

802. *Complex Halides of the Transition Metals. Part I.
Tetrahedral Nickel Complexes.*

By NAIDA S. GILL and R. S. NYHOLM.

The factors likely to favour the formation of tetrahedral complex halides of bivalent transition metals are discussed. The preparation of a series of complex halides of the type $R_2[M^{II}Hal_4]$, where $R = [Et_4N]^+$ or $[Ph_3MeAs]^+$, $M^{II} = Mn, Fe, Co, Ni, Cu, Zn$, and $Hal = Cl, Br, I$, is reported. The conductivity, spectra, magnetic susceptibility, and crystal structure of the Ni^{II} complexes have been studied and it is concluded that in these compounds the nickel atom is tetrahedrally co-ordinated. Relevant properties of the tetrahalogeno-complexes of Mn^{II} , Co^{II} , Cu^{II} , and Zn^{II} are reported.

As part of a systematic investigation of complex anionic metal halides we have been studying the compounds formed by the bivalent metals Cr^{II} , Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II} , using as cations large organic groups such as the tetraethylammonium and triphenylmethylarsonium ions. These are convenient as precipitants, partly because they form stable compounds and partly because they confer upon the products solubility in polar organic solvents such as nitromethane and nitrobenzene. We here outline the project and discuss the tetrahalogeno-nickel complexes in detail. Later papers will deal with Fe^{II} , Cr^{II} , and trivalent metals.

If one uses simple crystal-field theory as a guide (with a purely ionic model) one concludes¹ that, in the first Long Period, tetrahedral spin-free complex halides of the type $[M^{II}Hal_4]^{2-}$ are most likely to occur with the non-bonding configurations, d^0 , d_7^2 ,

¹ Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 381; see also Gillespie and Nyholm, *ibid.*, p. 339.

$d_{\gamma}^2 d_{\epsilon}^3$, $d_{\gamma}^4 d_{\epsilon}^3$, and d^{10} . These are exemplified severally by Ca^{II} , Ti^{II} , Mn^{II} , Co^{II} , and Zn^{II} . (A tetrahedral arrangement is also favoured for spin-paired d_{γ}^4 complexes, e.g., $[\text{ReCl}_4]^-$.) However, this theory does not take into account effects such as charge transfer due to covalent bonding or steric hindrance which, as we shall see, can lead to shapes different from those expected on the purely electrostatic model. Evidence for the existence of tetrahedral halogeno-complexes of Ca^{II} (d^0) or Ti^{II} (d^2) is lacking but recently² some tetrahedral d_{γ}^2 complexes of V^{III} , e.g., $[\text{Et}_4\text{N}][\text{VCl}_4]^-$, have been prepared. A number of complexes of Mn^{II} (d^5) believed to contain the $[\text{Mn}^{\text{II}}\text{Hal}_4]^{2-}$ ion have been described, and Jørgensen³ has recently examined the spectrum of the compound $[\text{Et}_4\text{N}]_2[\text{MnBr}_4]$, considering that this consistent with a tetrahedral anion. The well-known tetrahedral Co^{II} (d^7) complexes are usually blue, in contrast with the octahedral complexes which are generally pink or violet. For reasons discussed later, however, colour is not a very reliable guide to stereochemistry for Co^{II} complexes. The magnetic moment of spin-free Co^{II} complexes also bears a relation to stereochemistry⁴ (see p. 4002). The tetrahedral structure of the blue $[\text{CoCl}_4]^{2-}$ has been established by X-rays in compounds such as Cs_3CoCl_5 and Cs_2CoCl_4 .^{5,6} There is also good evidence from X-rays for the existence of tetrahedral Zn^{II} (d^{10}) complexes, e.g., the compound $\text{Cs}_2[\text{ZnCl}_4]$.⁷

This leaves us with d^3 (V^{II}), d^4 (Cr^{II}), d^6 (Fe^{II}), d^8 (Ni^{II}), and d^9 (Cu^{II}), there being no bivalent d^1 (Sc^{II}) compounds known. Crystal-field theory predicts that for spin-free d^4 and d^9 complexes, Cr^{II} and Cu^{II} respectively, a square planar quadricovalent or tetragonal sexicovalent arrangement is likely. The tetragonal arrangement has been reported in a large number of compounds of bivalent copper and the explanation of this in terms of the Jahn-Teller effect has been discussed by Orgel and Dunitz.⁸ Helmholtz and Kruh⁹ have, however, reported that the $[\text{CuCl}_4]^{2-}$ ion in crystalline Cs_2CuCl_4 is intermediate between a square planar and a tetrahedral shape (see p. 4002). In the cases of V^{II} , Fe^{II} , and Ni^{II} a tetrahedral arrangement involves the electronic configurations $d_{\gamma}^2 d_{\epsilon}^1$, $d_{\gamma}^4 d_{\epsilon}^2$, and $d_{\gamma}^4 d_{\epsilon}^4$ respectively for the ground state. Even allowing for some mixing-in of upper states, one might expect the unsymmetrical d_{ϵ} sub-shell in each of these ions to cause some distortion from a regular tetrahedral structure; calculations of the crystal-field stabilisation energy suggest that the octahedron is likely to be the more stable structure,¹⁰ but see below.

