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Bismuth Trihalide Complexes with Nitrogen and Phosphorus Chelating Ligands

G. ALONZO, M. CONSIGLIO

Istituto di Chimica Generale, Università di Palermo, Via Archirafi 26, I-90123 Palermo, Italy

N. BERTAZZI

Istituto di Tecnologie Farmaceutiche, Università di Palermo, Via Archirafi 32, I-90123 Palermo, Italy

and C. PRETI

Istituto di Chimica Generale ed Inorganica, Università di Modena, Via G. Campi 183, I-41100 Modena, Italy

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Abstract

Bismuth(III) halides react with 1,10-phenanthroline, 2-pyridinecarboxaldehyde-2-pyridylhydrazone and diphenylphosphynoethane in methanol. A stoichiometry differing from 1:1 is found only for $BiCl_3(Phen)_{1.33}$ and $BiCl_3(Dpe)_{1.5}$. Characterization of these compounds, which are not very soluble in common solvents, follows from analytical, mass and IR spectral data. In the low frequency region, the IR spectra proved to be useful to ascertain the presence of bridging halogens.

Introduction

Although a number of studies have been made in recent years on the complex formation between nitrogen donor ligands and the group VB elements antimony and bismuth, this field deserves further attention in consideration of the variety of stoichiometries and structures so far observed. The number of species which have been fully characterized is still small, particularly in the case of complexes with potential chelating ligands. We have recently studied a number of adducts formed by antimony(III) as well as phenylantimony(III) halides, with neutral bidentate and tridentate nitrogen donors [1, 2].

We are at the same time studying systematically trivalent bismuth systems, using the same ligands in order to make easier the comparison between the corresponding antimony and bismuth systems. In this respect, we attempted to extend our studies to BiF_3 derivatives in order to obtain a complete understanding of trihalide behaviour. However, all our efforts were unsuccessful because of the insolubility and the non-reactive nature of BiF_3, at variance with SbF_3.

The present work deals with the products obtained from the interaction between BiX_3 (X = Cl, Br, I) with examples of bidentate and tridentate nitrogen donors such as 1,10-phenanthroline (Phen) and 2-pyridinecarboxaldehyde-2-pyridylhydrazone (PaphyH). The latter is the Schiff base shown in Fig. 1 in the *sin* (*E*) and *anti* (*Z*) isomers. In the solid state, PaphyH exists in the (*E*)-form [3] whose structure has been recently solved [4]. The only two crystal structures known of complexes of this ligand, $CoCl_2$(PaphyH) [5] and PdCl(Paphy) [3], are examples of the neutral and monoanionic (*E*)-form which, in both cases, presents a meridional terdentate disposition of the coordinating nitrogens. Complexes of the (*Z*)-form have also been isolated depending on several factors [6, 7].

We have noticed in the literature the complete lack of information on the interaction between antimony(III) or bismuth(III) derivatives and Lewis bases containing phosphorus as donor atom. We have found that the well-known potentially bidentate ligand diphenylphosphynoethane (Dpe) easily forms adducts with bismuth trihalides and the solid products obtained are described in this paper. The characterization of related antimony(III) compounds appears at the present uncertain and the work is still underway.

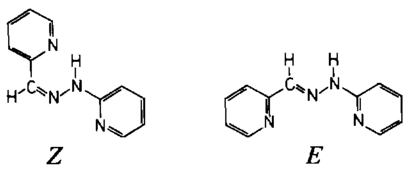

Fig. 1. *Sin* (*E*) and *anti* (*Z*)-isomers of 2-pyridinecarboxaldehyde-2-pyridylhydrazone (PaphyH).

Experimental

All the reagents were of the best chemical grade and were used without further purification. Manip-

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ulations involving $BiCl_3$ and $BiBr_3$ were carried out with vacuum line and dry-box techniques, while similar precautions were found unnecessary for BiI_3. The compounds were generally obtained upon mixing freshly prepared methanolic solutions of the bismuth halide and the ligand in 1:1 molar ratio. In most cases the product was immediately precipitated but 30 min stirring was always allowed. The solids, collected and washed several times with the same solvent, were dried *in vacuo* over silica gel and stored in the dark.

