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Bipyridyl and Terpyridyl Complexes of the Group VB Trihalides and their Far Infrared Spectra

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Metal–halogen and metal–ligand infrared frequencies have been assigned for MX_3.bipy and MX_3.2py compounds of arsenic, antimony and bismuth. Metal–halogen frequencies suggest that the complexes can be divided into two groups – those with and without halogen bridges. Terpyridyl complexes with antimony halides are constituted $[SbX_2.terpy^+]_2$ SbX_5^{2-}, and with arsenic halides $[AsCl_2.terpy^+]$ $AsCl_4^-$ and $[AsBr_2.terpy^+]$ Br^-. $BiCl_3$.terpy is covalent.

Introduction

There is known to be considerable diversity in the complexes formed by the Group VB trihalides, even though the number of full structure determinations is still rather small. Coordination numbers are variable. The mononuclear complexes $SbCl_3.PhNH_2$[1] and $SbCl_3.2Ph_3AsO$[2] provide examples of four- and five-coordination, with a stereochemically active lone pair in addition. Similarly, $(NH_4)_2SbCl_5$ contains antimony in a distorted square pyramidal configuration[3], but sixfold coordination is achieved through halogen bridging in other halogen anions of both antimony[4] and bismuth[5]; and the six-coordinate structure of $[AsCl_3.bipy]_2$ containing a stereochemically inactive lone pair has recently been reported[6].

In extending previous work on adducts with nitrogen bases[7] we have examined the low frequency infrared spectra of the mono(2,2′-bipyridyl) adducts and also evidence on the structures of several 2′,2″:6″,2‴-terpyridyl derivatives. The bipyridyl complexes are partially ionised (to give free halide) in nitrobenzene. Therefore terpyridyl, whose coordination can produce ionisation of halogen,[8] seemed of use in showing coordination preferences of these Group VB elements. Bis-pyridine adducts which might have been analogous to the mono-bipyridyl complexes were also sought, but only those from arsenic, antimony and bismuth tribromides were obtained.

TABLE I. Infrared Spectra of Bipyridyl and Bis-Pyridine Complexes.

Compound	ν (M–L)	ν (M–X)	Other Bands (below 300 cm^{-1})
Bipyridyl			218m, 168s, 150m, 105s
$AsCl_3 \cdot$ bipy	(360sh, 340m, 317s, 304m, 273s)[a]		[b]
$AsBr_3 \cdot$ bipy	280sh	[c]269s, 241s, 220s	[d]180m, 148s, 124m
$AsI_3 \cdot$ bipy	257m, 247w	202s, 182s, 170s	152w, 142w
$SbCl_3 \cdot$ bipy	(299m, 284s, 244s, 203s, 184s, 175s)[a]		142m, 123w, 105m
$SbBr_3 \cdot$ bipy[f]	254m, 243m	200s, 193s, 175s	[d]165m, 131m, 100m
$SbI_3 \cdot$ bipy[g]	236w	179m, [e]166m, 153s	135w, 126w, 110w
$BiCl_3 \cdot$ bipy	262m, 233m	179sh, 165s, 155s	[d]127s, 111m
$BiBr_3 \cdot$ bipy[f]	245w, 214m	188s, 160s	146sh, 125m, 104s
$BiI_3 \cdot$ bipy[g]	238w, 212m	142s, 123s	151m, 104m
$AsBr_3 \cdot$ 2py	(254m, 200s)[a]		
$SbBr_3 \cdot$ 2py	258m, 233m	191sh, 175m, 156s	137s, 123m, 110w
$BiBr_3 \cdot$ 2py	265m, 246m	182m, 158s	146m, 128m, 116m

[a] ν (M–L) and ν (M–X). [b] Spectrum not recorded below 200 cm^{-1}. [c] Possibly a ν (M–L) band. [d] Possibly a ν (M–X) band. [e] Possibly a ligand band. [f, g] Isomorphous pairs of compounds.