Until recently, definite proof that Ni^{II} was ever tetrahedrally co-ordinated was lacking. Indeed, the apparent non-existence of tetrahedral Ni^{II} complexes was generally assumed to be in accord with simple crystal-field theory.¹¹ The paramagnetic compound $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{Et}_3\text{P}$ appeared likely to be tetrahedral unless one postulated that the NO_3 group acted as a chelate, but no paramagnetic Ni^{II} compounds were known even to be quadricovalent with certainty. Venanzi and Powell¹² have, however, reported recently that complexes of the type $\text{NiHal}_2 \cdot 2\text{Ph}_3\text{P}$, which are monomeric, are tetrahedral after studying these by X-ray crystallography. They find that there is distortion from a perfect tetrahedron.

The presence of $[\text{NiCl}_4]^{2-}$ ions in aqueous solution had been suggested by several workers but this had not been proved definitely.¹³ Colour changes in melts of nickel chloride with alkali halides have been taken to indicate complex formation although the identity of the

² Scaife, 1959, unpublished work.

³ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 53.

⁴ Figgis and Nyholm, *J.*, 1954, 12.

⁵ Powell and Wells, *J.*, 1935, 359.

⁶ Porai-Koshits, *Kristallografiya*, 1956, **1**, 291.

⁷ Brehler, *Z. Krist.*, 1957, **109**, 68.

⁸ Orgel and Dunitz, *Nature*, 1957, **179**, 462.

⁹ Helmholtz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

¹⁰ See Orgel, Proceedings of the Xth Solvay Congress, Brussels, 1956, p. 308, and Jørgensen, *ibid.*, p. 355, for a discussion of this subject.

¹¹ Bjerrum and Jørgensen, *Rec. Trav. chim.*, 1956, **75**, 658.

¹² Venanzi, *J.*, 1958, 719; Powell and Venanzi, *Proc. Chem. Soc.*, 1956, 6.

¹³ Kiseleva and Kodeeva, *Trudy Moskov. Khim. Technol. Inst. un D.I. Mendeleeva*, 1956, **22**, 89; *Chem. Abs.*, 1957, **51**, 16183; Katzin, *Nature*, 1958, **182**, 1013.

complex was not definitely established.¹⁴ Also, it had been reported that a red colour is observed when nickel iodide and sodium iodide are dissolved in acetone.¹⁵ This is apparently due to the presence of some $[\text{NiI}_4]^{2-}$ ion. In 1944, Remy and Meyer¹⁶ noted that a blue colour was produced when CsNiCl_3 was melted with excess of caesium chloride. We have now found that the compound Cs_2NiCl_4 appears to be formed when equimolecular

TABLE 1. *Properties of tetrahalogeno-complexes.*

Compound	Colour in solid state	$\mu_{\text{eff.}}$ at 20° c. (B.M.)	Molar conductivity in	
			MeNO ₂ at 20° (c = 0.0005M)	PhNO ₂ at 25° (c = 0.0005M)
$[\text{Ph}_3\text{MeAs}]_2[\text{NiCl}_4]$	Blue	3.89	173	56
$[\text{Et}_4\text{N}]_2[\text{NiCl}_4]$	Blue	3.87	—	Insol.
$[\text{Et}_4\text{N}]_2[\text{NiBr}_4]$	Blue	3.79	179 (0.0008M)	Insol.
$[\text{Ph}_3\text{MeAs}]_2[\text{NiI}_4]$	Red	3.49	163	53
$[\text{Ph}_3\text{MeAs}]_2[\text{CoCl}_4]$	Blue	4.69	173	55
$[\text{Ph}_3\text{MeAs}]_2[\text{CoBr}_4]$	Blue	4.74	162	54
$[\text{Ph}_3\text{MeAs}]_2[\text{CoI}_4]$	Green	4.85	151	53
$[\text{Ph}_3\text{MeAs}]_2[\text{MnCl}_4]$	Pale green	5.88	188	57
$[\text{Et}_4\text{N}]_2[\text{MnCl}_4]$	Pale green	5.94	200	Insol.
$[\text{Ph}_3\text{MeAs}]_2[\text{MnBr}_4]$...	Yellow-green	5.87	179	—
$[\text{Et}_4\text{N}]_2[\text{MnBr}_4]$	Yellow-green	5.97	197	Insol.
$[\text{Ph}_3\text{MeAs}]_2[\text{MnI}_4]$	Pale yellow	5.87	—	—
$[\text{Ph}_3\text{MeAs}]_2[\text{ZnCl}_4]$...	White	Diamag.	174	53
$[\text{Ph}_3\text{MeAs}]_2[\text{ZnBr}_4]$...	White	(-0.56×10^{-6}) Diamag.	165	—
$\text{Ph}_3\text{MeAs}_2[\text{ZnI}_4]$	White	(-0.50×10^{-6}) Diamag.	153	—
$[\text{Ph}_3\text{MeAs}]_2[\text{CuCl}_4]$...	Yellow	(-0.44×10^{-6}) 1.91	171	60
$[\text{Ph}_3\text{MeAs}]_2[\text{CuBr}_4]$...	Purple	1.96	172	—
Reference compounds for conductivities:				
$[\text{Ph}_3\text{MeAs}]\text{I}$			85	—
$[\text{Et}_4\text{N}]\text{I}$	(1 : 1 Electrolyte)		97	—
$[\text{Co}(\text{diars})_2][\text{ClO}_4]_2$	(2 : 1 Electrolyte)		177	55 (0.00002M)
$[\text{Co}(\text{diars})_3][\text{ClO}_4]_3$	(3 : 1 Electrolyte)		262	92 (0.00002M)

