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The Hydrogen Bonding Effect on the Halobismuthate(III) Geometry: Thermal, Spectroscopic and Structural Properties of Halobismuthate Complexes of 4,6-Dimethylpyrimidine-2(1*H*)-thione

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Abstract

Reactions involving Bi(III) halides and 4,6-dimethylpyrimidine-2(1*H*)-thione (L) in HX solution result in the formation of $[HL]_3[BiX_6]\cdot 2H_2O$ (X = Cl, Br) and $[HL]_3[Bi_2I_9]$. These compounds together with the organic molecule in the form of the hydrochloride, (HLCl) were characterized by means of spectroscopic and thermogravimetric measurements. For $HLCl\cdot H_2O$ (**1**) and $[HL]_3[BiCl_6]\cdot 2H_2O$ (**2**), X-ray structures were determined. In **1**, which crystallizes in the space group $Pca2_1$, with four molecules in the cell, the structure consists of roughly planar protonated organic molecules stacked along the [100] axis and built up by hydrogen bonds involving chlorine atoms and water molecules. For **2**, the space group is $P2_1/n$, $Z = 4$, the structure contains $[BiCl_6]^{3-}$ anions, protonated organic molecules stacked along the [010] axis and water molecules which form strong hydrogen bonds with the $[BiCl_6]^{3-}$ anions. The final R indices are 0.0320 and 0.0465 for **1** and **2**, respectively.

Introduction

Pyrimidine-thiones play an important role in biological systems as sulphur-containing components of minor bases of nucleic acids. In fact the thio-bases 2- and 4-thiouracil and 2-thiocytosine are normal constituents of some t-RNA species, but their function is not well understood. They appear to be essential components, but they can, under certain conditions, inhibit RNA synthesis, leading to anti-tumor and anti-thyroid activity [1].

The ligand properties toward metal ions of these types of heterocyclic bases, particularly those regarding their neutral [2, 3] and deprotonated [3, 4] forms, were widely studied, demonstrating a great variety of coordination types. In fact S-donation, S,N-chelation or bridging as well as N-donation have been structurally established.

Since less interest has been shown in the effect of iminic nitrogen protonation on the coordination ability of these ligands, [3, 5] we have undertaken a systematic study of the coordinating ability of protonated 4,6-dimethylpyrimidine-2(1*H*)-thione toward metal ions. In this paper the results obtained with bismuth(III) halides are discussed. Further interest also derives from an inorganic point of view: because of the electronic structure of the group 5B atoms, the halobismuthate species may present some particularly interesting stereochemical possibilities, depending on the role of the lone pair. The presence of a lone pair on the metal ion can be adverse to regular octahedral geometries as is demonstrated by the very few reports in the literature of discrete hexahalobismuthate compounds [6].

Experimental

Starting Materials

The hydrohalide salts were prepared by adding the corresponding hydrohalide acid to an aqueous 4,6-dimethylpyrimidine solution.

Preparation of the Complexes

The compounds were synthetized by adding a solution of Bi_2O_3 (1 mmol) in 37% HCl (8 cm^3), in 48% HBr (6 cm^3) or in 57% HI (5 cm^3), respectively, to a hot aqueous solution (15 cm^3) of the corresponding hydrohalide salt (4 mmol).

While the red iodide compound instantaneously precipitated, the yellow chloride and bromide compounds separated after three days on cooling the solutions at 0 °C.

Carbon, hydrogen, nitrogen and sulphur were analyzed using a C. Erba Mod 1106 Elemental Analyzer. The water content was carried out on a

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TABLE I. Experimental Data for the Crystallographic Analyses

