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2,2′-Dipyridyl Adducts of the Group VB Trihalides and Their Ionization

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Received May 17, 1963

2,2′-Dipyridyl forms complexes dipy·MX_3 with the trihalides of arsenic, antimony, and bismuth. The compounds ionize in nitrobenzene solution, the dissociation increasing from chlorides to iodides but decreasing from arsenic to bismuth. This latter trend is consistent with the increasing preference for higher coordination numbers down the group.

The trihalides of phosphorus, arsenic, antimony, and bismuth are known to react with nitrogen bases to give crystalline complexes such as $(CH_3)_3N \cdot PCl_3$,[1] py·$AsCl_3$,[2] 2py·$AsCl_3$,[3] 3py·$2SbI_3$,[4] and 2py·BiX_3.[4] Composition types vary, but it is significant that only the unstable monoamine complexes from phosphorus trichloride and tribromide are known, suggesting lower acceptor properties for the phosphorus compounds.

Walden[5] in 1903 noted that a solution of pyridine in arsenic trichloride is an electrolyte, pointing to the formation of an ionized complex in this system. In the present investigation the bidentate ligand 2,2′-dipyridyl has been used to obtain a series of stable complexes of uniform composition dipy·MX_3 whose possible ionization trends could be examined. Though no direct evidence is available on the constitution of these compounds in the crystalline state, it seemed that their ionization in solution might be influenced in part by the coordination preferences of the central atom. For measurement of conductivities, nitrobenzene was chosen as being a solvent which does not solvate strongly.

Observations have been extended to organo-substituted halides RMX_2 which also form monodipyridyl adducts, and the dipyridinium salts of the complex anions $C_6H_5SbI_3^-$ and $C_6H_5BiBr_3^-$ have been characterized as reference compounds.

Experimental

Dipyridyl Complexes of the Arsenic, Antimony, and Bismuth Trihalides.—The arsenic and antimony compounds were precipitated by mixing toluene solutions of the ligand (1.0 mmole in 25 ml.) and halide (1.0 mmole in 50 ml.). For the less soluble bismuth halides dry acetone was used as solvent. The adducts were collected on a fritted filter and washed with the pure solvent, all manipulations being made in a drybox. The product was removed from the drybox in a capsule which was then attached to a vacuum line (10^{-4} mm.) for pumping off solvent. It was determined that the compositions of the adducts were uninfluenced by the proportions in which the reactants were used. Arsenic trichloride, antimony tribromide, and bismuth tribromide were distilled immediately before use. Freshly opened reagent grade samples of the remaining halides were used as received.

dipy·$AsCl_3$ suffers rapid hydrolysis on exposure to air. X-Ray powder photographs showed arsenic(III) oxide to be a decomposition product. The other trihalide complexes are unchanged in air.

The complexes were analyzed (see Table I) for halogen by the Volhard titration. In the combustion analyses samples were mixed with tungsten(VI) oxide for carbon determination and with cobalt(III) oxide for nitrogen.

Behavior of Phosphorus Trihalides toward Dipyridyl.—The chloride and bromide (purified in a high-vacuum system) showed no reaction at ordinary temperature. Phosphorus triiodide and dipyridyl in benzene produced a brown precipitate in low (*ca.* 10%) yield. The X-ray powder photograph was identical with that of a sample of dipyridinium triiodide from dipyridinium iodide and iodine. Repeated tests, all made with rigorous exclusion of moisture, failed to eliminate this product. Pyridine reacted similarly to give pyridinium triiodide.

Anal. Calcd. for $C_{10}H_9N_2I_3$: C, 22.3; H, 1.7; N, 5.2. Found: C, 22.7; H, 2.0; N, 4.8.

Complexes from Organosubstituted Halides. (1) Dipyridyl Derivatives.—dipy·CH_3AsI_2 was precipitated from benzene, dipy·$C_6H_5SbI_2$ from methylene chloride, and dipy·$C_6H_5BiBr_2$ from warm benzene, using the same procedure as for the trihalide adducts. The parent halides were prepared as in the literature.[6-8]

Dipyridyl did not react with diphenylchlorostibine, diphenylchlorobismuthine, or diphenyliodobismuthine under the same conditions.

(2) **Anion Complexes.**—The dipyridinium salt of $C_6H_5SbI_3^-$ separated as orange-red needles upon addition of 0.16 g. of dipyridyl to 0.5 g. of phenyldiiodostibine in 25 ml. of ethanol and 6 ml. of constant-boiling hydriodic acid freshly distilled from red phosphorus. A solution 0.8×10^{-3} *M* in nitrobenzene gave $\Lambda_m = 17.5$ at 25°. In methylene chloride solution the salt showed an absorption maximum at 360 mμ characteristic of the anion.