proportions of these compounds are melted together, but the complex is stable at high temperatures only; it reverts to the starting materials when cooled below about 70°. More recently, Jørgensen¹⁷ deduced the expected positions of the absorption bands due to $[\text{NiCl}_4]^{2-}$ in melts containing NiCl_2 by allowing for the absorption due to the (suggested) $[\text{NiCl}_6]^{4-}$ ion.

By using alcohol as a solvent we have been able to isolate stable salts of the $\text{Ni}[\text{Hal}_4]^{2-}$ ion without difficulty. The tetraethylammonium and triphenylmethylarsonium cations are suitable; the properties of the complex chlorides, bromides, and iodides are given in Table 1, together with the corresponding data for certain similar complexes of Mn^{II} , Co^{II} , Cu^{II} , and Zn^{II} . It has not been found possible to isolate all tetrahalogeno-complexes of both cations, e.g., neither the $[\text{Ph}_3\text{MeAs}]_2[\text{NiBr}_4]$ complex nor the $[\text{Et}_4\text{N}]_2\text{NiI}_4$ compound was obtained pure. It appears that whether one can isolate a particular $\text{M}_2[\text{M}^{\text{II}}\text{Cl}_4]$ complex depends on the relative stability of the complex anion and the lattice energy of the precipitated salt, the latter being dependent on relative sizes of ions.

The conductivity data indicate that all compounds are uni-bivalent electrolytes in the solvents used. Unfortunately, molecular-weight studies by freezing-point depression were not feasible owing to the low solubilities in nitrobenzene and other suitable solvents.

The colours of the quadricovalent nickel complexes are much more intense than those of the corresponding octahedral hexa-aquanickel(II) compounds. This has also been

¹⁴ Gruen, *J. Inorg. Nuclear Chem.*, 1957, **4**, 74; Boston and Smith, *J. Phys. Chem.*, 1958, **62**, 409.

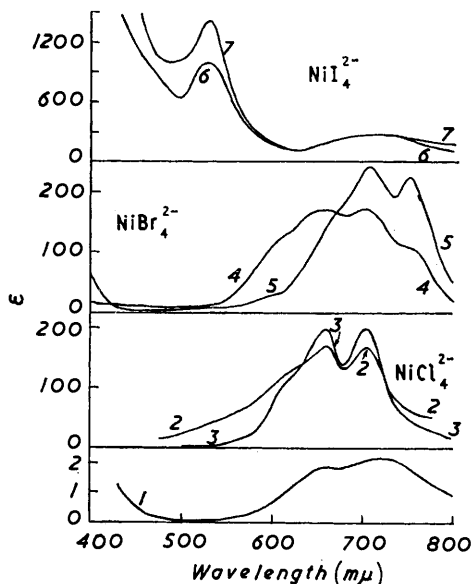
¹⁵ Cambi, *Gazzetta*, 1909, **39**, 361.

¹⁶ Remy and Meyer, *Ber.*, 1944, **77**, 679.

¹⁷ Jørgensen, *Molec. Phys.*, 1958, **1**, 410.

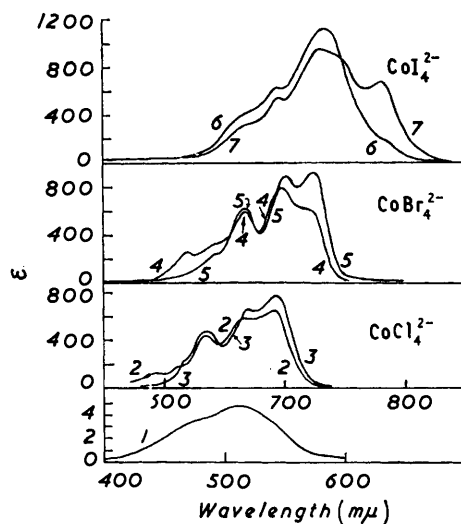
observed in the case of Co^{II} complexes, the blue $[\text{CoCl}_4]^{2-}$ ion having an intensity of colour * about 100 times that of the pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion. This intensity effect has led to some confusion when workers have attempted to correlate the stereochemistry of Co^{II} complexes with the colour. Thus, the pink colour of a hexa-aquocobalt(II) solution changes to blue when as little as 2% of the complex has been changed to the tetrahedral form. The spectra of the various halogenonickel(II) complexes in nitromethane are given in Fig. 1

FIG. 1. Absorption spectra in nitromethane.



