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Syntheses and Spectroscopic Study of Some New Mixed-Ligand Bi(III) 1,1-Dithiolate Complexes

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The reaction between halogenobis(dialkyldithiocarbamate) complexes of Bi(III) and sodium dialkyldithiocarbamate or potassium O-ethylxanthate yields mixed-ligand Bi(III) 1,1-dithiolate complexes. A series of ten new mixed-ligand complexes have been synthesized and studied spectroscopically. The new complexes have been characterized by elemental analysis, molecular weights, i.r., ^1H n.m.r., electronic and mass spectra. From the spectroscopic study it is deduced that the presence of the two types of 1,1-dithiolate ligands does not influence greatly the electronic properties of the complexes compared to those of the corresponding tris(1,1-dithiolate) complexes. It is also deduced that the xanthate group is a chelated ligand weaker than the dithiocarbamate group in the case of the Bi(III) complexes.

Introduction

We are presently engaged in the synthesis and study of mixed-ligand 1,1-dithiolate complexes. In a previous paper [1], we reported the syntheses and spectroscopic study of some new mixed-ligand Iron(III) 1,1-dithiolate complexes, focusing our interest on the influence of the two chemically nonequivalent 1,1-dithiolate ligands on the electronic and magnetic properties of the complexes.

Extending our work on this field we present here the results of the study of some new mixed-ligand Bi(III) 1,1-dithiolate complexes of the general formula $Bi(Y\text{-}CSS)_2(X\text{-}CSS)$ where $X = NR_2$ or OR and $Y = NR'_2$.

Results and Discussion

The halogenobis(dialkyldithiocarbamate) complexes of Bi(III), which were prepared by the reaction of tris(dialkyldithiocarbamate) complexes with halogens [2, 3], were used as starting materials for the preparation of mixed-ligand 1,1-dithiolate complexes.

The synthesis of the mixed-ligand complexes was achieved by reacting the halogenobis(dialkyldithiocarbamate) complex either with sodium dialkyldithiocarbamate, $Na(R'_2dtc)$, according to the general equation

$$Bi(R_2dtc)_2X + Na(R'_2dtc) \rightarrow NaX + Bi(R_2dtc)_2(R'_2dtc) \quad (1)$$

or with carbon disulfide and dialkylamine, according to the general equation

$$Bi(R_2dtc)_2X + CS_2 + 2R'_2NH \rightarrow Bi(R_2dtc)_2(R'_2dtc) + R'_2NH{\cdot}HX \quad (2)$$

where $R_2dtc = Et_2dtc$, Pyrrdtc, Pipdtc and $R'_2dtc = Et_2dtc$, Pyrrdtc, Bz_2dtc, THPyrdtc*.

The mixed-ligand dithiocarbamate–xanthate complexes were prepared by the reaction of Bismuth(III) iodobis(dialkyldithiocarbamate) complexes with potassium O-ethylxanthate:

$$Bi(R_2dtc)_2I + KSC(S)OEt \rightarrow KI + Bi(R_2dtc)_2[SC(S)OEt] \quad (3)$$

The ten new mixed-ligand complexes obtained by the reactions (1), (2) and (3) are given in Table I. Also in Table I are given the results of the stoichiometric analysis of the complexes, their melting points and the $\nu(C\overset{\cdot\cdot\cdot}{-}N)$ frequencies (cm^{-1}) in their i.r. spectra. All the complexes are stable in air both in the solid state and in solutions. An important feature of the dithiocarbamate–xanthate mixed-ligand complexes of Bi(III) is that they are more stable than the Bi(III) tris(O-ethylxanthate) complex.

The infrared spectra of the new complexes are consistent with the well-known characteristic bands of the coordinated dithiocarbamate groups [2]. The band attributed to the stretching vibration of the $C\overset{\cdot\cdot\cdot}{-}N$ bond of the dithiocarbamate group absorbs strongly in the case of the mixed-ligand 1,1-dithiolate complexes. The maximum of the band depends on

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*Abbreviations used throughout: Et = Ethyl, Pyrr = Pyrrolidyl, Pip = Piperidyl, Bz = Benzyl, and THPyr = 1,2,5,6-Tetrahydro-pyridyl.