Results and Discussion

Bipyridyl Complexes

The infrared spectra of these compounds show one or two medium to weak bands between 300 and 200 cm^{-1} which can be assigned to a metal–ligand stretching vibration (Table I). The frequencies lie close to those assigned to the metal–ligand vibration in bipyridyl complexes of the tin tetrahalides[9] and are consistent with those which have been identified in other bipyridyl complexes.[10] In addition, a group of strong overlapping bands whose positions are halogen dependent can be assigned to ν (M–X) vibrations. In most cases these ν (M–X) bands lie at lower frequencies than the ν (M–L); for the arsenic and antimony trichloride derivatives the two regions merge, but the stronger ν (M–Cl) bands can be distinguished. The ranges of these ν (M–X) bands from individual compounds suggest that the compounds fall into two structural groups – those with halogen bridging, as is known to be the case for $[AsCl_3.bipy]_2$,[6] and those without bridging, as exemplified by the triphenylarsine oxide complex, $SbCl_3.2Ph_3AsO$.[2]

X-ray powder photographs show that $SbBr_3$.bipy is isomorphous with $BiBr_3$.bipy, and also that these two bromides are of closely similar structure to the pair of isomorphous iodides, SbI_3.bipy and BiI_3.bipy. For halides of similar structure typical frequency ratios ν (M–Cl) : ν (M–Br) : ν (M–I) are 1 : 0.70–0.75 : 0.55–0.60. Moreover it is known that the ν (M–X) frequencies for bridging halogens are 0.60–0.85 of those for terminal halogens in the same molecule.[11] The ratio between the ν (M–X) frequencies for the bromides and iodides is that expected for similarly constituted compounds. Next, taking $SbCl_3.2Ph_3AsO$ and $SbBr_3.2Ph_3AsO$ as a reference chloride–bromide pair it is found that the ν (Sb–Cl) bands lie at 224, 208 and 188 cm^{-1}, and ν(Sb–Br) at 155, 143 and 135 cm^{-1}, so that the usual ν (M–Cl) : ν (M–Br) relationship holds in this case. But with respect to the chlorides and bromides of the bipyridyl series it will be seen from Table I that the strong ν (M–Cl) vibrations appear over a wide range and extend to lower frequencies in comparison with the bromides than would have been anticipated if the two series were similarly constituted. It is inferred that $SbCl_3$.bipy and $BiCl_3$.bipy resemble the arsenic trichloride compound in being halogen bridged, but that the bromides and iodides are mononuclear. The case of $AsBr_3$.bipy remains in doubt, however, because the medium intensity band at 180 cm^{-1} which is not generally shown by the other complexes may also be a ν (As–Br) vibration. This would extend the range to considerably lower frequency and indicate halogen bridging.

Pyridine Complexes

Despite previous reports[12] it did not prove possible to obtain bis-pyridine adducts from arsenic triiodide, antimony trichloride or bismuth trichloride, the highest adducts found being AsI_3.py, $2SbCl_3$.3py and $2BiCl_3$.3py.

Of the bis-pyridine compounds, $BiBr_3$.2py gives an infrared spectrum with metal–halogen bands corresponding closely to those from $BiBr_3$.bipy (Table I), thus indicating a structural similarity.

Terpyridyl Complexes

With these halides, as for those of other groups, the tridentate terpyridyl ligand emphasises differences in the coordination behaviour of the acceptor molecules. Combining ratios vary, as shown in Table III. The arsenic compounds are 1 : 1 electrolytes in nitrobenzene, the antimony compounds 2 : 1 electrolytes and $BiCl_3$.terpy is essentially a non-electrolyte. The inferred formulations (Table III) involve a common cation type $[MX_2.terpy^+]$ associated with different anions, $AsCl_4^-$, Br^- and SbX_5^{2-}. The compounds $3SbBr_3$.2terpy and $AsBr_3$.terpy would contain the respective anions $SbBr_5^{2-}$ and Br^-, and in accord with expectations the spectrum of the antimony compound shows more bands in the ν (M–Br) region (Table II). Confirmation of the presence of the $SbCl_5^{2-}$ anion in the crystalline compound $3SbCl_3$.2terpy is afforded by the presence of the characteristic shoulder at 360 nm which appears in the ultraviolet reflectance spectrum of $(NH_4)_2SbCl_5$.