- (1) $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in water; (2) $[\text{NiCl}_4]^{2-}$, 0.0005M; (3) $[\text{NiCl}_4]^{2-}$, 0.0006M, with added Cl^- ; (4) $[\text{NiBr}_4]^{2-}$, 0.0007M; (5) $[\text{NiBr}_4]^{2-}$, 0.0008M, with added Br^- ; (6) $[\text{NiI}_4]^{2-}$, 0.00025M; (7) $[\text{NiI}_4]^{2-}$, 0.00025M, with added I^- .

FIG. 2. Absorption spectra in nitromethane.



- (1) $\text{Co}(\text{H}_2\text{O})_6^{2+}$ in water; (2) $[\text{CoCl}_4]^{2-}$, 0.0005M; (3) $[\text{CoCl}_4]^{2-}$, 0.0005M, with added Cl^- ; (4) $[\text{CoBr}_4]^{2-}$, 0.0005M; (5) $[\text{CoBr}_4]^{2-}$, 0.0005M, with added Br^- ; (6) $[\text{CoI}_4]^{2-}$, 0.0005M; (7) $[\text{CoI}_4]^{2-}$, 0.0005M, with added I^- .

together with the spectrum of the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion. In Fig. 2 the spectra of the corresponding cobalt compounds are recorded for comparison.

The cobalt spectra, measured in the presence of excess of halide ions, have ϵ values considerably higher than previously reported; these are discussed below. Values of λ_{max} and ϵ for all complexes of Mn^{II} , Co^{II} , Ni^{II} , and Co^{II} are given in Table 2. A solution of $[\text{Et}_4\text{N}]_2\text{NiCl}_4$ on standing in nitromethane slowly became cloudy with deposition of a little anhydrous nickel chloride. Before opalescence develops an ϵ_{max} of 170 at 660 and 700 $\mu\mu$ is observed; addition of $[\text{Et}_4\text{N}]\text{Cl}$ increases the value of ϵ_{max} to 200 but there is no change in the position of the maxima. This suggests an equilibrium of the type, $[\text{NiCl}_4]^{2-} \rightleftharpoons \text{NiCl}_2(\text{c}) + 2\text{Cl}^-$ which is reversed by the addition of chloride ions. Since there is no change in the position of the band on addition of chloride ions in the large excess necessary to obtain a constant value of ϵ , it is not considered that any significant concentration of $[\text{NiCl}_6]^{4-}$ is formed. The same effect of an increased ϵ with CoCl_4^{2-} and CoBr_4^{2-} is also observed (see Fig. 2).

The frequencies and values of the extinction coefficients of these bands call for comment, especially in relation to those observed for octahedral complexes. Three types of band are observed in the spectra of octahedral transition-metal complexes.^{10,18} First, charge-transfer bands, having large ϵ_{max} values (1000—10,000); these usually occur in the 200—400 $\mu\mu$ region but may overlap the visible region. Secondly, Laporte-forbidden $d-d$ bands

* As estimated from the extinction coefficient only.

¹⁸ Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

which are observed in the visible, near-ultraviolet, and near-infrared regions for octahedral complexes and have ϵ_{\max} values in the range 1—10. Thirdly, bands which are *both* Laporte- and spin-forbidden which are observed in the case of spin-free d^5 complexes (e.g., Mn^{II}), these have much smaller ϵ_{\max} values (ca. 0.01).

In the octahedral hexa-aquo-bivalent-metal complexes the d_e-d_γ separation (Δ) is about 8000—13,000 cm^{-1} . The value estimated for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ being 8500 cm^{-1} , the band observed at 723 $\text{m}\mu$ has been assigned to one of the two possible $d_e^6d_\gamma^2 \rightarrow d_e^5d_\gamma^3$ transitions. A similar $d_e^5d_\gamma^2 \rightarrow d_e^4d_\gamma^3$ band for the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion is also shown. In the tetrahedral complexes the d_e and d_γ levels are inverted and the separation between them is less