Compound	1	2
Formula	$C_6H_{11}ClN_2OS$	$C_{18}H_{31}BiCl_6N_6O_2S_3$
Molecular weight	194.68	881.36
Space group	$Pca2_1$	$P2_1/n$
a (Å)	14.821(1)	11.844(4)
b (Å)	8.907(1)	14.854(4)
c (Å)	7.2576(7)	18.462(5)
β (°)	90	99.82(3)
V (Å^3)	958.1(2)	3200(2)
Z	4	4
D_c (g cm^{-3})	1.83	1.35
D_o (g cm^{-3})	1.81	1.33
F(000)	408	1720
Temperature (K)	293	293
Crystal size (mm)	0.33 × 0.53 × 0.53	0.26 × 0.26 × 0.33
Diffractometer	Siemens AED	Philips PW 1100
μ (cm^{-1})	5.58	62.13
Absorption correction (min–max)		1.00–1.16
Scan speed (°/min)	2.5	6
Scan width (°)	1.20 + 0.35 tanθ	1.80 + 0.35 tanθ
Radiation (λ = 0.7093 Å)	Mo Kα_1	Mo Kα_1
θ range (°)	3.0–25.0	2.5–25.0
Scan mode	$\omega-2\theta$	$\omega-2\theta$
No. of measured reflections	1020	6042
Condition for observed reflections	$I > 2\sigma(I)$	$I > 3\sigma(I)$
Number of reflections used in the refinement	598	3612
Number of refined parameters	99	326
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.0320	0.0465
$R_w = \{\Sigma w(\Delta F)^2/\Sigma w F_o^2\}^{1/2}$	0.0332	0.0524
k, g ($w = k/[\sigma^2(F_o) + gF_o^2]$)	1.0, 0.0056	1.0, 0.0057

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Anal. Found for $[HL]_3[BiCl_6]\cdot 2H_2O$: C, 24.3; H, 3.5; N, 9.5; S, 10.8; H_2O, 4.1%. Calc. for $C_{18}H_{31}BiCl_6N_6O_2S_3$: C, 24.51; H, 3.54; N, 9.53; S, 10.90; H_2O, 4.08%.

Found for $[HL]_3[BiBr_6]\cdot 2H_2O$: C, 18.8; H, 2.7; N, 7.3; S, 8.3; H_2O, 3.1%. Calc. for $C_{18}H_{31}BiBr_6N_6O_2S_3$: C, 18.81; H, 2.72; N, 7.31; S, 8.37; H_2O, 3.14%.

Found for $[HL]_3[Bi_2I_9]$: C, 10.9; H, 1.4; N, 4.2; S, 4.8. Calc. for $C_{18}H_{27}Bi_2I_9N_6S_3$: C, 10.89; H, 1.37; N, 4.23; S, 4.84%.

Physical Measurements

IR spectra were obtained on the solids in KBr pellets [4000–250 cm^{-1}) and in Nujol mulls on polythene (500–50 cm^{-1}) with Perkin-Elmer 521 and 180 spectrophotometers respectively. Raman spectra (400–20 cm^{-1}) could not be obtained because the solid compounds were highly fluorescent in the laser beam.

X-ray Data Collection and Structure Determination

Crystal data and details of parameters associated with data collection are given in Table I. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and put on an absolute scale by least-squares; for 2 an empirical absorption correction was also applied [7]. The structures were solved by the heavy-atom method and refined by full-matrix least-squares cycles and anisotropic thermal parameters for non-hydrogen atoms. In 2 hydrogen atoms were not located, while in 1 only those of the water molecule were located and refined, the others, placed at the calculated positions were introduced in the last refinement cycle as fixed contributors; four reflections (400, 020, 002, 112) which can be affected by extinction or counting errors were excluded from the final refinement; Table II lists the atomic coordinates. The atomic scattering factors used, corrected for anomalous dispersion, were taken from International Tables [8]; the major calculations were performed by using the CYBER 76 of the 'Consorzio per la gestione del Centro di Calcolo

TABLE II. Fractional Atomic Coordinates (×10^4)