TABLE I. Analytical Data and the $\nu(\mathrm{C\overset{\cdots}{-}N})$ Frequencies ($\mathrm{cm^{-1}}$) in the I.r. Spectra of the Mixed-ligand Bi(III) 1,1-Dithiolate Complexes.

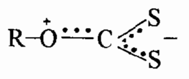
Compound	Yield %	M.P. °C	% C	% H	% N	% Bi	M.W.	$\nu(\mathrm{C\overset{\cdots}{-}N})$
$\mathrm{Bi(Et_2dtc)_2(Pyrrdtc)}$	90	166 d[a]	27.89 (27.64)[b]	4.12 (4.33)	6.26 (6.44)	31.9 (32.07)	702 (651.7)	1483vs[c] 1460vs
$\mathrm{Bi(Pyrrdtc)_2(Et_2dtc)}$	83	229–230 d	27.41 (27.73)	3.71 (4.03)	6.21 (6.46)	31.9 (32.17)	677 (649.7)	1480s, sh 1460vs
$\mathrm{Bi(Et_2dtc)_2(Bz_2dtc)}$	58	69 d	38.28 (38.60)	4.06 (4.40)	5.32 (5.40)	26.6 (26.87)	851 (777.9)	1486vs
$\mathrm{Bi(Pyrrdtc)_2(Bz_2dtc)}$	64	90 d	38.63 (38.80)	3.68 (3.91)	4.98 (5.43)	27.0 (27.00)	788 (773.8)	1460vs
$\mathrm{Bi(Pipdtc)_2(Et_2dtc)}$	88	185 d	29.85 (30.12)	4.37 (4.46)	5.96 (6.20)	30.6 (30.83)	669 (677.7)	1477vs
$\mathrm{Bi(Pipdtc)_2(Bz_2dtc)}$	85	85 d	40.62 (40.44)	4.16 (4.27)	4.88 (5.24)	26.3 (26.06)	815 (801.9)	1493vs, sh 1470vs
$\mathrm{Bi(Pyrrdtc)_2(THPyrdtc)}$	86	214–215	28.83 (29.13)	3.38 (3.67)	6.14 (6.37)	31.3 (31.68)	682 (659.7)	1470vs, sh 1455vs
$\mathrm{Bi(Pipdtc)_2(THPyrdtc)}$	80	188 d	31.29 (31.43)	4.02 (4.10)	6.14 (6.11)	30.7 (30.88)	699 (687.8)	1466vs
$\mathrm{Bi(Et_2dtc)_2(EtXanth)}$	58	102–103	24.71 (24.91)	3.77 (4.02)	4.26 (4.47)	33.3 (33.35)	681 (626.7)	1488vs
$\mathrm{Bi(Pyrdtc)_2(EtXanth)}$	97	135 d	25.37 (25.07)	3.41 (3.40)	4.12 (4.50)	33.5 (33.56)	625 (622.7)	1462vs

[a] d = decomposition. [b] Figures in parentheses are the theoretically calculated values. [c] vs = very strong, s = strong, sh = shoulder.

the dithiocarbamate group which has a higher proportion in the mixed-ligand complex and appears at about the same frequency at which the respective tris(dialkyldithiocarbamate) complex absorbs. As the proportion of dithiocarbamate group diminishes, the intensity of its $\nu(\mathrm{C\overset{\cdots}{-}N})$ band diminishes too. This band appears as a shoulder which cannot always be seen as it is, sometimes, obscured by the stronger $\nu(\mathrm{C\overset{\cdots}{-}N})$ band of the dithiocarbamate group which is present in higher proportion. Similar behaviour is observed in the case of the $\mathrm{C\overset{\cdots}{-}S}$ stretching vibrations. All the bands due to the stretching vibration of the $\mathrm{C\overset{\cdots}{-}S}$ bond of both types of dithiocarbamate groups are present in the i.r. spectra of the mixed-ligand complexes.