Conductance measurements were performed at 20 °C on methanolic solutions with a LKB 5300 B instrument.

Mass spectra were recorded on a Jeol JMS-01SG-2 double-focusing spectrometer at an exciting voltage of 70 eV (100 μA).

Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer as Nujol and HCBD mulls between CsI plates. The far IR spectra were obtained with a Perkin-Elmer 180 spectrophotometer as Nujol mulls supported between polyethylene sheets; atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

The complexes are listed in Table I together with their physical and microanalytical data.

Discussion

Characteristic properties of the new complexes are the rather high melting points and the low solubility in polar but unreactive solvents. The latter prevented us from obtaining reliable measurements in solution. The conductivities of methanolic saturated solutions at concentrations only slightly less than 10^{-3} M have been determined for the most soluble complexes. The qualitative results obtained are reported in Table I. These clearly show a different behaviour in solution between $BiCl_3(Phen)_{1.33}$ and $BiBr_3(Phen)$, possibly reflecting their different stoichiometry. In this respect, one possibility for the chloride is to assume the presence of ionic species such as, for example, $[BiCl_2(Phen)_2{}^+]_2[BiCl_5{}^{2-}]$.

The conductivity of the 1:1 complexes is reasonably accounted by considering the following equilibrium:

$$BiX_3(ligand) = BiX_2(ligand)^+ + X^-$$

analogous to that proposed for $BiX_3(Bipy)$ adducts [8]. In the present case, the conductivity values for the PaphyH adducts are expected to be greater than those measured for the Bipy adducts if PaphyH acts as a terdentate ligand. However, this hypothesis cannot be confirmed on the basis of present qualitative results.

Mass Spectra

The relevant species in the mass spectra for the three series of complexes are given in Table II. The absence in all cases of the molecular peak has been previously [9] observed in similar complexes, and appears to be consistent with a relatively easy dissociation of the ligand. This may occur both during

TABLE I. Physical and Microanalytical Data[a].

Complex	m.p. (°C)	Colour	C%	H%	N%	Conductivity in MeOH[b]
$BiCl_3(Phen)_{1.33}$	295–300 dec	white	34.20 (34.54)	1.88 (1.93)	6.99 (6.71)	i
$BiBr_3(Phen)$	330 dec	yellow	23.13 (22.91)	1.31 (1.28)	4.50 (4.45)	wi
$BiI_3(Phen)$	312 dec	red	18.18 (18.72)	0.98 (1.05)	3.86 (3.64)	ns
$BiCl_3(PaphyH)$	258 dec	yellow	25.56 (25.73)	2.04 (1.96)	10.85 (10.91)	i
$BiBr_3(PaphyH)$	252	yellow	20.62 (20.42)	1.68 (1.56)	8.60 (8.66)	i
$BiI_3(PaphyH)$	171 dec	red	17.10 (16.77)	1.41 (1.28)	7.30 (7.11)	ns
$BiCl_3(Dpe)$	185–187	yellow	51.64 (51.31)	3.65 (3.97)		wi
$BiBr_3(Dpe)$	180–182	yellow	37.16 (36.86)	3.00 (2.86)		wi
$BiI_3(Dpe)$	178–180	red	32.04 (31.60)	2.42 (2.45)		wi

[a] Percent calcd values in brackets. [b] Only very qualitative information was obtained as consequence of a generalized low solubility of the compounds and results are expressed as i = ionized; wi = weak ionized; ns = not soluble.

TABLE II. Fragments in the Mass Spectra of the Complexes (relative intensity and assignment in parenthesis. See Refs. 10, 11 and Table III for the proposed structures of ligands' fragments).