Atom	x/a	y/b	z/c
1			
S	8736(1)	7504(2)	1452(5)
C1	7642(4)	7289(6)	1380(11)
N1	7233(3)	5961(6)	927(8)
C2	6009(5)	4261(9)	253(14)
C3	6321(4)	5780(9)	816(9)
N2	7055(3)	8448(6)	1758(9)
C4	5781(4)	6994(9)	1198(12)
C5	6158(4)	8309(10)	1644(11)
C6	5624(6)	9711(11)	2055(15)
Cl	6540(1)	3236(2)	5000(0)
O	2815(4)	9025(7)	3073(10)
H1	7652(0)	5046(0)	438(0)
H2	5275(0)	4492(0)	386(0)
H3	6135(0)	3167(0)	827(0)
H4	6202(0)	4337(0)	−1133(0)
H5	5232(0)	6632(0)	1063(0)
H6	4897(0)	9666(0)	2057(0)
H7	5843(0)	10482(0)	966(0)
H8	5864(0)	10131(0)	3360(0)
H9	7339(0)	9521(0)	2155(0)
H1W	3048(59)	8367(92)	1861(162)
H2W	2457(71)	8210(100)	3359(128)
2			
Bi	−1854(0)	2410(0)	5998(0)
Cl1	−2802(3)	4017(2)	5554(2)
Cl2	−1696(3)	2852(3)	7430(2)
Cl3	316(3)	3042(2)	5906(2)
Cl4	−997(3)	791(2)	6440(2)
Cl5	−3990(3)	1791(2)	5978(2)
Cl6	−2041(3)	1945(2)	4528(2)
S1	644(3)	1543(2)	3463(2)
C1	606(10)	2644(9)	3471(6)
N1	−154(9)	3132(7)	3820(5)
N2	1313(9)	3189(7)	3141(6)
C3	−185(10)	4060(8)	3841(6)
C2	−1125(13)	4469(10)	4216(8)
C4	540(10)	4534(8)	3533(6)
C5	1325(11)	4105(8)	3168(7)
C6	2251(13)	4563(10)	2827(8)
S2	6404(3)	−1113(2)	3062(2)
N3	7429(10)	−2595(6)	2673(6)
N4	5876(9)	−2841(7)	3251(5)
C7	6554(10)	−2213(8)	3006(6)
C9	7583(11)	−3471(8)	2609(7)
C8	8586(12)	−3761(10)	2252(9)
C10	6848(11)	−4076(9)	2848(7)
C11	5947(11)	−3737(8)	3155(7)
C12	5106(12)	−4311(10)	3420(9)
S3	2977(3)	3636(2)	4895(2)
C13	3004(12)	2514(8)	4855(7)
N5	2223(9)	1997(6)	5154(6)
N6	3744(9)	2039(7)	4527(6)
C15	2163(10)	1080(9)	5107(7)
C14	1194(14)	637(11)	5390(9)
C16	2969(12)	632(9)	4763(7)
C17	3757(12)	1131(9)	4469(6)
C18	4653(13)	704(11)	4090(8)
O1	6012(9)	3590(7)	2760(6)
O2	5584(10)	3081(9)	4171(6)

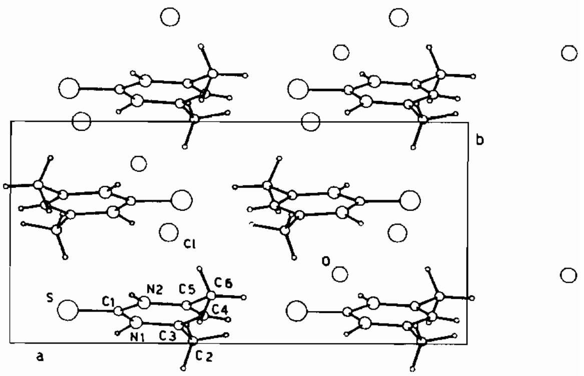

Fig. 1. Projection of the structure of 1 along the [001] axis.

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Results and Discussion

Description of the Structures

Figure 1 shows the structure of 4,6-dimethylpyridine-2(1*H*)-thione hydrochloride monohydrate in projection along the [010] axis. The roughly planar organic molecules are stacked in ribbons along the *a* axis, so that the shorter distances involve the thiourea moiety of each molecule and the carbon atoms of an adjacent one. Chlorine ions and water molecules are placed between the stacks and complete the packing forming strong hydrogen bonds with thioureic nitrogen atoms (Table III). Bond distances and angles are quoted in Table IV. The S–C bond, 1.634(6) Å, is slightly shorter than the values found in similar compounds, 1.671(1) Å in 4-amino-2-thioxo-6-pyrimidinone monohydrate [10], 1.694(3) Å in imidazolidine-2-thione [11], 1.659(2) Å in the 6-amino-8-mercaptopurinium cation [5]. The other bond lengths N–C (sp^2) 1.378(8), 1.338(8) Å; C(sp^2)–C(sp^2) 1.37(1), 1.34(1) Å; C(sp^3)–C(sp^2) 1.51(1), 1.49(1) Å are regular and similar to those found above, in 6-amino-8-mercaptopurinium. As expected in accordance with the empirical rule of Singh [12] for six-membered nitrogen heterocycles, all the endocyclic angles at the protonated nitrogens are significantly greater than 120, whereas the N–C–N angles are significantly smaller. This fact can also be connected to the geometric constraints exerted by the planarity condition in the rings with larger angles at the nitrogens so that the values of the N–C–N angles

