680. *Bipyridyl and Terpyridyl Complexes from Halides of Group* IVB *Elements*

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Bipyridyl complexes formed by halides of tetravalent germanium, tin, and lead are usually of 1 : 1 composition and little ionised in nitrobenzene. The germanium tetraiodide complex of exceptional 2 : 1 composition is formulated as $[2Bipy,GeI_2]^{2+} 2I^-$. Terpyridyl forms ionic 1 : 1 complexes with germanium and tin tetraiodides, but undissociated 1 : 1 complexes with diphenyl-lead dihalides. Derivatives from the remaining tin tetrahalides are formulated as $[Terpy,SnX_3]^+_2 SnX_6^{2-}$. Organotin halides form complexes of 1 : 1, 2 : 3, and 1 : 2 compositions through anion variation, but all contain a six-co-ordinate cation. In failing to react with germanium tetrachloride, germanium tetrabromide, and the trimethyltin halides, terpyridyl is a weaker ligand than bipyridyl.

Comparison of the constitution of complexes from germanium, tin, and lead halides shows that in critical cases ionic character decreases from germanium to lead.

THE complexes formed by halides of silicon, germanium, and tin with monodentate ligands are usually of composition MX_4,L_2 corresponding to the development of six-co-ordination.[1] Yet there is also evidence of structural diversity. The tetrapyridine adduct from silicon tetraiodide [2] is formulated *cis*-$[4Py,SiI_2]^{2+} 2I^-$ with six-co-ordinate silicon as in $2Py,SiCl_4$, but the complex $Bipy,Ph_3SiI$ [3] which is ionised in methylene chloride may contain five-co-ordinate silicon. Silicon tetrachloride forms only a 1 : 1 compound with trimethylamine.[4] The crystalline complex Py,Me_3SnCl contains five-co-ordinate tin [5] as in several polymerised organotin compounds, R_3SnX,[6] and probably also the halide-ion complexes of equimolar composition.[7]

While bipyridyl complexes of most of the germanium [8] and tin [9] tetrahalides have been prepared, polydentate ligands have not been used extensively with these elements. The requirements by a ligand of more than one co-ordination position can in itself emphasise differences in co-ordination behaviour. For this reason we have examined complexes

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[1] Beattie, *Quarterly Rev.*, 1963, **17**, 382.
[2] Beattie, Gilson, Webster, and McQuillan, *J.*, 1964, 238.
[3] Corey and West, *J. Amer. Chem. Soc.*, 1963, **85**, 4034.
[4] Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 4318; Fergusson, Grant, Hickford, and Wilkins, *J.*, 1959, 99.
[5] Hulme, *J.*, 1963, 1524.
[6] Van der Kerk, Luijten, and Janssen, *Chimia*, 1962, **16**, 10; Hathaway and Webster, *Proc. Chem. Soc.*, 1963, 14; Clark, O'Brien, and Trotter, *ibid.*, p. 85; Clark and O'Brien, *Inorg. Chem.*, 1963, **2**, 540.
[7] Seyferth and Grim, *J. Amer. Chem. Soc.*, 1961, **83**, 1610; Gielen, Nasielski, and Yerneaux, *Bull. Soc. chim. belges*, 1963, **72**, 594; Sharp and Sheppard, *J.*, 1957, 674.
[8] Lebedev and Tronev, *Zhur. neorg. Khim.*, 1960, **5**, 1725.
[9] Allison and Mann, *J.*, 1949, 2915.

formed by halides of tetravalent germanium, tin, and lead with 2,2′-bipyridyl and 2,2′:6′,2″-terpyridyl. It is known that terpyridyl differs from bipyridyl in failing to react with silicon tetrachloride.[10] This difference was found to persist in limiting cases with germanium and tin compounds, *e.g.*, towards germanium tetrachloride and the trimethyltin halides, but the strengthened electron-acceptor properties of the heavier elements minimises this disability.