$BiCl_3$(Phen)$_{1.33}$
m/e: 77(75,C_5H_3N), 127(58,C_9H_5N), 154(80,$C_{10}H_6N_2$), 180(100,$C_{12}H_8N_2$), 209(29,Bi), 244(23,BiCl), 279(20,$BiCl_2$), 314(8,$BiCl_3$), 424(3,$C_{12}H_8N_2BiCl$)

$BiBr_3$(Phen)
m/e: 77(10,C_5H_3N), 127(18,C_9H_5N), 154(54,$C_{10}H_6N_2$), 180(100,$C_{12}H_8N_2$), 209(60,Bi), 288(20,BiBr), 367(32,$BiBr_2$), 446(9,$BiBr_3$)

BiI_3(Phen)
m/e: 77(18,C_5H_3N), 127(32,C_9H_5N), 154(18,$C_{10}H_6N_2$), 180(100,$C_{12}H_8N_2$), 209(22,Bi), 336(20,BiI), 463(42,BiI_2), 904(72,BiI_3)

$BiCl_3$(PaphyH)
m/e: 78(14,C_5H_4N), 91(10,C_6H_5N), 92(17,$C_5H_4N_2$), 105(6,$C_6H_5N_2$), 120(100,$C_6H_6N_3$), 169(13,$C_{11}H_9N_2$), 198(17,$C_{11}H_{10}N_4$), 209(13,Bi), 244(7,BiCl), 279(8,$BiCl_2$), 314(7,$BiCl_3$)

$BiBr_3$(PaphyH)
m/e: 78(12,C_5H_4N), 91(15,C_6H_5N), 92(9,$C_5H_4N_2$), 105(6,$C_6H_5N_2$), 120(100,$C_6H_6N_3$), 169(12,$C_{11}H_9N_2$), 198(17,$C_{11}H_{10}N_4$), 209(15,Bi), 288(8,BiBr), 367(11,$BiBr_2$), 446(4,$BiBr_3$)

BiI_3(PaphyH)
m/e: 78(18,C_5H_4N), 91(4,C_6H_5N), 92(19,$C_5H_4N_2$), 105(5,$C_6H_5N_2$), 120(100,$C_6H_6N_3$), 169(14,$C_{11}H_9N_2$), 198(19,$C_{11}H_{10}N_4$), 209(2,Bi), 336(3,BiI), 463(3,BiI_2), 590(3,BiI_3)

$BiCl_3$(Dpe)$_{1.5}$
m/e: 108(42,C_6H_5P), 121(15,C_7H_6P), 133(17,C_8H_6P), 152(20,$C_{12}H_8$), 183(100,$C_{12}H_8P$), 185(70,$C_{12}H_{10}P$), 199(15,$C_{13}H_{12}P$), 209(3,Bi), 213(35,$C_{14}H_{14}P$), 262(40,$C_{18}H_{15}P$), 275(5,$C_{19}H_{16}P$), 289(55,$C_{20}H_{18}P$), 321(7,$C_{20}H_{19}P_2$), 370(32,$C_{24}H_{20}P_2$), 398(75,$C_{26}H_{24}P_2$), 244(4,BiCl), 279(8,$BiCl_2$), 314(2,$BiCl_3$)

$BiBr_3$(Dpe)
m/e: 108(34,C_6H_5P), 121(21,C_7H_6P), 133(19,C_8H_6P), 152(25,$C_{12}H_8$), 183(100,$C_{12}H_8P$), 185(89,$C_{12}H_{10}P$), 199(8,$C_{13}H_{12}P$), 209(33,Bi), 213(9,$C_{14}H_{14}P$), 262(70,$C_{18}H_{15}P$), 275(22,$C_{19}H_{16}P$), 289(86,$C_{20}H_{18}P$), 321(6,$C_{20}H_{19}P_2$), 370(41,$C_{24}H_{20}P_2$), 398(98,$C_{26}H_{24}P_2$), 288(9,BiBr), 367(16,$BiBr_2$), 446(7,$BiBr_3$)