Some notable features exist in the i.r. spectra of the mixed-ligand dithiocarbamate–xanthate complexes. The salient feature, due to the xanthate moiety, is the band in the region 1200–1300 $\mathrm{cm^{-1}}$. This band is attributed [4] to the asymmetric stretching vibration of the $\mathrm{C\overset{\cdots}{-}O}$ bond in the $\mathrm{OCS_2}$ group.

The position of this band indicates that the contribution from the resonance form



of the xanthate group to the structure of the complexes is, as one would expect, less than the corresponding structure of the dithiocarbamate group. This is due to the fact that the alkoxy group (OR) is a weaker electron donor than the dialkylamino group ($\mathrm{NR_2}$).

The absorption of the $\nu(\mathrm{C\overset{\cdots}{-}O})$ band in the mixed-ligand complexes (1198s, br for $\mathrm{Bi(Et_2dtc)_2}$-(EtXanth) and 1190 s, br for $\mathrm{Bi(Pyrrdtc)_2(EtXanth)}$ complex), is shifted to lower frequencies relative to that of the tris(O-ethylxanthate) complex (1222vs, 1210vs, 1178vs). One plausible explanation is the stronger electron releasing ability of the dithiocarbamate ligand than that of the xanthate one. This results in an increase of the electron density on the metal atom, which as a consequence acts as a weaker electron acceptor. The shift of the band increases as the basicity of the amine group increases.

The band absorbing in the region 1110 $\mathrm{cm^{-1}}$ is also due to the xanthate moiety. It is assigned to the symmetric stretching vibration of the C–O group. The position of this band is not affected by the presence of the dithiocarbamate group in the mixed-ligand complexes.

The electronic spectral data of the mixed-ligand complexes and their assignments are summarised in Table II. The salient point in the electronic spectra of

TABLE II. Electronic Spectral Data of the Mixed-ligand Bi(III) 1,1-Dithiolate Complexes.

Compound	n → σ*	π → π* NCS_2	π → π* CS_2	n → π*
$Bi(Et_2dtc)_2(Pyrrdtc)$	–	38.9[a](4.90)[b]	–	27.8(4.03)
$Bi(Pyrrdtc)_2(Et_2dtc)$	–	38.8 (4.84)	–	27.8(3.97)
$Bi(Et_2dtc)_2(Bz_2dtc)$	–	38.6 (4.66)	–	26.8(3.84)
$Bi(Pyrrdtc)_2(Bz_2dtc)$	–	38.6 (4.79)	–	27.5(3.92)
$Bi(Pipdtc)_2(Et_2dtc)$	–	38.6 (4.75)	–	27.5(3.92)
$Bi(Pipdtc)_2(Bz_2dtc)$	–	38.3 (4.79)	–	27.4(3.95)
$Bi(Pyrrdtc)_2(THPyrdtc)$	–	38.9 (4.69)	–	27.8(3.80)
$Bi(Pipdtc)_2(THPyrdtc)$	–	39.5 (4.74) 38.3 (4.74)	–	26.8(3.89)
$Bi(Et_2dtc)_2(EtXanth)$	41.0(4.72)	41.0 (4.72)	34.3sh(4.33)	27.8(3.82)
$Bi(Pyrrdtc)_2(EtXanth)$	40.2(4.76)	40.2 (4.76)	34.0sh(4.16)	28.2(3.87)

[a] Band maximum in kK. [b] Figures in parentheses are the logϵ_{mol}.

the mixed-ligand dithiocarbamate complexes is a strong band in the region 38.0–40.0 kK (logϵ_{mol} 4.5–5.0) and another in the region 27.5 kK. These bands are strong enough to obscure partly the characteristic bands of the xanthate moiety in the mixed-ligand dithiocarbamate–xanthate complexes.

Thus, the band in the region 41.0 kK of the xanthate ligand which is attributed to an n → σ* electronic transition [5] is partly obscured by the π → π* band of the dithiocarbamate ligands. Therefore, it is rather difficult in a mixed-ligand dithiocarbamate–xanthate complex to assign the bands unambiguously to either the dithiocarbamate or the xanthate moiety.

The small effect of the two types of 1,1-dithiolate ligands used in the mixed-ligand complexes on their electronic properties is also observed in the ^1H n.m.r. spectra of these compounds.