The bipyridyl adducts (Table 1) of this group are typically of 1 : 1 composition and show low molar conductivities in nitrobenzene. The bidentate ligand therefore reinforces the development of six-co-ordination throughout the group. The exceptional compound 2Bipy,GeI$_4$, having the conductivity characteristic of a 2 : 1 electrolyte in nitrobenzene, is presumably [2Bipy,GeI$_2$]$^{2+}$ 2I$^-$. It is thus analogous to the tetrapyridine complex [4Py,SiI$_2$]$^{2+}$ 2I$^-$. Introduction of organic substituents must reduce the electron-acceptor properties of germanium halides markedly because the diphenylgermanium dihalides did not react with bipyridyl. Triphenylgermanium iodide was found, however, to give an unstable derivative of approximate composition Bipy,Ph$_3$GeI, which is ionised in nitrobenzene. Bipyridyl co-ordination by tin extends over R$_2$SnX$_2$ halides to the formation of unstable *covalent* complexes with trimethyltin (but not triphenyltin) halides.

TABLE 1

Bipyridyl complexes and molar conductivities (ohm^{-1} cm.^{2} mole^{-1}) at 10^{-3}M in nitrobenzene (at 25°)

Bipy,GeCl$_4$	0·7 [a]	Bipy,GeBr$_4$ [c]		[2Bipy,GeI$_2$]$^{2+}$ 2I$^-$	42·8
Bipy,SnCl$_4$	0·45 [b]	Bipy,SnBr$_4$	0·25 [a]	Bipy,SnI$_4$	0·5 [a]
		Bipy,MeSnBr$_3$	0·5	Bipy,MeSnI$_3$	2·4
Bipy,Me$_2$SnCl$_2$	0·3	Bipy,Me$_2$SnBr$_2$	0·5	Bipy,Me$_2$SnI$_2$	1·2
Bipy,Me$_3$SnCl	0·35	Bipy,Me$_3$SnBr	0·1	Bipy,Me$_3$SnI	0·1
Bipy,Ph$_2$PbCl$_2$	0·3	Bipy,Ph$_2$PbBr$_2$	0·9	Bipy,Ph$_2$PbI$_2$	0·6

[a] At 0·6 × 10^{-3}M. [b] At 0·35 × 10^{-3}M. [c] Ref. 8. This compound was not prepared in the present work.

Towards germanium tetrahalides terpyridyl was found to react only with the iodide, but it combines with tin halides (Table 2) of all types except R$_3$SnX. Of these tin complexes those from the iodides are equimolecular compounds behaving as 1 : 1 electrolytes in nitrobenzene, this pointing to the typical formulation [Terpy,SnI$_3$]$^+$ I$^-$. The cation from Terpy,Me$_2$SnI$_2$ was characterised by preparation of a tetraphenylborate [Terpy,Me$_2$SnI]$^+$ BPh$_4$$^-$. Tin tetrachloride and tetrabromide differ from the tetraiodide in forming complexes of composition 2Terpy,3SnX$_4$. A solution of the chloride in nitrobenzene had a molar conductivity, as based on this formula, of 37·3 ohm^{-1} cm.^{2} mole^{-1}, which points to the constitution [Terpy,SnCl$_3$]$^+{}_2$SnCl$_6{}^{2-}$. This complex (like those from the other tetrahalides) was insufficiently soluble in alcohol to permit conversion into derivatives, but a tetraphenylborate [Terpy,n-BuSnCl$_2$]$^+$ BPh$_4$$^-$ was prepared from the

TABLE 2

Terpyridyl complexes and molar conductivities (ohm^{-1} cm.^{2} mole^{-1}) at 10^{-3}M in nitrobenzene (at 25°)