BiI_3(Dpe)
m/e: 108(21,C_6H_5P), 121(12,C_7H_6P), 133(5,C_8H_6P), 152(15,$C_{12}H_8$), 183(100,$C_{12}H_8P$), 185(50,$C_{12}H_{10}P$), 199(5,$C_{13}H_{12}P$), 209(14,Bi), 213(2,$C_{14}H_{14}P$), 262(36,$C_{18}H_{15}P$), 275(44,$C_{19}H_{16}P$), 289(48,$C_{20}H_{18}P$), 321(3,$C_{20}H_{19}P_2$), 370(22,$C_{24}H_{20}P_2$), 398(60,$C_{26}H_{24}P_2$), 336(17,BiI), 463(12,BiI_2), 590(15,BiI_3)

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the vaporization process as well as under the electron impact, leading to a similar fragmentation pattern of the halide-ligand stoichiometry. Indeed, ions having *m/e* values corresponding to the ligand constitute the most abundant species for the phenanthroline complexes and show very intense peaks in the case of remaining adducts with PaphyH and Dpe.

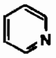
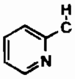
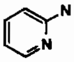
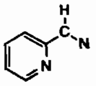
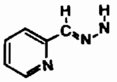
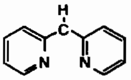
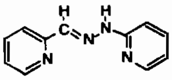
The fragmentation patterns of the free Phen and Dpe ligands have been previously reported [10, 11]; the relevant fragments in the spectrum of PaphyH are reported in Table III. Noticeably, the fragmentation of the ligand part of the complexes appears very similar to that observed for the free ligands. Other major fragments are easy explained on the basis of the presence of species BiX_n (n = 0, 1, 2, 3) with the exception of a peak at *m/e* = 424 in the spectrum of $BiCl_3$(Phen)$_{1.33}$, corresponding to BiCl(Phen).

Infrared Spectra

The low frequency IR spectra (400–80 cm^{-1}) of the complexes are reported in Tables IV–VI, together with the most relevant absorptions above 400 cm^{-1}. As found for other bismuth derivatives, the recorded spectra show an intrinsic low intensity and poor resolution of the vibrational features, especially in the low frequency range.

Assignments of the highest-lying Bi–halide stretching modes are supported by the typical [12] ratios ν(Bi–Cl):ν(Bi–Br):ν(Bi–I) observed: 1:0.68:0.56 for Phen; 1:0.67:0.56 for PaphyH and 1:0.66:0.53 for Dpe complexes. For the same halide ligand the ν(Bi–X) modes show a decreasing frequency going from Phen to PaphyH and to Dpe complexes. Even taking into account possible different structures, what we observed probably reflects an inverse trend for the coordinating strength of the chelating ligand.

TABLE III. Mass Spectral Fragmentation of PaphyH.

	m/e	Abundance %
	78	29
	91	3
	92	20
	105	3
	120	100
	169	16
	198	18

An analogous trend is observed for the ν(Sn–X) frequencies with SnX_4(Phen) and SnX_4(Dpe) adducts [13]. With respect to previously reported studies [14] on BiX_3L (L = Bipy, X = Cl, Br, I; L = Terpy, X = Cl) complexes, we note that the assigned frequencies for ν(Bi–Cl) and ν(Bi–N) modes are substantially higher.

Phen Complexes

The coordination of the ligand is inferred from the typical small shifts and splittings of certain bands of free Phen, Table IV, upon chelation (see for example [15, 16]). The data for the chloride are not of much help for proposing a definite structure at the solid state. As far as the previously advanced cation–anion formulation is concerned, we observe that the strong band at 268 cm^{-1} would be consistent with the highest ν(Bi–Cl) frequency reported for isolated $BiCl_5^{2-}$ units [17, 18 and refs. therein]. On the other hand, one expects the ν(Bi–Cl) modes of any counter–cation $BiCl_2(Phen)_2^+$ as hardly distinguishable from those of the anion. At any rate, the bands at frequencies as low as 180–165 cm^{-1} are in the expected range for ν(Bi–Cl) for bridging chlorines, so that in respect of salt formulation, cation–anion and anion–anion interactions via halogen bridges cannot be exluded.