TABLE 2. *Spectra of tetrahalogeno-complexes in visible region.*

Complex ion	ϵ_{\max}	λ_{\max}	Ref.	Concn. of $\text{CH}_3\cdot\text{NO}_2$ soln. (M)	Complex ion	ϵ_{\max}	λ_{\max}	Ref.	Concn. of $\text{CH}_3\cdot\text{NO}_2$ soln. (M)
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$...	4.8	513	<i>c, d</i>		$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	2.2	723	<i>b, c, d</i>	
	(sh.)	454				2.0	663		
$[\text{CoCl}_4]^{2-}$	653	693	<i>a, b, h</i>	0.0005		5.1	395		
	580	668			$[\text{NiCl}_4]^{2-}$	167	700	<i>b</i>	0.005
	419	635				167	660		
	(sh.)	613				(sh.)	610		
	122	593			$[\text{NiBr}_4]^{2-}$...	(sh.)	750	<i>b</i>	0.0008
$[\text{CoBr}_4]^{2-}$	(sh.)	723	<i>b, h</i>	0.0005		173	698		
	790	698				168	652		
	595	668				(sh.)	608		
	332	645			$[\text{NiI}_4]^{2-}$	278	~725*	<i>b</i>	0.00025
	254	618				1096	530		
$[\text{CoI}_4]^{2-}$	(sh.)	783	<i>b, h</i>	0.0005	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	0.017	532	<i>c, f</i>	
	1126	733				0.014	435		
	634	693				0.036	402		
	(sh.)	663				(sh.)	397		
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$...	13	~800*	<i>c, e</i>			0.023	357		
$\text{CuCl}_4]^{2-}$	88	~890*	<i>b, g</i>	0.0005		0.021	337		
	(sh.)	435			$[\text{MnCl}_4]^{2-}$...	0.71	445	<i>b</i>	0.1
	~4000	360				0.47	430		
$[\text{CuBr}_4]^{2-}$	122	~870*	<i>b</i>	0.0005	$[\text{MnBr}_4]^{2-}$...	(sh.)	465	<i>b</i>	0.05
	1774	643				1.91	452		
	1995	433				1.00	437		
	~3000	369				2.37	371		

* = Broad.

^a Ballhausen and Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 397. ^b This work. ^c Orgel, *J. Chem. Phys.*, 1955, **23**, 1004. ^d Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1495. ^e Bjerrum, Ballhausen, and Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1275. ^f Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1502. ^g Helmholtz and Krulh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176. ^h Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 53.

than half (theoretically 4/9) of the value of Δ for an octahedral complex. The single-electron transitions between d_e^1 and d_γ levels then occur at much longer wavelengths. In the case of tetrahedral cobalt complexes the two transitions from the singlet (4A_2) ground state to the first (4T_1) and second (4T_2) triplet levels of the *F* state have frequencies in the vicinity of 3000 cm^{-1} and 5000 cm^{-1} , respectively, well outside the visible region. The band observed for $[\text{CoCl}_4]^{2-}$ in the visible region is generally considered¹⁹ to correspond to a transition from the singlet level of the *F* state (4A_2) to the 4P state (4T_2). For the $[\text{NiCl}_4]^{2-}$ complex the observed band at about 700 $\text{m}\mu$ is presumably due to a transition from the lowest-lying triplet of the *F* state (3T_1) to the 3P state. The position of these bands corresponds fairly closely to those deduced by Jørgensen¹⁷ for $[\text{NiCl}_4]^{2-}$ from considerations of spectra of melts of nickel chloride with alkali halides. There is, however, no agreement with the predicted extinction coefficients. In all cases a change from the octahedral hexa-aquo- to the quadri-covalent halogeno-complexes of Mn^{II} , Co^{II} , and Cu^{II} results in at least a 100-fold increase in the extinction coefficient. This is observed also for the $[\text{NiHal}_4]^{2-}$ complexes and may be taken as additional support for their formulation

¹⁹ Ballhausen and Liehr, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

as quadri-covalent halogeno-complexes in solution. Scaife² has observed a similar increase in passing from the $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ to the $[\text{VCl}_4]^-$ ion.

The reason for the high intensity of the $[\text{CoHal}_4]^{2-}$ bands is not fully understood. A commonly accepted explanation is that the presence of $4p$ orbitals having the same symmetry as the d_ϵ orbitals enhances the intensity. However, the transition from the A_2 level, arising from the ion F term, to the T_2 level arising from the ion P term, is not Laporte-forbidden and hence in this instance a considerable intensity can be expected. It has also been suggested that the intensity may arise partly from a charge-transfer contribution. It is noteworthy that the complexes of the iodide ion (the most readily polarised ion) have the largest ϵ_{max} values of the three halogens; however, the ratio of intensities $[\text{CoCl}_4]^{2-} : [\text{CoI}_4]^{2-}$ is still only about 2 : 1. Charge-transfer effects would make it easier to understand the large ϵ values for the $[\text{CuCl}_4]^{2-}$ and $[\text{CuBr}_4]^{2-}$ ions in nitromethane, in which solvent a tetrahedral arrangement is not at all certain. Thus, Helmholtz and Kruh have reported that the $[\text{CuCl}_4]^{2-}$ ion in crystalline Cs_2CuCl_4 is an irregular tetrahedron. One expects for a perfect tetrahedron a relatively large orbital contribution to the magnetic moment, leading to a μ_{eff} of about 2.2 B.M.²⁰ We find a value of 1.96, in agreement with Figgis and Harris²¹ who report 2.0 B.M. For the $[\text{Ph}_3\text{MeAs}]_2\text{CuCl}_4$ complex we obtained a value of 1.91 B.M. These values support the view that there is marked deviation from any regular tetrahedral arrangement in the solid state. We find, moreover, that μ_{eff} for $[\text{Ph}_3\text{MeAs}]_2\text{CuCl}_4$ in nitromethane solutions is 1.95 B.M. Although in this solvent one might expect to minimise forces between the complex ions and hence to favour the formation of a regular tetrahedron as suggested by Ballhausen and Liehr,¹⁹ the low moment obtained certainly does not support the postulated regular tetrahedral arrangement. A more detailed discussion of these spectra will be published shortly by Dr. T. M. Dunn.