(GeCl$_4$) [a]		(GeBr$_4$) [a]		[Terpy,GeI$_3$]$^+$ I$^-$	24·2
[Terpy,SnCl$_3$]$^+{}_2$ SnCl$_6{}^{2-}$	37·3 [b]	[Terpy,SnBr$_3$]$^+{}_2$ SnBr$_6{}^{2-}$ [c]		[Terpy,SnI$_3$]$^+$ I$^-$	23·2
[Terpy,BuSnCl$_2$]$^+{}_2$ BuSnCl$_5{}^{2-}$		[Terpy,MeSnBr$_2$]$^+$ MeSnBr$_4{}^-$	22·9 [d]	[Terpy,MeSnI$_2$]$^+$ I$^-$	23·2 [d]
[Terpy,Me$_2$SnCl]$^+$ Me$_2$SnCl$_3{}^-$	13·8	[Terpy,Me$_2$SnBr]$^+$ Me$_2$SnBr$_3{}^-$	15·3	[Terpy,Me$_2$SnI]$^+$ I$^-$	18·5
[Terpy,Ph$_2$SnCl]$^+$ Ph$_2$SnCl$_3{}^-$	14·1	[Terpy,Ph$_2$SnBr]$^+$ Ph$_2$SnBr$_3{}^-$	10·2		
Terpy,Ph$_2$PbCl$_2$	1·9	Terpy,Ph$_2$PbBr$_2$	2·1	Terpy,Ph$_2$PbI$_2$	2·3

[a] No complex formed. [b] At 0·3 × 10^{-3}M. [c] Too insoluble for measurement of conductivity. [d] At 0·4 × 10^{-3}M.

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[10] Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.

more soluble n-butyltin trichloride adduct 2Terpy,$3Bu^nSnCl_3$ of the same composition type. The ultraviolet reflectance spectrum of 2Terpy,$3SnBr_4$ shows a maximum at 350 mμ as does the hexabromostannate ion in its potassium and tetramethylammonium salts.

Methyltin tribromide and the organotin dichlorides and dibromides yield 1 : 2 adducts. These compounds have molar conductivities consistent with the formulations $[Terpy,MeSnBr_2]^+ [MeSnBr_4]^-$ and $[Terpy,R_2SnX]^+ [R_2SnX_3]^-$, and yield the corresponding tetraphenylborates. The evidence does not enable a decision between a monomeric (five-co-ordinate) or a polymeric (six-co-ordinate, halogen bridged) anion, but the existence of varied five-co-ordinate tin complexes [5-7] makes the former probable.

The reactions of the tin halides with terpyridyl thus all lead to formation of a six-co-ordinated cation through ionisation of one halogen, but the stoicheiometric composition of the product is determined by the capacity of the excess of tin halide for co-ordinating this anion. Due to the low stability of hexaiodostannate [11] the iodide ion from tin tetraiodide remains free. With the other tetrahalides formation of hexahalogenostannate determines the composition. With the organotin compounds yielding complexes of composition terpyridyl : halide = 1 : 2 reduction of the acceptor properties of the tin through substitution of chlorine by bromine, or of halogen by an organic group apparently limits co-ordination within the anion to one additional halide ion. That the different compositions of the 1 : 2 and 1 : 1 terpyridyl complexes arise from a different stoicheiometry of the primary reactions leading to the dissolved products, and not to some structural feature peculiar to the solid was shown by conductometric titration in nitrobenzene. Though addition of terpyridyl to dimethyltin dichloride and di-iodide beyond the respective 1 : 2 and 1 : 1 molar ratios gave a slow continuing increase in conductivity in each case (perhaps through repression of non-ionic dissociation) the end-points at these ratios were clear.

The diphenyl-lead dihalides differ markedly from organotin halides in forming a uniform series of 1 : 1 terpyridyl adducts which are little ionised. Their formation is evidence of the stronger electron acceptor properties of lead and of its ability to increase its co-ordination number beyond six.

Comparing bipyridyl and terpyridyl co-ordination by the lighter elements there is evidence of more than one factor restricting the formation of terpyridyl complexes. The failure of terpyridyl to react with silicon and germanium tetrachlorides is attributable to difficulty in ionisation of a halogen rather than to an intrinsically low electron donor-acceptor interaction. The situation is reversed with trimethyltin iodide because the co-ordination of terpyridyl by other tin iodides does cause ionisation. The co-ordinate linkage is already weak in the unstable bipyridyl complexes Bipy,Me_3SnX; in possible terpyridyl derivatives the bonding would be still weaker due to unfavourable angles and deformation of the ligand. This occurs in Terpy,$ZnCl_2$ [12] and would be accentuated by the larger tin atom.