The salt dipy·$H[C_6H_5BiBr_3]$ was obtained similarly from phenyldibromobismuthine (0.4 g. in 30 ml. of ethanol and 5 ml. of concentrated hydrobromic acid). Λ_m was 23.0 at 0.8×10^{-3} *M*.

Anal. Calcd. for $C_{16}H_{14}N_2SbI_3$: C, 26.1; H, 1.9; N, 3.8. Found: C, 25.7; H, 2.2; N, 3.7.

Anal. Calcd. for $C_{16}H_{14}N_2BiBr_3$: C, 28.1; H, 2.1; N, 4.1; Br, 35.1. Found: C, 27.0; H, 2.2; N, 4.4; Br, 35.9.

Physical Measurements.—All solutions were made up in a drybox. Glassware was preflushed with dry air while hot (120°). Conductivities were measured using a Philips GM4249 bridge and a cell (constant 0.331) with removable dip-type smooth platinum electrodes. Nitrobenzene (Hopkin and Williams "Analar") dried over calcium chloride[9] or calcium sulfate and fractionally distilled under reduced pressure gave a specific conductivity less than 10^{-7} ohm^{-1} cm.$^{-1}$. Storage over Linde 4A Molecular Sieve pellets reduced the conductivity to less than

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TABLE I

Complex	Color	Calcd., % C	H	N	X	Found, % C	H	N	X
dipy·$AsCl_3$	Pale yellow	35.6	2.4	8.3	31.6	...	...	...	32.5
dipy·$AsBr_3$	Bright yellow	25.5	1.7	6.0	50.9	25.8	1.9	5.2	50.6
dipy·AsI_3	Brown	19.6	1.3	4.6	62.2	18.9	1.9	4.6	...
dipy·$SbCl_3$	Cream	31.2	2.1	7.3	27.7	29.3	2.2	7.2	27.7
dipy·$SbBr_3$	Bright yellow	23.2	1.6	5.4	46.3	23.0	1.7	4.5	45.9
dipy·SbI_3	Dark red	18.2	1.2	4.3	57.8	17.7	1.0	2.8	57.3
dipy·$BiCl_3$	White	25.5	1.7	5.9	22.6	25.7	1.9	5.9	22.6
dipy·$BiBr_3$	Cream	19.9	1.3	4.6	39.6	20.3	1.6	4.6	39.3
dipy·BiI_3	Bright red	16.1	1.1	3.8	51.6	16.1	1.3	3.2	50.6
dipy·CH_3AsI_2	Golden yellow	24.0	1.6	5.6	50.8	...	...	...	49.8
dipy·$C_6H_5SbI_2$	Red	31.4	2.1	4.7	41.7	30.6	2.6	4.7	40.9
dipy·$C_6H_5BiBr_2$	Cream	31.9	2.2	4.7	26.6	33.0	2.6	4.2	26.4

10^{-8} ohm^{-1} cm.$^{-1}$, but this further treatment did not alter the conductivities of the dipyridyl adducts. Conductivities were reproducible as between different batches of solvent and solute. Dimethylformamide was purified according to Prue and Sherrington[10] and stored over molecular sieve pellets.

X-Ray powder photographs were obtained using a Philips-11.48 cm. diameter camera with copper Kα radiation.

Results

Conductometric titration of the trihalides against dipyridyl (Fig. 1, lower curve) confirms that the conductivity has almost reached its limiting value at the equimolecular ratio. Table II gives molar conductivities of the trihalide complexes. Though the low solubility of dipy·$BiBr_3$ in nitrobenzene made reliable measurement impossible, the conductivities of the bismuth complexes in dimethylformamide show the same increasing order from chloride to iodide.

TABLE II

MOLAR CONDUCTIVITIES (OHM^{-1} CM.^{2} MOLE^{-1}) OF dipy·MX_3 COMPLEXES AT 10^{-3} M IN NITROBENZENE[a]

	Cl	Br	I
As	19.0	23.9	27.3
Sb	10.8	14.9	20.0
Bi	2.5	...	3.4[b]
	3.3[c]	5.0[c]	6.2[c]

[a] Λ_m = 25–35 for a 1:1 strong electrolyte. [b] At 0.5 × 10^{-3} M. [c] In dimethylformamide (Λ_m = 60–80).