TABLE II. Infrared Spectra of Terpyridyl Complexes.

Compound	ν (M–L)	ν (M–X)	Other Bands (below 300 cm^{-1})
terpyridyl			244vw, 220vw, 191s, 150w, 140w, 118m
$2AsCl_3 \cdot$ terpy	(364s, 334s, 283s, 240m)[a]		[b]
$AsBr_3 \cdot$ terpy	275sh, 260m	235m, 221s	182m, [c]174m, 158m, 132m, 110m
$3SbCl_3 \cdot$ 2terpy	(305m, 284s, 260s, 220s)[a]		[c]172m, 149m, 118m
$3SbBr_3 \cdot$ 2terpy	260m	205sh, 189s, 173s, 163s, 144s	155m, 123m, 110s
$3SbI_3 \cdot$ 2terpy	260m, 253m	165s, 145s, 136s, 125s	183m, 114m
$BiCl_3 \cdot$ terpy	248m, 240m	199s, 180s, 170s	134m, 120m

[a] Probably ν (M–X) and ν (M–L). [b] Not recorded below 200 cm^{-1}. [c] Possibly a ν (M–L) band.

TABLE III. Terpyridyl Complexes.

Compound	Λ_m[a] (ohm^{-1} mole^{-1} cm^2)	Probable Formulation
$2AsCl_3 \cdot terpy$	28.6	$[AsCl_2 \cdot terpy^+]\ AsCl_4^-$
$AsBr_3 \cdot terpy$	24.3	$[AsBr_2 \cdot terpy^+]Br^-$
$3SbCl_3 \cdot 2terpy$	41.1	$[SbCl_2 \cdot terpy^+]_2SbCl_5^{2-}$
$3SbBr_3 \cdot 2terpy$	35.8	$[SbBr_2 \cdot terpy^+]_2SbBr_5^{2-}$
$3SbI_3 \cdot 2terpy$	36.3	$[SbI_2 \cdot terpy^+]_2SbI_5^{2-}$
$BiCl_3 \cdot terpy$	[b]	$[BiCl_3 \cdot terpy]$

[a] In nitrobenzene, in which a 1:1 electrolyte gives Λ_m 20–30.
[b] Insoluble in nitrobenzene; $\Lambda_m = 5.7$ in dimethylformamide.

The infrared spectra (1400–600 cm^{-1}) attributable to coordinated terpyridyl are all closely similar for the arsenic and antimony compounds for which the common cation type is suggested; but the spectrum of the covalent bismuth compound, which is assumed to be six-coordinate, shows distinct differences (Figure 1). Few metal–terpyridyl stretching frequencies have been reported. In the present compounds bands of medium strength in the 250 cm^{-1} region and at 170–180 cm^{-1} are possibilities (see Table II).

Overall, the evidence from these terpyridyl compounds points to a predominance of five-coordination, as in the ions $[MX_2.terpy^+]$ and SbX_5^{2-}, but with a preference for increasing coordination number down the group, as in $BiCl_3$.terpy.

Experimental Section

Preparation of Complexes

The chlorides and bromides of arsenic and antimony were freshly distilled before use. Bismuth trichloride was sublimed under vacuum. Preparation and manipulation of the complexes was carried out in a dry-box, except that arsenic trichloride compounds were obtained by vacuum distillation of the halide into the ligand and solvent. Products were collected on a filter, washed with petrol ether (b.p. 50–70° C) and dried under high vacuum. The arsenic compounds are particularly sensitive to hydrolysis.