The chemical shifts (τ, ppm) of the protons of the compounds studied are given in Table III. There are no significant differences between the τ values of the mixed-ligand 1,1-dithiolate complexes and those of the corresponding simple tris(dialkyldithiocarbamate) complexes.

In benzene solution there is a change in chemical shift due to a solvent effect. This effect, the aromatic solvent induced shift (ASIS), is attributed to the formation of collision complexes [6]. This type of benzene complexes of dithiocarbamates has been isolated recently by E. Sinn [7].

The ASIS observed was of about the same magnitude as in the corresponding tris(1,1-dithiolate) complexes. The implication is that the ASIS in the case of the studied compounds depends mainly on the type of ligand and partly on the stereochemistry of the complex.

The mass spectra of the studied mixed-ligand 1,1-dithiolate complexes follows the same fragmentation pattern as in the case of the tris(1,1-dithiolate) complexes [8]. Again, the molecular ion was not observed. The peaks with higher m/e values correspond to fragments $[(R_2dtc)_2M]^+$ and or $[(R_2dtc)(R'_2dtc)M]^+$. Fragments of the formula $[(R_2dtc)_2M]^+$ were the only ones in the case of the dithiocarbamate–xanthate complexes. The absence of peaks containing the xanthate moiety is characteristic. This observation confirms the wide-held opinion that the xanthate ligand is a weaker chelating agent than the dithiocarbamate ligand.

The fragmentation of the complexes is partly due to thermolytic decomposition [8]. The fragmentation pattern changes considerably with the probe temperature and polynuclear metal ions and their sulfides appear as the temperature is increased.

The mass spectra of a representative compound of the mixed-ligand 1,1-dithiolate complexes over a range of temperatures are given in Table IV. From Table IV it is easily deduced that these compounds undergo thermolysis.

The base peak in the mass spectra of the compounds studied corresponds to the ion $[CS_2]^{+\cdot}$. The other peaks are easily indentified as fragments of either the dithiocarbamate or the xanthate moieties.

Experimental

Materials

The iodobis(dialkyldithiocarbamate) complexes of Bi(III) were prepared according to the method reported in the literature [2].

Potassium O-ethylxanthate and sodium dialkyldithiocarbamate salts were prepared by standard methods [9, 10].

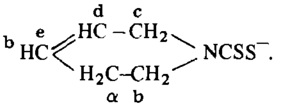
Measurements

Infrared spectra were recorded in the region 4000–650 cm^{-1}, with a Perkin–Elmer 257 spectrophotometer.

TABLE III. ^{1}H N.m.r. Chemical Shifts (τ, ppm) of the Mixed-ligand Bi(III) 1,1-Dithiolate Complexes in $CDCl_3$ and C_6H_6 Solutions.