The conductivities of the dipyridyl adducts from methyldiiodoarsine, phenyldiiodostibine, and phenyldibromobismuthine at 21.1, 8.2, and 1.5 ohm^{-1} cm., mole^{-1}, respectively, are lower than those from the corresponding trihalide adducts. For phenyldiiodostibine–dipyridyl the variation in molar conductivity over the range 4 × 10^{-3} to 2 × 10^{-4} M in nitrobenzene is given by $\Lambda_m = 10.8 - 83\sqrt{c}$.

The triiodides [dipy·SbI_2]I_3 and [dipy·C_6H_5SbI]I_3 obtained by iodination of iodides have Λ_m = 33.6 and 30.6, respectively. These higher values enable the conversion of iodide to triiodide to be followed by conductometric titration (Fig. 1, upper curve). With [dipy·C_6H_5SbI]I_3 the absence of interfering bands enabled the characteristic I_3^- spectral absorption at 362 mμ[11] with the expected extinction coefficient (24,000) to be recorded in methylene chloride solution.

X-Ray powder patterns (Table III) showed each of the pairs dipy·$SbBr_3$, dipy·$BiBr_3$ and dipy·SbI_3, dipy·BiI_3 to be isomorphous, and the crystalline bromides and iodides to be of closely similar structure, despite widely different molar conductivities.

TABLE III

d VALUES AND INTENSITIES OF X-RAY POWDER LINES

dipy·$SbBr_3$	dipy·$BiBr_3$	dipy·SbI_3	dipy·BiI_3
8.02 (s)	8.24 (s)	8.26 (s)	8.51 (s)
7.05 (m)	7.05 (m)	7.35 (m)	7.38 (m)
6.09 (m)	6.09 (m)	6.32 (w)	6.32 (w)
5.06 (w)	5.10 (w)	5.09 (m)	5.14 (s)
3.73 (m)	3.83 (m)	3.93 (m)	3.98 (m)
3.54 (m)	3.61 (m)	3.72 (m)	3.77 (m)
3.04 (s)	3.09 (s)	3.24 (s)	3.29 (s)
2.69 (m)	2.70 (m)	2.93 (m)	2.94 (m)
2.42 (w)	2.40 (w)	2.78 (w)	2.78 (w)
2.16 (w)	2.15 (w)	2.23 (m)	2.23 (m)

Discussion

The possibility that the variations in the conductivities of the trihalide adducts arise from reversibility of the equilibrium

$$\text{dipy} + MX_3 \rightleftharpoons \text{dipy}\cdot MX_3$$

rather than from varying ionization is excluded because an excess of dipyridyl produces little increase in conductivity. Moreover, simple interpretation based on atomic sizes and bond polarities would suggest that tne equilibrium should lie furthest to the right with bismuth trichloride and least with arsenic triiodide, and so give the reverse order.

In specific cases there is evidence for a simple ionization

$$\text{dipy}\cdot MX_3 \rightleftharpoons [\text{dipy}\cdot MX_2]^+ + X^-$$

rather than a more complicated type leading to the formation of a complex halide anion. For example, the absorption spectrum of dipy·$C_6H_5SbI_2$ in methylene chloride does not show the peak at 360 mμ which is characteristic of the anion $C_6H_5SbI_3^-$, which might arise from an alternative ionization

$$2\text{dipy}\cdot C_6H_5SbI_2 \rightleftharpoons [(\text{dipy})_2C_6H_5SbI]^+ + C_6H_5SbI_3^-$$

The reaction of the iodides with iodine to produce the triiodide shows the availability of the halide ion. For the triiodide derived from dipy·$C_6H_5SbI_2$, the I_3^-