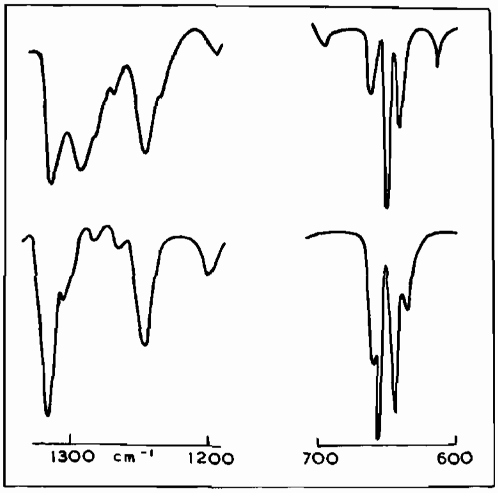

Figure 1. Infrared spectra of terpyridyl complexes. Upper, $[SbBr_2.terpy^+]_2SbBr_5^{2-}$; lower, $BiCl_3$.terpy.

Details of preparation of the bipyridyl compounds have been reported.[7a] The terpyridyl compounds were obtained by reacting the components in equimolar proportions in toluene (or acetone for $BiCl_3$.terpy). Pure samples of the arsenic trichloride derivative were obtained by shaking excess halide with ligand in benzene. Analytical results are given in Table IV.

Pyridine Compounds

Toluene and excess pyridine (Analar grade, dried over barium oxide) were vacuum distilled onto the halide. The reaction vessel was sealed, shaken, and opened in the dry-box for collection of the product.

TABLE IV. Analytical Data.

Compound	Colour	Found, %			Calculated, %		
		C	H	X	C	H	X
$AsBr_3 \cdot 2py$	yellow	25.9	2.8	50.6	25.4	2.1	50.7
$AsI_3 \cdot py$	orange	10.7	0.97	70.7	11.2	0.94	71.4
$SbCl_3 \cdot py$	white	19.5	2.0	34.0	19.5	1.6	34.6
$2SbCl_3 \cdot 3py$	white	–	–	30.7	–	–	30.7
$SbBr_3 \cdot 2py$	yellow	24.5	2.6	46.2	23.1	1.9	46.1
$2BiCl_3 \cdot 3py$	white	20.6	1.9	24.1	20.7	1.7	24.5
$BiBr_3 \cdot 2py$	yellow	20.8	2.1	39.7	19.8	1.7	39.5
$2AsCl_3 \cdot terpy$	yellow	30.8	2.0	35.6	30.2	1.8	35.7
$AsBr_3 \cdot terpy$	orange	–	–	43.5	–	–	43.8
$3SbCl_3 \cdot 2terpy$	yellow	30.5	2.5	27.8	31.3	1.9	27.7
$3SbBr_3 \cdot 2terpy$	orange	23.9	1.6	46.1	23.2	1.4	46.4
$3SbI_3 \cdot 2terpy$	red	18.9	1.3	57.0	18.2	1.1	57.9
$BiCl_3 \cdot terpy$	cream	32.9	2.6	19.1	32.8	2.0	19.4

Drying under vacuum was continued for only the 3–4 min required to remove the petrol ether used for washing. Therefore the higher pyridine adducts reported in the literature,[12] but for which no evidence was found, viz. $AsBr_3.3py$, $AsI_3.2py$, $AsI_3.3py$, $SbCl_3.2py$ and $BiCl_3.2py$, must be very unstable, if indeed they were formed at all. Repeated attempts to obtain $SbCl_3.2py$ without vacuum drying were unavailing. Distillation of excess pyridine (7 ml) without additional solvent onto antimony trichloride (1.1 g) gave a clear solution. When a portion of the solvent pyridine was removed crystals of composition $2SbCl_3.3py$ separated. They gave a distinctive X-ray powder pattern, and the absence of an undisplaced ligand band at 601 cm^{-1} showed there was no uncoordinated pyridine.[13] However, loss of pyridine under vacuum leaves $SbCl_3.py$ (m.p. 185°).

Spectra

Infrared spectra were recorded on nujol mulls using Perkin-Elmer 337 (to 400 cm^{-1}) and Grubb Parsons DM4 (500–200 cm^{-1}) spectrometers and an R.I.I.C. FS-720 interferometer (below 400 cm^{-1}).

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