In the range and composition of its complexes with bipyridyl and terpyridyl germanium resembles silicon more closely than tin. Towards terpyridyl tin and lead show progressive differences arising from increasing acceptor properties. Formation of the compound Terpy,GeI_4 is assisted by ionisation of the Ge–I bond which offsets accumulation of negative change on the germanium. The tin halides, in reacting with terpyridyl also through ionisation, form a wide range of derivatives in which there is co-operative formation of anion complexes. With lead, co-ordination of terpyridyl is no longer dependent upon ionisation. There is thus some parallel between ionisation in nitrobenzene of complexes of Group IVB and VB halides,[13] with lower ionisation for the heavier elements. As between germanium and tin it is significant that germanium tetraiodide forms a complex

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[11] Auger and Karantassis, *Compt. rend.*, 1925, **180**, 1845; Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[12] Corbridge and Cox, *J.*, 1956, 594.

[13] Roper and Wilkins, *Inorg. Chem.*, 1964, **3**, 500.

$[2\text{Bipy},\text{GeI}_2]^{2+}\ 2\text{I}^-$, whereas the tin adduct Bipy,SnI_4 is little ionised. The inability of triphenyltin iodide to react with bipyridyl when triphenylsilicon iodide forms an ionised complex is a further example of the same trend.

EXPERIMENTAL

Adducts were prepared by direct combination of halide and ligand, usually in petroleum for the tin compounds. The insoluble complex was washed in a sintered-glass crucible and residual solvents removed under vacuum. In no case did variation of the proportions in which the components were mixed influence the composition of the product. The tin and lead adducts seemed unaffected by atmospheric moisture, but undue exposure to air was avoided.

Halides sensitive to moisture were handled in a dry-box. Prior purification of germanium tetrachloride was carried out in a vacuum line. Organosubstituted halides were prepared by methods described in the literature. Samples of n-butyltin trichloride, dimethyltin dichlororide, and trimethyltin chloride were kindly supplied by M and T Chemicals, Inc., Rahway, New Jersey.

Conductivities in nitrobenzene were measured as described previously.

Halide was usually determined by the Volhard method. Prolonged boiling with alkali was necessary for complete hydrolysis of certain bipyridyl complexes, *e.g.*, those from stannic halides, but terpyridyl complexes were more easily decomposed. Carbon, hydrogen, and nitrogen were determined in the microanalytical laboratory, University of Otago.

Adducts from the Germanium Halides.—Germanium tetrachloride was distilled from a vacuum line directly into a frozen solution of bipyridyl in benzene. Reaction occurred on warming. The bipyridyl–germanium tetrachloride complex was transferred to a dry-box for collection and washing (Found: C, 32·5; H, 2·45; N, 7·2; Cl, 38·5. Calc. for $\text{C}_{10}\text{H}_8\text{Cl}_4\text{GeN}_2$: C, 32·45; H, 2·2; N, 7·6; Cl, 38·4%). Terpyridyl gave no precipitate with germanium tetrachloride and only a trace of precipitate with the tetrabromide.

The bipyridyl complex from germanium tetraiodide was precipitated from benzene, and the terpyridyl compound from toluene. Both *complexes* were red-brown and were rapidly hydrolysed to germanium dioxide on exposure to air (Found for 2Bipy,GeI_4: I, 57·3. $\text{C}_{20}\text{H}_{16}\text{GeI}_4\text{N}_4$ requires I, 57·0%. Found for Terpy,GeI_4: I, 61·2. $\text{C}_{15}\text{H}_{11}\text{GeI}_4\text{N}_3$ requires I, 62·4%).

No insoluble bipyridyl adducts were obtained from diphenylgermanium dichloride, diphenylgermanium di-iodide, or triphenylgermanium bromide on mixing concentrated solutions in petroleum. The pale yellow bipyridyl complex from triphenylgermanium iodide was obtained by crystallisation from a methylene chloride solution evaporated under dry nitrogen, but recrystallisation failed to give an analytically pure product. An approximate value of Λ_m in nitrobenzene is 12 $\text{ohm}^{-1}\text{cm.}^2\text{mole}^{-1}$.