[Note added in proof: Gruen and McBeth (*J. Phys. Chem.*, 1959, **63**, 393) have recently published the spectrum of $[\text{NiCl}_4]^{2-}$ in a melt made from nickel chloride and pyridinium chloride and this agrees closely with our Fig. 1.]

On the question of the stereochemistry of the nickel complexes the magnetic data are specially significant (see Table 1). Since the stereochemistry of the attached ligands affects the quenching of orbital magnetism, the size of the latter may in suitable cases be used as a guide to stereochemistry. Thus, octahedral spin-free Co^{II} complexes usually have moments in the region 4.8—5.2 B.M., whereas the moments of tetrahedral complexes are usually considerably less (4.3—4.8 B.M.) (see however, $[\text{CoI}_4]^{2-}$ p. 3999). For octahedral Co^{II} complexes the lowest-lying level of the F state is a triplet, hence a large orbital contribution in excess of the spin-only moment of 3.88 B.M. is expected. For tetrahedral Co^{II} complexes the lowest-lying level is a singlet, but the moment still exceeds 3.88 B.M. because spin-orbit coupling can "mix in" some of the first (and even second) excited state, which is a triplet, since this is only about 3000 cm^{-1} higher in energy. This separation Δ becomes gradually smaller in the sequence $[\text{CoCl}_4]^{2-} > [\text{CoBr}_4]^{2-} > [\text{CoI}_4]^{2-}$, which explains the steadily increasing moments obtained along this series (see Table 1). Similar results have been obtained by Cotton.²² Thus in this instance the moment alone is not a safe guide to stereochemistry.

The moments of the tetrahalogeno-nickel complexes (3.6—4.0 B.M.) are much higher than those observed for octahedral Ni^{II} complexes (2.9—3.2 B.M.), and especially so in the case of the tetrachloro-ion. This is what one would expect for a bivalent nickel atom surrounded by a perfect tetrahedron of negative charges; the situation is opposite to that obtaining with bivalent cobalt, an orbital triplet lying lowest in $[\text{NiCl}_4]^{2-}$. In Table 3 are shown the μ_{eff} values calculated for various circumstances. The moment of the $[\text{NiCl}_4]^{2-}$ complex has been measured over a temperature range (-178° to $+25^\circ$) and this gives a θ value of approximately 35° ; the μ_{eff} calculated by using this value of θ is 4.1₂ B.M. Fig.

²⁰ Figgis, *Nature*, 1958, **182**, 1568.

²¹ Figgis and Harris, *J.*, 1959, 855.

²² Cotton, 1959, personal communication.

3 shows the plot of susceptibility against temperature. The moment in solution in nitromethane is 4.0 B.M., a little larger than in the solid but the difference is not significant for this discussion. The moment does show, however, that the $[\text{NiCl}_4]^{2-}$ ion does not distort in this solvent so as to remove the degeneracy and hence that the presumed tetrahedral arrangement still obtains in solution.

The interpretation of the order of the moments ($[\text{NiCl}_4]^{2-} > [\text{NiBr}_4]^{2-} > [\text{NiI}_4]^{2-}$) is not as straightforward as in the corresponding tetrahalogenocobalt(II) complexes. In

TABLE 3. *Predicted magnetic moments for spin-free bivalent nickel complexes.*

No.	Environment of Ni ^{II} atom	μ_{eff} (B.M.) (calc.)
1	Free Ni ²⁺ ion (3F_4). No electrical field. $S = 1, L = 3$. Assume $\lambda = 0$	4.47*
2	As in (1) but assuming usual value of λ ($\sim -335 \text{ cm.}^{-1}$)	5.56
3	As in (1) but assuming $\lambda = \infty$	5.59†
4	Ni ²⁺ ion in perfect octahedral field of negative charges; assume $\lambda = 0$	2.83
5	Octahedral Ni ^{II} , e.g., $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, using accepted value of λ (varies from ~ 200 to ~ 324)	~ 3.1 — 3.2
6	Ni ²⁺ in tetrahedral field of negative charges assuming $\lambda = 0$ and large value of Δ (assume $L = 1$)	3.16*
7	As in (6) but using same value of λ as in octahedral case and assuming Δ is very large, i.e., only configuration to be considered is $d_{xy}^4 d_{z^2}$	~ 3.6
8	As in (7) but with Δ small enough to permit configuration interaction (i.e., weak field). Moment can be as large as 4.1	~ 4.1

λ = Spin-orbit coupling constant.

* Using $\mu = \sqrt{4S(S+1) + L(L+1)}$.