TABLE III. Hydrogen Bond Systems[a]

1					
N(1)...Cl^{i}	3.107(5)	H(1)...Cl^{i}	2.03	N(1)–H(1)...Cl^{i}	170
N(2)...O^{ii}	2.692(8)	H(9)...O^{ii}	1.62	N(2)–H(9)...O^{ii}	170
O...Cl^{iii}	3.153(7)	H1W...Cl^{iii}	2.06(9)	O–H1W...Cl^{iii}	168(8)
O...Cl^{iv}	3.096(7)	H2W...Cl^{iv}	2.22(9)	O–H2W...Cl^{iv}	158(8)
2					
N(1)...Cl(6)	3.29(1)	H(1)...Cl(6)	2.35	N(1)–H(1)...Cl(6)	156
N(5)...Cl(3)	3.24(1)	H(5)...Cl(3)	2.33	N(5)–H(5)...Cl(3)	151
N(6)...O(2)	2.84(2)	H(6)...O(2)	1.86	N(6)–H(6)...O(2)	164
N(2)...Cl(2^{v})	3.28(1)	H(2)...Cl(2^{v})	2.29	N(2)–H(2)...Cl(2^{v})	169
N(3)...O(1^{vi})	2.77(2)	H(3)...O(1^{vi})	1.83	N(3)–H(3)...O(1^{vi})	154
N(4)...Cl(5^{vii})	3.25(1)	H(4)...Cl(5^{vii})	2.27	N(4)–H(4)....Cl(5^{vii})	166

[a] Distances (Å), angles (°). Symmetry code: i = $\frac{3}{2} - x, y, z - \frac{1}{2}$, ii = $x + \frac{1}{2}, 2 - y, z$, iii = $1 - x, 1 - y, z - \frac{1}{2}$, iv = $x - \frac{1}{2}, 1 - y, z$, v = $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$, vi = $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$, vii = $\bar{x}, \bar{y}, 1 - z$.

TABLE IV. Selected Bond Distances (Å) and Angles (°)

1		2	
S–C(1)	1.634(6)	Bi–Cl(1)	2.705(3)
C(1)–N(1)	1.369(8)	Bi–Cl(2)	2.700(4)
C(1)–N(2)	1.378(8)	Bi–Cl(3)	2.769(4)
N(1)–C(3)	1.364(8)	Bi–Cl(4)	2.683(3)
N(2)–C(5)	1.338(8)	Bi–Cl(5)	2.686(4)
C(2)–C(3)	1.487(11)	Bi–Cl(6)	2.772(4)
C(3)–C(4)	1.374(10)		
C(4)–C(5)	1.338(11)	Cl(1)–Bi–Cl(2)	92.2(1)
C(5)–C(6)	1.508(13)	Cl(1)–Bi–Cl(3)	91.4(1)
		Cl(1)–Bi–Cl(4)	177.7(1)
S–C(1)–N(1)	123.3(5)	Cl(1)–Bi–Cl(5)	87.5(1)
S–C(1)–N(2)	122.2(5)	Cl(1)–Bi–Cl(6)	87.9(1)
N(1)–C(1)–N(2)	114.6(5)	Cl(2)–Bi–Cl(3)	93.9(1)
C(1)–N(1)–C(3)	123.7(6)	Cl(2)–Bi–Cl(4)	87.7(1)
C(1)–N(2)–C(5)	123.1(6)	Cl(2)–Bi–Cl(5)	90.3(1)
C(2)–C(3)–N(1)	115.6(6)	Cl(2)–Bi–Cl(6)	179.3(1)
N(1)–C(3)–C(4)	118.2(6)	Cl(3)–Bi–Cl(4)	90.9(1)
C(2)–C(3)–C(4)	126.2(6)	Cl(3)–Bi–Cl(5)	175.8(1)
C(3)–C(4)–C(5)	119.7(6)	Cl(3)–Bi–Cl(6)	86.8(1)
C(4)–C(5)–N(2)	120.7(6)	Cl(4)–Bi–Cl(5)	90.2(1)
C(4)–C(5)–C(6)	123.6(6)	Cl(4)–Bi–Cl(6)	92.1(1)
N(2)–C(5)–C(6)	115.6(6)	Cl(5)–Bi–Cl(6)	89.1(1)