Adducts from Tin Tetrahalides.—Bipyridyl complexes were prepared analytically pure both from petroleum and from alcohol, following Allison and Mann.[9] Terpyridyl derivatives were precipitated from petroleum. The *chloride complex* was white, the *bromide complex* pale cream, and the *iodide* dark red [Found for the chloride: C, 29·5; H, 2·3; Cl (gravimetric), 33·3; N, 6·2. $\text{C}_{30}\text{H}_{22}\text{Cl}_{12}\text{N}_6\text{Sn}_3$ requires C, 28·9; H, 1·8; Cl, 34·0; N, 6·7%. Found for the bromide: C, 20·1; H, 1·5; Br (gravimetric), 53·6; N, 4·2. $\text{C}_{30}\text{H}_{22}\text{Br}_{12}\text{N}_6\text{Sn}_3$ requires C, 20·2; H, 1·2; Br, 53·9; N, 4·8%. Found for the iodide: C, 21·3; H, 1·5; I, 60·0; N, 4·3; Sn, 14·0. $\text{C}_{15}\text{H}_{11}\text{I}_4\text{N}_3\text{Sn}$ requires C, 21·0; H, 1·3; I, 59·1; N, 4·9; Sn, 13·8%].

Bipyridyl Complexes from Organotin Halides.—The following *complexes* were obtained: (*a*) Bipy,Me_2SnCl_2, m. p. 238—239°, separating as white microcrystals from benzene (Found: C, 38·5; H, 3·9; N, 7·0. Calc. for $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Sn}$: C, 38·4; H, 3·7; N, 7·4%). (*b*) Bipy,Me_3SnCl, white silky needles, m. p. 70° (Found: Cl, 9·8. $\text{C}_{13}\text{H}_{17}\text{ClN}_2\text{Sn}$ requires Cl, 10·0%). (*c*) Bipy,MeSnBr_3, m. p. 245° (decomp.) [Found: C, 25·6; H, 2·3; Br (gravimetric), 44·9; N, 5·4. $\text{C}_{11}\text{H}_{11}\text{Br}_3\text{N}_2\text{Sn}$ requires C, 24·9; H, 2·1; Br, 45·3; N, 5·3%]. (*d*) Bipy,Me_2SnBr_2, m. p. 224° (Found: C, 30·8; H, 3·45; Br, 34·3; N, 5·6. $\text{C}_{12}\text{H}_{14}\text{Br}_2\text{N}_2\text{Sn}$ requires C, 30·0; H, 3·0; Br, 34·4; N, 6·0%). (*e*) Bipy,Me_3SnBr, long needles, m. p. 65° (Found: C, 37·6; H, 4·6; N, 6·6. $\text{C}_{13}\text{H}_{17}\text{BrN}_2\text{Sn}$ requires C, 39·0; H, 4·3; N, 7·0%). (*f*) Bipy,MeSnI_3, yellow needles, m. p. 260° (decomp.) (Found: C, 19·7; H, 1·6; N, 4·2. $\text{C}_{11}\text{H}_{11}\text{I}_3\text{N}_2\text{Sn}$ requires C, 20·0; H, 1·9; N, 3·7%). (*g*) Bipy,Me_2SnI_2, crystals, m. p. 214° (Found: C, 26·1; H, 2·7; N, 4·6. $\text{C}_{12}\text{H}_{14}\text{I}_2\text{N}_2\text{Sn}$ requires C, 25·8; H, 2·5; N, 5·0%). (*h*) Bipy,Me_3SnI, white silky needles, m. p. 71° (Found: I, 27·7. $\text{C}_{13}\text{H}_{17}\text{IN}_2\text{Sn}$ requires I, 28·4%).

The complexes from the trimethyltin halides are very unstable, losing the tin halide quantitatively on exposure to air. They are easily soluble in organic solvents and are best prepared from petroleum (b. p. 35—60°). Triphenyltin iodide gave no reaction with bipyridyl.