† Using $\mu = g\sqrt{J(J+1)}$.

tetrahedral Ni^{II} both the lowest level and the first excited level are orbital triplets; "mixing-in" of the latter by spin-orbit coupling is not expected to lead to a reduction in moment. However, the moment could be reduced by mixing-in some of the second excited state since this is a singlet. By analogy with $[\text{CoCl}_4]^{2-}$ this level is presumed to be about 6000 cm.^{-1} above the ground state, and the separation (Δ') is expected to decrease in the sequence $[\text{NiCl}_4]^{2-} > [\text{NiBr}_4]^{2-} > [\text{NiI}_4]^{2-}$; hence a greater singlet contribution which is proportional to Δ' , is expected as we pass along $\text{Cl} \longrightarrow \text{Br} \longrightarrow \text{I}$ with a consequent reduction in moment, as observed. The spin-orbit interaction will increase in the sequence $\text{Cl} < \text{Br} < \text{I}$, and this also will reduce the moment, the decrease being greatest for the iodide and least for the chloride. There will, of course, be a contribution from the 3T_2 level arising from the 3P free-ion term in each case, but this is not expected to be of such a size as to be of major importance in deciding the *order* of the moments of these ions.

Finally, the appreciably large and positive value of θ calls for comment. This suggests at first sight the possibility of some antiferromagnetic interaction, but alternatively the explanation could be the same as that proposed by Figgis and Lewis²³ for octahedral V^{III} complexes. They suggest that there is an appreciable temperature-independent paramagnetism arising from a splitting of the lowest-lying triplet. We propose to study the susceptibility of a number of these complexes over a range of temperature to throw more light on this problem.

It is noteworthy that tetrahedral complexes of the type $\text{NiX}_2 \cdot 2\text{Ph}_3\text{P}$ do not have a large orbital contribution, moments of the order 2.9—3.1 B.M. being reported. However, in these compounds there are two different kinds of attached ligand which can provide an asymmetric field, as discussed by Griffith, Lewis, and Wilkinson for $\text{NiNO}(\text{OH})_3$.²⁴ Further, there is in any case appreciable distortion of the tetrahedron which also leads to removal of orbital degeneracy and hence a reduction in the moment closer to the spin-only value. It should be emphasised that the absence of a large orbital contribution does not prove that a Ni^{II} complex is octahedral, but the *presence* of a large orbital moment can be taken as highly suggestive of a tetrahedral arrangement.

²³ Figgis and Lewis, 1959, personal communication.

²⁴ Griffith, Lewis, and Wilkinson, *J.*, 1959, 1775.

The conclusion that these complex $[\text{NiHal}_4]^{2-}$ ions are tetrahedral is supported by *X*-ray studies carried out by Mr. Peter Pauling.²⁵ These will be reported later by him in detail. The arsonium salts of MnCl_4^{2-} , MnBr_4^{2-} , FeCl_4^{2-} , CoCl_4^{2-} , CoBr_4^{2-} , NiCl_4^{2-} , ZnCl_4^{2-} , and ZnBr_4^{2-} are isomorphous, forming cubic crystals with cell edge 15.5 Å (Ni), space-group $P2_1/3$ with four molecules in the unit cell. If it be accepted that $[\text{CoCl}_4]^{2-}$ is tetrahedral in the above compound, then it follows that all these complex ions have this arrangement, although very slight distortions are not ruled out. Further, the crystal symmetry is such that the metal atom lies on a three-fold axis, and taken in conjunction with the results of other physicochemical measurements leads to the conclusion that, *if* there is any slight distortion at all, it is in the sense of there being three equivalent halide ions and one non-equivalent ion also on the three-fold axis; this is also in agreement with the deductions from consideration of the spectrum of $[\text{NiCl}_4]^{2-}$.²⁶ Work is in progress on the complete elucidation of the structure of $[\text{Ph}_3\text{MeAs}]_2[\text{NiCl}_4]$. *X*-Ray studies on single crystals also show that the arsonium salts of MnI_4^{2-} , CoI_4^{2-} , NiI_4^{2-} , and ZnI_4^{2-} are isomorphous with one another but not with the tetrabromo- or tetrachloro-compounds. Undoubtedly these too contain tetrahedral complex ions, the change in crystal type being due to the larger size of the I^- ion.

The fact that it is possible to obtain tetrahedral complexes of Ni^{II} and Fe^{II} (to be described in Part II) shows that factors other than the ligand-field effects are important in determining the stereochemistry of complex ions, and in some cases can be of greater importance. The first of these is considered to be the effect of covalent bonding. When an easily polarised ligand is used, the charge transfer per bond from the ligand to the bivalent metal ion must become appreciable. It is considered that this effect plays a major part in deciding the co-ordination number of the metal in accordance with the electroneutrality principle. As pointed out by Pauling,²⁷ the preferred co-ordination number of a metal atom increases with the valency, and he has suggested that as a rough rule the co-ordination number is twice the valency of the metal atom. However, two or more co-ordination numbers can occur with the same metal ion, *e.g.*, $[\text{FeF}_6]^{3-}$ and $[\text{FeCl}_4]^-$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$. This may be considered to arise, not so much from steric factors as a rule, but from differences in polarisability of the ligands. If it be accepted that charge transfer from F^- to Fe^{3+} in an $\text{Fe}-\text{F}$ bond is less than from Cl^- to Fe^{3+} in an $\text{Fe}-\text{Cl}$ bond, then clearly the number of Cl^- ligands needed to effect near electroneutrality of the Fe^{3+} ion is smaller than the number of F^- ligands. However, there is no doubt that steric factors can be of major importance in deciding both co-ordination number and stereochemistry in other cases. If some covalent binding occurs, the most readily available orbitals are $4s4p^3$ which, as with ionic binding, give rise to tetrahedral co-ordination.

