a 9% in the bromo-derivative solutions. In the same solvent $BiI_3$·2MTC decomposes to solid $BiI_3$; the orange solution shows the well-resolved free ligand signals (≃55%) and a series of broad unresolved

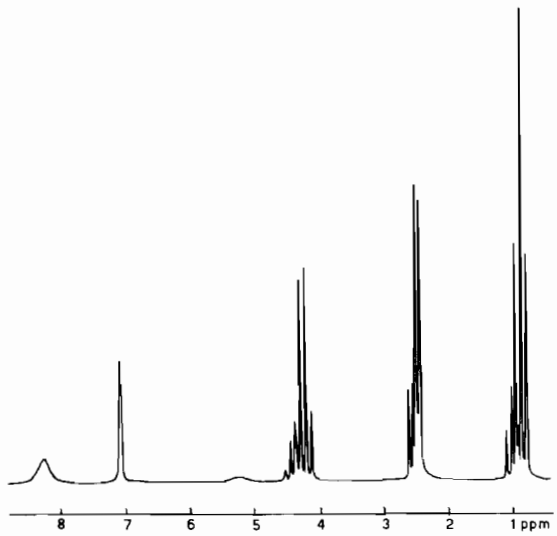


Fig. 1. $^1$H NMR Spectrum of $BiBr_3$·2MTC in $d_6$-benzene.

signals, indicative of a ligand exchanging complex, as $Hg(MTC)_2Cl_2$ [21]. The behaviour of $BiX_3 \cdot 2MTC$ in $CDCl_3$ is similar to that in $d_6$-benzene. The solutions consist mainly of coordinated ligand, except for the iodo derivative which decomposes as usual. In $d_6$-DMSO (and in $d_6$-benzene/$d_6$-DMSO mixtures) the three complexes behave as the DMTC analogues: the $^1H$ NMR spectrum of $BiBr_3 \cdot 2MTC$, reported as an example in Table III, coincides with that of free MTC, indicating total ligand release; in the same conditions the platinum halide–MTC adducts released all but one ligand molecule to give mixed complexes [27]. The $^1H$ NMR spectra in $d_6$-acetone are consistent with free and coordinated ligand; the $BiX_3 \cdot 2MTC$ (X = Cl, Br) spectra, in $d_6$-benzene/$d_6$-acetone from 10% to 50% in volume, are as the one of Fig. 2, which suggests dissociation to give the 1:1 complex and free ligand in equal amounts.

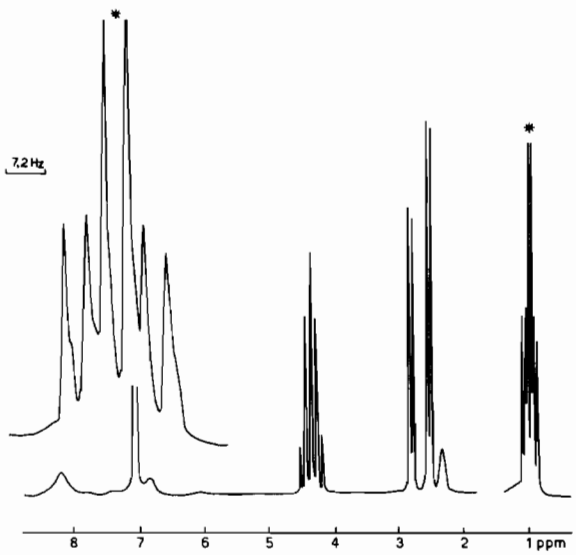


Fig. 2. $^1H$ NMR Spectrum of $BiBr_3 \cdot 2MTC$ in $d_6$-benzene containing $\simeq 10\%$ $d_6$-acetone in volume.

The $^1H$ NMR data indicate competition between sulfur and oxygen donors towards bismuth halides. It seems then of interest to correlate the complexes reported here with the analogous carbamic ester derivatives, and this study is in progress.

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