Bi(Et$_2$dtc)(Pyrrdtc)	Pyrrdtc:	7.97(8.89)[a] (m, 4H, β-CH_2-),	6.10(6.46) (m, 4H, α-CH_2-)
	Et$_2$dtc:	8.66(9.07) (t, 12H, -CH_3),	6.16(6.59) (m, 8H, -CH_2-)
Bi(Pyrrdtc)$_2$(Et$_2$dtc)	Et$_2$dtc:	8.67(9.06) (t, 6H, -CH_3)	6.06(6.43) (m, 4H, -CH_2-)
	Pyrrdtc:	7.97(8.86) (m, 8H, β-CH_2),	6.06(6.43) (m, 8H, α-CH_2-)
Bi(Et$_2$dtc)$_2$(Bz$_2$dtc)	Bz$_2$dtc:	4.91(5.02) (5.4H, -CH_2-),	2.63(-) (s, 10H, C_6H_5)
	Et$_2$dtc:	8.65(9.10) (t, 12H, -CH_3),	6.15(6.65) (q, 8H, -CH_2-)
Bi(Pyrrdtc)$_2$(Bz$_2$dtc)	Bz$_2$dtc:	4.89(4.95) (s, 4H, -CH_2-),	2.63(-) (s, 10H, C_6H_5)
	Pyrrdtc:	7.96(8.88) (m, 8H, β-CH_2-),	6.04(6.43) (m, 8H, α-CH_2-)
Bi(Pipdtc)$_2$(Et$_2$dtc)	Et$_2$dtc:	8.67(9.06) (t, 6H, -CH_3),	6.17(6.57) (q, 4H, -CH_2-)
	Pipdtc:	8.26(8.89) (m, 12H, β, γ, -CH_2),	5.96(6.27) (m, 8H, α-CH_2-)
Bi(Pipdtc)$_2$(Bz$_2$dtc)	Bz$_2$dtc:	4.88(4.90) (s, 4H, -CH_2-),	2.62(-) (s, 10H, C_6H_5)
	Pipdtc:	8.27(8.90) (m, 12H, β, γ, -CH_2),	5.92(6.30) (m, 8H, α-CH_2-)
Bi(Pyrrdtc)$_2$(THPyrdtc)	THPyrdtc:[b]	7.50(8.24) (m, 2H, α-CH_2-),	5.76(6.08) (m, 2H, b-CH_2-)
		5.37(5.61) (m, 2H, c-CH_2-),	4.07(-) (m, 1H, d = CH-)
		4.20(-) (m, 1H, e = CH-)	
	Pyrrdtc:	7.96(8.83) (m, 8H, β-CH_2-),	6.04(6.40) (m, 8H, α-CH_2-)
Bi(Pipdtc)$_2$(THPyrdtc)	THPyrdtc:	7.72(8.28) (m, 2H, α-CH_2-),	5.80(6.13) (m, 2H, b-CH_2-)
		5.40(5.65) (m, 2H, c-CH_2-),	4.07(-) (m, 1H, d = CH-)
		4.20(-) (m, 1H, e = CH-)	
	Pipdtc:	8.30(8.88) (m, 12H, β, γ, -CH_2-),	5.90(6.29) (m, 8H, α-CH_2-)
Bi(EtXanth)$_3$	EtXanth:	8.47(9.09) (t, 9H, -CH_3),	5.23(5.73) (q, 6H, -CH_2-)
Bi(Et$_2$dtc)$_2$(EtXanth)	EtXanth:	8.52(8.99) (t, 3H, -CH_3),	5.27(5.60) (q, 2H, -CH_2-)
	Et$_2$dtc:	8.65(9.10) (t, 12H, -CH_3),	6.16(6.66) (q, 8H, -CH_2-)
Bi(Pyrrdtc)$_2$(EtXanth)	EtXanth:	8.52(9.02) (t, 3H, -CH_3),	5.28(5.58) (q, 2H, -CH_2-)
	Pyrrdtc:	7.94(8.88) (m, 8H, β-CH_2-),	6.05(6.48) (m, 8H, α-CH_2-)

[a] Figures in parentheses ate the τ values for the benzene solutions. [b]



^{1}H n.m.r. spectra were obtained on a Varian A 60A (60 MHz) instrument in $CDCl_3$ and C_6H_6 solutions using TMS as an internal standard.

Mass spectra were measured on an RMU-6L Hitachi Perkin–Elmer mass spectrometer with an ionization source AT-2P operating at ~70 eV electron beam energy.

Electronic spectra were obtained by a Zeiss PMQ II spectrophotometer with freshly prepared chloroform solutions at ~30 °C.

Molecular weights were determined using a Perkin–Elmer molecular weight apparatus Model 115 at a concentration range 3×10^{-3} to 6×10^{-4} m in chloroform solution.

Preparation of the Complexes

Preparation of the mixed-ligand Bi(III) dialkyldithiocarbamate complexes.

Bi(R$_2$dtc)$_2$(R$'_2$dtc). Two general methods were used for the preparation of the mixed-ligand Bi(III) dialkyldithiocarbamate complexes.