TABLE IV. Far Infrared Spectra (400–80 cm^{-1}) and Relevant Bands Above 400 cm^{-1}. L = Phen.

Description	L•H_2O	$BiCl_3$•$L_{1.33}$	$BiBr_3$•L	BiI_3•L
ν(Bi–N)			270mw(br) 254(sh)	278(sh) 266mw 254(sh)
ν(Bi–X)		268s[a] 218s 200s 180vs 165vs	182vs 170vs(br) 175vs(br) 145vs(br) 125vs(br)	151vs 134vs 118vs 106vs
Def. modes		150s(br) 130vs(br) 115vs(br)	88vs	75vs
Other bands below 400 cm^{-1}	240mw 220(sh) 200vw 146w 114w 95w 85w	245(sh) 98(sh) 90(sh) 75(sh)	244mw 222vw(br) 120(sh)	244mw 222vw(br) 198vw(br) 124(sh) 90w
Relevant bands above 400 cm^{-1}	1615w 1505m 854vs 842mw 734vs 722m	1618w 1515ms 865m 850s 730s 722s	1620w 1517m 863mw 850s 725s 720vs	1616w 1512m 862mw 850s 720s

(continued on facing page)

TABLE IV *(continued)*

Description	L·H$_2$O	BiCl$_3$·L$_{1.33}$	BiBr$_3$·L	BiI$_3$·L
		716vs		
	622m	642mw	640m	640m
		633mw		
	410mw	416m	417m	415m

[a] Also ν(Bi–N).

TABLE V. Far Infrared Spectra (400–80 cm^{-1}) and Relevant Bands Above 400 cm^{-1}. L = PaphyH.

Description	L	BiCl$_3$·L$_{1.33}$	BiBr$_3$·L	BiI$_3$·L
ν(Bi–N)		328m	322mw	324mw
		292ms	287s	278s
		282(sh)	268(sh)	270(sh)
ν(Bi–X)		254s	170vs	142s
		210vs	140s	116vs(br)
		198vs(br)	108s	
		175vs(br)		
		155vs(br)		
Def. modes		114m		
		92s		
Other bands below 400 cm^{-1}	305w((br)			298(sh)
			255(sh)	255(sh)
	236ms		228m	222mw
	215mw			
	190m			
		142(sh)	152m	
		134(sh)	132m	134(sh)
	120w(br)	128m	126w	128(sh)
	95w(br)	100mw	95(sh)	
Relevant bands[a] above 400 cm^{-1}				
ν(N–H)	3200w(br)	3175w(br)	3200w(br)	3200w(br)
py I	1595s	1610ms	1610ms	1605ms
py II	1570s	1590(sh)	1600(sh)	
		1575w	1578w	1575w
ν(C–N)	1540m	1535m	1535ms	1530m
py III	1470s	1485m	1485ms	1485m
ring	990m	1008mw	1008mw	1005w
		1000mw	998mw	995(sh)
		580m(br)	557m(br)	

[a] For assignments see also refs. 3, 5, 6.

TABLE VI. Far Infrared Spectra (400–80 cm^{-1}) and Relevant Bands Above 400 cm^{-1}. L = Dpe.

Description	L	BiCl$_3$·L$_{1.5}$	BiBr$_3$·L	BiI$_3$·L
ν(Bi–X)		250ms	164s	132vs
		228mw	144ms	117vs
			114ms	100(sh)
Def. modes			85m	
Other bands below 400 cm^{-1}	396w	372vw	370vw	372vw
		350vw	354vw	352w
	335mw	325w	326w	325w

(continued overleaf)