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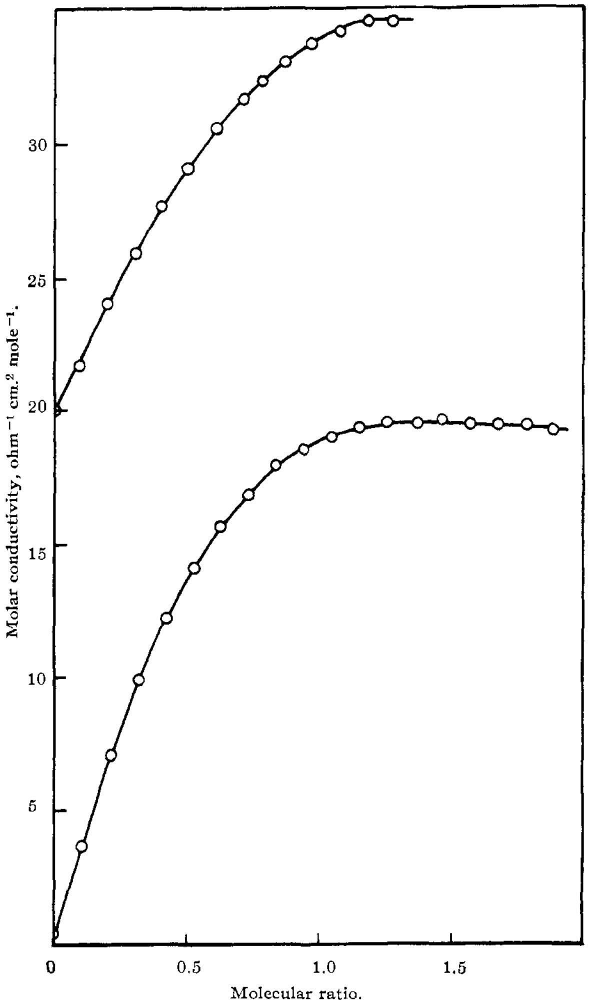

Fig. 1.—Molar conductivity plotted against molecular ratio for titration of (i) dipy·SbI_3 with iodine (upper curve), and (ii) arsenic trichloride with dipyridyl (lower curve).

absorption band is superimposed upon the otherwise unchanged spectrum of the parent iodide, thus confirming the constitution of the dissolved compounds to be $[dipy \cdot C_6H_5SbI]^+I_3^-$ and $[dipy \cdot C_6H_5SbI]^+I^-$. There remains the possibility that the mode of ionization within the series of complexes may vary, but the regular trends toward conductivity values characteristic of 1:1 electrolytes render this unlikely. With the diarsine adducts of the trihalides,[12] where higher solubilities enabled molecular weight determinations and anion replacement, the results indicated simple dissociation of halide ion from the monomeric complexes.

The ionization trends accord with those to be expected simply on steric grounds. The increasing dissociation from chlorides to iodides can be linked more specifically with several interrelated properties. Thus "ionic bond energies"[13] fall progressively from chlorides to iodides, *viz.*: As–Cl, 229; As–Br, 216; As–I, 209; Sb–Cl, 184; Sb–Br, 173; Sb–I, 165 cal. Solvation energies of the halide ions in aprotic solvents,[14] increasing from chloride to iodide, would enhance the trend, as would also the lower electronegativity of the halogen atoms within the cation. However, the variation down the group is the reverse of that expected from the ionization potentials of arsenic, antimony, and bismuth, from the polarities of the halogen bonds,[15] and from the probable charge transfer from nitrogen to the coordination center. The order also runs counter to that expected from the aqueous chemistry of the elements, but direct comparison with aqueous systems is not justifiable since solvolysis of the halide occurs in protic solvents.

The decreasing ionization down the group seems part of a more general effect common to several series of compounds. The diarsine complexes[12] in which there can be little or no resultant charge transfer to the coordination center are less strongly ionized than the dipyridyl compounds but the ionization trends are similar and continue to the phosphorus halides. Ionization is therefore assisted by electron accession from a coordinating base, but is not conditional upon it. The same ionization order appears with oxidation state V compounds without the stimulus of complex formation. Halides of types R_3PX_2[16] and R_3AsX_2[17] are ionic or easily ionized, but $(CH_3)_3SbX_2$[18] halides are poorly ionized and bismuth compounds $(C_6H_5)_3BiX_2$[19] are covalent. Crystalline phosphorus pentahalides are ionic but antimony pentachloride is covalent.[20] The variation in ionization within each of these classes of compounds is consistent with that to be expected if the dissociation were influenced primarily by the preference of the lighter elements for lower coordination numbers. The inability of the phosphorus halides to form dipyridyl complexes, when they yield (unstable) trimethylamine derivatives, can be ascribed to the low acceptor properties of the halides in conjunction with the preference for lower coordination numbers.

The reduced electron acceptor properties of organo-substituted halides would account for the inability of the R_2MX halides to form complexes, as also for the lower conductivities of dipy·RMX_2 adducts than the corresponding dipy·MX_3 compounds. Ionization in the dipy·RMX_2 series, nevertheless, follows the same order and bears the same relationship to the coordination preference of the central atom.

Acknowledgment.—The authors are indebted to Dr. J. E. Fergusson for his helpful interest. W. R. R. participated in the work as holder of a Research Fund Fellowship.

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