appear inversely related to those of the C–N–C angles. Figure 2 shows the structure of the $(LH)_3[BiCl_6]$ compound in projection. The asymmetric structural unit contains one $[BiCl_6]^{3-}$ anion, three N-protonated organic cations and two water molecules. The three organic molecules are roughly planar and mutually nearly parallel, the dihedral angles formed by mean planes being in the range 4.6(2)–2.9(2)°. As revealed by intermolecular contacts the organic molecules are stacked along the [010] axis in a similar way to that found in the hydrochloride compound.

The geometry of the hexachlorobismuthate ion is slightly distorted octahedral (bond angles range: *cis* 93.9(1)–86.8(1)°, *trans* 179.3(1)–175.8(1)°); the Bi–Cl bonds (Table IV) 2.683(3)–2.772(4) Å are close to the 2.66(1) Å value found in the $[BiCl_6]^{3-}$ anion of μ_4-chloro-{tris[trichloro(thiosemicarbazide)Bi(III)} [tris(thiosemicarbazide)bismuth(III)] hexachlorobismuthate(III) chloride [6b] and comparable with those found in some chloro-bismuth derivatives: e.g. 2.709(6)–2.763(10) Å in di-μ-chlorobis[chlorotris(thiourea)bismuth(III)]pentachlorothioureabismuthate(III) [13]. All these bonds are

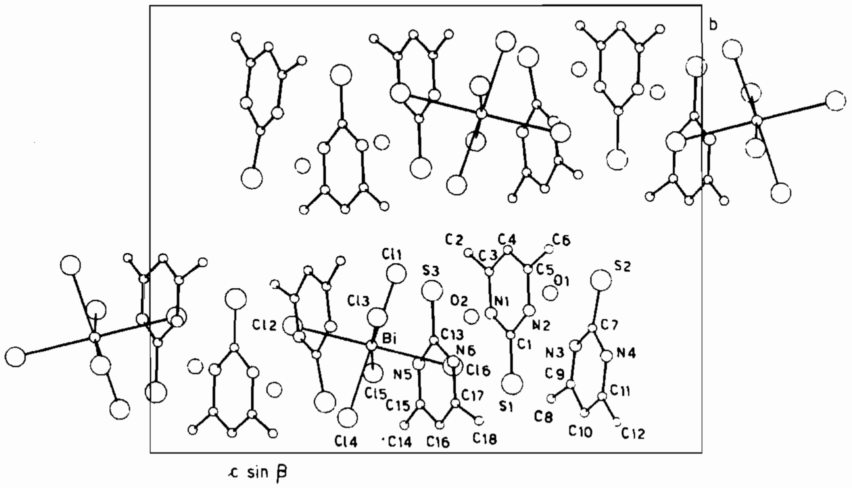

Fig. 2. Projection of the structure of 2 along the [100] axis.

longer than the corresponding ones in $BiCl_3$ (2.468(4)–2.518(7) Å) [14]. A very extended and complex network of hydrogen bonds is found, involving water molecules, nitrogen and chlorine atoms (Table III). These extensive and strong hydrogen bonding, on which the crystal packing depends, may have a fundamental role in stabilizing discrete $[BiCl_6]^{3-}$ units, as, on diminishing the charge density at the halide atoms, they minimize ligand–ligand electron repulsion. This allows the arrangement of six ligand anions around the metal ion, making inactive the role of the lone pair. The presence of discrete $[BiCl_6]^{3-}$ ions is rather unusual, the trend among chlorobismuthates being to form polynuclear entities as in $(C_6H_5NH)_6Bi_4Cl_8$ (tetrameric) [15] or in $Cs_3Bi_2Cl_9$ (polymeric) [16].

Thermogravimetric and Spectroscopic Results

The differing thermogravimetric behaviour of the two hydrated complexes, summarized in the following equations

$$[HL]_3[BiCl_6]\cdot 2H_2O \xrightarrow[-H_2O]{110-153\ ^\circ C} [HL]_3[BiCl_6]\cdot H_2O$$

$$\xrightarrow[-H_2O]{153-185\ ^\circ C} [HL]_3[BiCl_6]$$

$$[HL]_3[BiBr_6]\cdot 2H_2O \xrightarrow[-2H_2O]{118-153\ ^\circ C} [HL]_3[BiBr_6]$$

is consistent with the presence of stronger hydrogen bonding involving H_2O and $[BiX_6]^{3-}$ anions in the chloride than in the bromide compound.