Terpyridyl Complexes from Organotin Halides.—These *compounds* were precipitated quantitatively as fine crystals from petroleum. Yields therefore served as a preliminary indication of compositions. The compounds are soluble in alcohol, with the solubilities decreasing from chlorides to iodides, but increasing with the number of organic substituents. The complexes were characterised as follows: (*a*) 2Terpy,3BuSnCl$_3$, m. p. 223° (decomp.) [Found: C, 37·3; H, 3·9; Cl (gravimetric), 24·3; N, 5·9. $\mathrm{C_{42}H_{49}Cl_9N_6Sn_3}$ requires C, 38·4; H, 3·8; Cl, 24·35; N, 6·4%]. (*b*) Terpy,2Me$_2$SnCl$_2$, m. p. 182—186° (Found: C, 34·7; H, 3·8; N, 5·5. $\mathrm{C_{19}H_{23}Cl_4N_3Sn_2}$ requires C, 34·0; H, 3·4; N, 6·2%). (*c*) Terpy,2Ph$_2$SnCl$_2$, m. p. 104° (Found: C, 51·0; H, 3·5; N, 4·4. $\mathrm{C_{39}H_{31}Cl_4N_3Sn_2}$ requires C, 50·8; H, 3·4; N, 4·6%). (*d*) Terpy,2MeSnBr$_3$, decomposes above 210° [Found: C, 21·9; H, 1·9; Br (gravimetric), 48·1; N, 4·3. $\mathrm{C_{17}H_{17}Br_4N_3Sn_2}$ requires C, 20·8; H, 2·1; Br, 49·0; N, 5·1%]. (*e*) Terpy,2Me$_2$SnBr$_2$, m. p. 178—180° (Found: C, 27·2; H, 2·9; Br, 36·8; N, 4·6. $\mathrm{C_{19}H_{23}Br_4N_3Sn_2}$ requires C, 26·8; H, 2·7; Br, 37·5; N, 5·0%). (*f*) Terpy,2Ph$_2$SnBr$_2$, a cream powder, m. p. 120° (Found: C, 42·8; H, 3·1; Br, 29·3; N, 3·7. $\mathrm{C_{39}H_{31}Br_4N_3Sn_2}$ requires C, 42·7; H, 2·8; Br, 29·1; N, 3·8%). (*g*) Terpy,MeSnI$_3$, an orange brown powder decomposing above 170° (Found: C, 25·4; H, 2·3; I, 50·2; N, 5·0. $\mathrm{C_{16}H_{14}I_3N_2Sn}$ requires C, 25·7; H, 1·9; I, 50·9; N, 5·6%). (*h*) Terpy,Me$_2$SnI$_2$, a yellow powder, m. p. 202° (decomp.) (Found: C, 31·9; H, 3·2; I, 39·7; N, 5·9. $\mathrm{C_{17}H_{17}I_2N_3Sn}$ requires C, 32·0; H, 2·7; I, 39·8; N, 6·6%).

Tetraphenylboron Derivatives.—For conversion into these *derivatives* the terpyridyl complex was dissolved in the minimum quantity of warm alcohol (below 40°) and sodium tetraphenylborate added in approximately equimolar proportion. In the (typical) preparation of (*a*) [Terpy,Ph$_2$SnCl]$^+$ BPh$_4^-$, sodium tetraphenylborate (0·1 g. in 5 ml. of alcohol) was added to diphenyltin dichloride (0·3 g. in 30 ml. of alcohol). The pale yellow crystals which separated were washed with the solvent and pumped dry. The tetraphenylborate, m. p. 82°, had Λ_m = 17·9 ohm^{-1} cm.^{2} mole^{-1} (Found: C, 71·1; H, 4·8; N, 4·9. $\mathrm{C_{51}H_{41}BClN_3Sn}$ requires: C, 70·7; H, 5·3; N, 4·6%). Other *tetraphenylborates* were characterised as follows: (*b*) [Terpy,Ph$_2$SnBr]$^+$ BPh$_4^-$, m. p. 186°, Λ_m = 18·3 (Found: C, 66·1; H, 4·7; N, 4·3. $\mathrm{C_{51}H_{41}BBrN_3Sn}$ requires C, 67·7; H, 4·5; N, 4·6%). (*c*) [Terpy,MeSnBr$_2$]$^+$ BPh$_4^-$, decomposing above 210°, Λ_m = 22·9 (Found: C, 56·0; H, 4·2; N, 4·5. $\mathrm{C_{40}H_{34}BBr_2N_3Sn}$ requires C, 56·7; H, 4·0; N, 5·0%). (*d*) [Terpy,BuSnCl$_2$]$^+$ BPh$_4^-$, m. p. 223° (decomp.), Λ_m = 19·4 (Found: C, 63·2; H, 5·0; N, 5·1. $\mathrm{C_{43}H_{40}BCl_2N_3Sn}$ requires C, 64·5; H, 5·0; N, 5·1%). (*e*) [Terpy,Me$_2$SnI]$^+$ BPh$_4^-$, m. p. 190° (decomp.), Λ_m = 24·8 (Found: C, 58·5; H, 4·2; N, 4·6. $\mathrm{C_{41}H_{37}BIN_3Sn}$ requires C, 59·4; H, 4·5; N, 5·1%).