Method A

A two necked flask, equipped with a separatory funnel and a reflux condenser was used for the synthesis of the complexes. Stirring was performed magnetically. The flask was charged with 2.0 mmol of the Bi(III) iodo-bis(dialkyldithiocarbamate) complex, 2.0 mmol of CS_2 and 100 cm^3 of CCl_4 as a solvent. The mixture was stirred to form a suspension and 4.0 mmol of the amine R'_2NH, dissolved in ~30 cm^3 of CCl_4, was added dropwise at room temperature under continuous stirring. After one hour's stirring the mixture was refluxed for 3–4 hours and then the solvent was distilled until the contents of the flask were condensed to a small volume (*ca.* 30 cm^3). Upon addition of either EtOH or petroleum ether the mixed-ligand complex was obtained as a crystalline precipitate.

The product obtained was recrystallized by dissolving the crude solid in a small volume of $CHCl_3$ or benzene and precipitating it by addition of EtOH or petroleum ether. The products were dried under vacuum.

TABLE IV. Mass Spectral Data of the Compound $Bi(Et_2dtc)_2(EtXanth)$ at Various Probe Temperatures.

m/e	Relative Intensity			Possible Formula of the Fragment
	160 °C	195 °C	210 °C	
30	–	7.5	40.7	$[CH_2O]^{+\cdot}$
31	10.0	17.5	–	$[CH_3O]^{+}$
43	–	6.8	20.3	$[C_2H_5N]^{+\cdot}$
44	16.6	26.8	70.3	$[CS]^{+\cdot}$
45	38.8	38.1	11.1	$[C_2H_5O]^{+}$
55	1.6	6.2	22.2	$[C_2H_5NC]^{+}$
57	3.0	6.8	25.9	$[C_2H_5OC]^{+}$
72	–	8.7	20.3	$[(C_2H_5)_2N]^{+}$
76	100.0	100.0	100.0	$[CS_2]^{+\cdot}$
87	–	4.3	51.8	$[C_2H_5NCS]^{+\cdot}$
88	2.7	9.3	17.7	$[C_2H_4OCS]^{+\cdot}$
89	2.2	–	–	$[C_2H_5OCS]^{+}$
116	2.7	9.3	94.4	$[(C_2H_5)_2NCS]^{+}$
122	2.2	–	–	$[C_2H_5OCSSH]^{+\cdot}$
149	4.4	15.0	90.7	$[(C_2H_5)_2NCSSH]^{+\cdot}$
357	–	0.4	12.9	$[Bi[SCSN(C_2H_5)_2]_2]^{+}$
418	traces	traces	traces	$[Bi_2]^{+}$
505	traces	2.2	40.7	$[Bi[(SCSN(C_2H_5)_2]_2]^{+}$
627	traces	0.1	1.3	$[Bi_3]^{+}$

Method B

The reaction was carried out in a conical flask in which was placed 3.0 mmol of the bismuth(III) iodobis(dialkyldithiocarbamate) complex, suspended in 60 cm^3 of chloroform. Then, 3.0 mmol of sodium dialkyldithiocarbamate salt dissolved in 15 cm^3 of ethanol was added slowly under continuous magnetic stirrig at room temperature. After 1 hour's period the mixture was filtered and the filtrate was condensed up to a small volume (*ca.* 20 cm^3). Upon addition of ethanol or petroleum ether the complex was precipitated and then isolated by filtration. The crude product was purified by dissolving it in a small volume of chloroform or benzene and reprecipitating it by addition of EtOH or petroleum ether.

Preparation of the mixed-ligand dithiocarbamate–xanthate complexes

$Bi(R_2dtc)_2(EtXanth)$. The mixed-ligand Bi(III) dithiocarbamate–xanthate complexes were prepared by a method similar to method B above.

Thus, 2.5 mmol of iodobis(dialkyldithiocarbamato)bismuthine suspended in ~60 cm^3 of chloroform was treated with 2.5 mmol of potassium O-ethylxanthate dissolved in 10 cm^3 of ethanol. After 1 hour the reaction mixture was filtered and the filtrate was condensed to a small volume (~20 cm^3). Addition of petroleum ether resulted in the precipitation of the mixed-ligand complex.

The crude product was purified by dissolving it in a small volume of benzene and reprecipitating it by adding petroleum ether (b.p. 60–80 °C).

All the compounds prepared are yellow crystalline solids, soluble in chloroform, benzene, and methylene chloride.

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