Other information on the hydrogen bonding strengths may be obtained by comparing the IR spectra of the complexes with those of the hydrohalide salts and their deuterated analogues, although they are very similar to one another.

The hydrohalide salts contain a strong bulky maximum centered at 2850 cm^{-1}, which may be assigned to both NH and ^+NH stretching vibrations, indistinguishable from each other since the resonance stabilization spreads the positive charge equally on both the nitrogen atoms of the heterocyclic cation, as confirmed by the very similar C(1)–N(1) = 1.369(8) Å and C(1)–N(2) = 1.378(8) Å distances. The position of this band maximum was considered to be characteristic of NH and ^+NH stretching vibrations perturbed by strong hydrogen bonding [17]. In the complexes this band maximum is shifted to higher frequencies (65–70 cm^{-1}) with respect to the hydrohalide salts, indicating a lowering of the hydrogen bonding strength as a consequence of the substitution of a $[BiX_6]^{3-}$ anion to halide anions. Identical behaviour was previously observed for similar ligands when $[SnCl_6]^{2-}$ or $[SbCl_6]^{3-}$ anions replaced halide anions [18, 19].

Also the in-plane bending NH and ^+NH modes fall at lower frequencies in the complexes (1560–80, 1530–40 cm^{-1}) than in the hydrohalide salts (1640–50, 1552–55 cm^{-1}), confirming a decrease in hydrogen bonding strength in the former.

As reported above, the bismuth atom in $[HL]_3$-$[BiCl_6]\cdot 2H_2O$ has a distorted octahedral coordination, the deviation from octahedral symmetry being revealed both by inequivalences in metal–chlorine distances and by the angular distortion (Cl–Bi–Cl) from the octahedral value. Consequently, more Bi–Cl vibrational bands than those calculated from ideal octahedral symmetry should be expected.

In the far-IR spectrum of the $[BiX_6]^{3-}$ compounds (Table V) four bands may be associated with Bi–X vibrations. In fact, two bands at 163 and 126 cm^{-1} are assignable to the two (F_{1u}) infrared-active Bi–Cl modes, respectively, for an undistorted octahedral structure two medium absorptions at 244 and 200 cm^{-1} are also present which may be associated with (A_{1g}) and (E_g) modes, even if these modes should be infrared-inactive.

TABLE V. Metal–Halogen Vibrations (cm^{-1}) of BiX_6^{3-} and $Bi_2I_9^{3-}$ Complexes

	A_{1g}(R)	E_g(R)	F_{1u}(IR)	F_{1u}(IR)
$BiCl_6^{3-}$	244mb	200sh	163vsb	126m
$BiBr_6^{3-}$	152m	131s	117s	98sh
		$(A_2^{II} + E^{I})$ (IR)		
	terminal		bridging	
$Bi_2I_9^{3-}$	130vsb		86ms	

Since a similar set of bands was observed in the far-IR spectrum of the corresponding bromine-derivative (Table V), we can reasonably assume that in the $[BiBr_6]^{3-}$ anion, too, the bismuth atom has a distorted octahedral symmetry very similar to that found for the $[BiCl_6]^{3-}$ anion.

Finally, the far-IR spectrum of the $[HL]_3[Bi_2I_9]$ compound shows a set of absorption bands assignable to metal–halogen stretching vibrations closely resembling those of the complexes having D_{3h} symmetry [20] in which the $[Bi_2I_9]^{3-}$ anion presents a binuclear structure (two octahedra sharing a face) [21]. For a $[M_2X_9]^{n-}$ ion having D_{3h} symmetry two terminal ($A_2'' + E'$) and two bridging ($A_2'' + E'$) stretching modes, which are IR-active, are expected. Therefore from our complex the higher frequency intense broad band at 130 cm^{-1}, which can be resolved into two contributions, may be probably associated with the former, while the medium intense band at 86 cm^{-1} may be one of the bridging ν(Bi–I) modes.

Supplementary Material

Tables of observed and calculated structure factors and thermal parameters are available from the authors on request.

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