TABLE VI *(continued)*

Description	L	$BiCl_3 \cdot L_{1.5}$	$BiBr_3 \cdot L$	$BiI_3 \cdot L$
	290vw(br)	301w	303w	300w
	280vw(br)	275(sh)	290w	288w
			280w	279w
	260vw(br)		267w	266w
			254mw	255w
	242vw		246w	245mw
	218w(br)	222(sh)	222w	223w
	200vw	200vw	200vw	200vw
			190vw	190w
	146mw(br)	156w	155(sh)	156w
	130mw(br)	144w(br)		142(sh)
	83w(br)			88w
Relevant bands above 400 cm^{-1}	530w	535ms	535w	530m
		530ms	522s	515s
	502ms	502ms	518s	510(sh)
		490vw		490vw
	472ms	475ms	470ms	470m
			460(sh)	460(sh)
	442m	442m		
	400w	410w	415w	410w(br)

The number of ν(Bi–Cl) modes observed for the bromide and iodide derivatives and the frequency values of the lowest-lying bands suggest a polymeric configuration with bridging halogens for these complexes.

PaphyH Complexes

The ligand is acting in the neutral form, as confirmed by the presence of a ν(N–H) band, Table V. The principal difference between the two PaphyH isomers is the presence of intermolecular hydrogen bonds in the (*Z*)-form which lowers the ν(N–H) frequency to 3150 cm^{-1} (KBr disks) [3]. However, reported studies on a number of PaphyH complexes with transition metals [6, 7] indicate that the tridentate (*E*)-form and the bidentate (*Z*)-form behaviour of the ligand does not clearly result from IR spectral data.

The coordination of PaphyH in the present complexes is indicated by the expected [6, 7] shifts and modifications of the py(I), py(II), py(III) and the 'breathing' modes of the pyridine ring. Indicative also is the bathocromic shift and intensity enhancement of the 1540 cm^{-1} band of free PaphyH assigned as ν(C–N) [3, 6, 7]. The number of ν(Bi–X) absorptions observed with the chloride, and their frequencies extended down to 175–155 cm^{-1}, strongly suggest the presence of bridging chlorines. As a consequence it appears reasonable to assume a bidentate PaphyH in this compound. For the bromide and iodide complexes, data are consistent with the absence of bridging interactions and, in these cases, a tridentate behaviour of the ligand which would satisfy the coordination demand from the central atom is the most reasonable hypothesis.

Dpe Complexes

Analogously to findings on tin(IV) Dpe adducts [13], metal–phosphorus stretching absorptions have not been localized in the spectra of present bismuth compounds, probably because of their intrinsic very low intensity. A part from the assigned ν(Bi–X) vibrations, practically all bands must be attributed to ligand vibrations, Table VI. Diagnostic of the coordination from the ligand appears the 600–400 cm^{-1} region, Fig. 2, where the y and t modes of substituted phenyls (Whiffen's notation [19]) occur. Shifts of these bands have been observed in the series Ph_3P and Ph_3PE (E = O, S, Se) and described as ν_{as} and ν_s(P–Ph) [20]. In this region the chloroderivative shows a more complex pattern which, considering its stoichiometry, may arise from nonequivalent Dpe moieties. A possible structure for this complex appears a dimeric one with a Dpe ligand bridging two $BiCl_3(Dpe)$ units. The spectra of the bromo- and iodo-complexes appear very similar to each other and give no evidence of halogen bridges.

Acknowledgements

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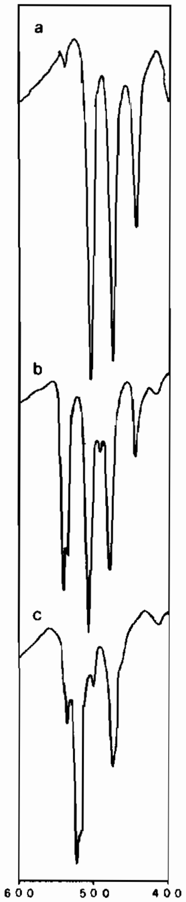

Fig. 2. IR spectra in the 600–400 cm^{-1} range of: (a) Dpe, (b) $BiCl_3(Dpe)_{1.5}$, and (c) $BiBr_3(Dpe)$.

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