Complexes from the Biphenyl-lead Dihalides.—The *monobipyridyl complexes* separated crystalline on mixing the reactants in acetone. No alternative products were obtained even when using a three-fold excess of ligand, despite the existence of tetrapyridine adducts 4Py,Ph$_2$PbX$_2$.[14] (*a*) Bipy,Ph$_2$PbCl$_2$, m. p. above 300° (Found: C, 45·0; H, 3·6; N, 4·4. $\mathrm{C_{22}H_{18}Cl_2NPb}$ requires C, 44·9; H, 3·0; N, 4·8%). (*b*) Bipy,Ph$_2$PbBr$_2$, m. p. 250° (decomp.) (Found: C, 39·5; H, 3·1; Br, 23·2; N, 3·7. $\mathrm{C_{22}H_{18}Br_2N_2Pb}$ requires C, 39·0; H, 2·7; Br, 23·6; N, 4·1%). (*c*) Bipy,Ph$_2$PbI$_2$, pale yellow crystals, m. p. 180° (decomp.) (Found: C, 34·0; H, 2·6; N, 3·2. $\mathrm{C_{22}H_{18}Br_2N_2Pb}$ requires C, 34·2; H, 2·3; N, 3·6%).

The *terpyridyl complexes* crystallised when equimolar proportions of halide and ligand were mixed in alcohol. (*a*) Terpy,Ph$_2$PbCl$_2$, needles, m. p. 253—255° (Found: C, 48·4; H, 3·6; N, 5·9. $\mathrm{C_{27}H_{21}Cl_2N_3Pb}$ requires C, 48·6; H, 3·2; N, 6·3%). (*b*) Terpy,Ph$_2$PbBr$_2$, needles, m. p. 233—234° (Found: C, 43·4; H, 3·2; Br, 21·9; N, 5·3. $\mathrm{C_{27}H_{21}Br_2N_3Pb}$ requires C, 43·0; H, 2·8; Br, 21·2; N, 5·6%). (*c*) Terpy,Ph$_2$PbI$_2$, yellow needles, m. p. 150° (Found: C, 37·7; H, 2·9; N, 4·6. $\mathrm{C_{27}H_{21}I_2N_3Pb}$ requires C, 38·2; H, 2·5; N, 5·0%).

The terpyridyl complexes are noticeably more soluble than the corresponding bipyridyl complexes in alcohol and acetone. In dimethyl sulphoxide, there is evidence of non-ionic dissociation. The apparent molecular weight of Terpy,Ph$_2$PbCl$_2$ at 0·1M was 365 (Calc.: 665), and a 1·07 × 10^{-3}M solution had Λ_m = 11·5, as compared with 50—60 for a 1 : 1 electrolyte.

One of the authors (W. R. R.) participated in the work during tenure of a Research Fund Fellowship.

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[14] Pfeiffer, Truskier, and Disselkamp, *Ber.*, 1916, **49**, 2446.