Crystal-field stabilisation energies (C.F.S.E.) have often been used to predict the relative stabilities of different stereochemical arrangements. In particular, they have been used to support the view that tetrahedral Ni^{II} complexes are unlikely to be stable; some comment thereon is called for. The C.F.S.E. of an octahedral Ni^{II} complex is 1.2Δ , where Δ is the separation between the d_e and d_v levels; hence, for the hexa-aquonickel(II) ion C.F.S.E. is about 28.5 kcal./g.-atom. For a tetrahedral complex the C.F.S.E. is only $0.8\Delta'$, where Δ' is the separation between d_e and d_v levels in a tetrahedral complex. Since $\Delta' = \frac{4}{9}\Delta$, we calculate that the C.F.S.E. for a tetrahedral complex is only about 9 kcal./g.-atom of Ni^{II} . However, this stabilisation energy is small compared with the energy evolved in producing the tetrahedral or octahedral ligand field and, further, other effects due to covalent binding could easily be more important. However, the C.F.S.E. is of great importance in considering the relative stabilities of a series of complexes of the *same* kind, *e.g.*, the hexa-aquo-complexes of bivalent metals.

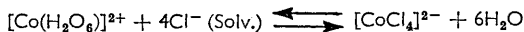
In the light of the above it is of interest to examine the circumstances favouring the

²⁵ P. Pauling, 1959, personal communication.

²⁶ T. Dunn, 1959, personal communication.

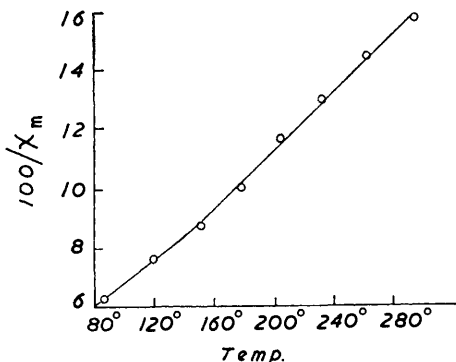
²⁷ L. Pauling, *J.*, 1948, 1461.

formation of these tetrahalogeno-complexes, especially in aqueous solution. Consider the reaction



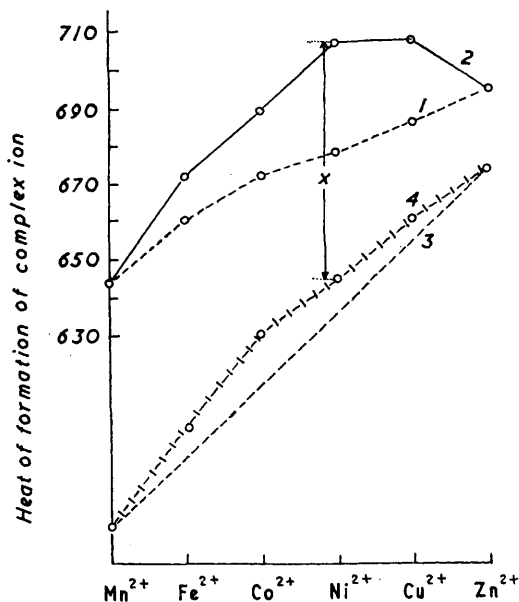
in various solvents. In water the large hydration energy of Cl^- tends to keep the equilibrium well to the left-hand side. To help to force the reaction to the right, one could change to a solvent of smaller solvating power; alcohol is effective in this way. An increase in temperature also moves the equilibrium to the right, presumably owing to a decrease in the solvation of the chloride ion. This is reflected in the marked colour change, usually from green to blue, as the temperature is increased.

FIG. 3. *Magnetic susceptibility of $[\text{NiCl}_4]^{2-}$.*



Plot of $1/\chi_m$ against T (°K) for $(\text{Ph}_3\text{MeAs})_2[\text{NiCl}_4]$.

FIG. 4.



(1) Corrected (C.F.S.E.) heat of hydration of ions $[\text{M}(\text{H}_2\text{O})_6]^{2+}$. (2) Experimental heat of hydration of ions $[\text{M}(\text{H}_2\text{O})_6]^{2+}$. (3) Corrected (C.F.S.E.) heat of formation of ions MCl_4^{2-} (hypothetical). (4) Hypothetical heat of formation of ions MCl_4^{2-} .

The problem remaining is to explain why Ni^{II} does not form NiCl_4^{2-} complexes in water whilst both the preceding element (Co^{II}) and the next one (Cu^{II}) do. Fig. 4 suggests an explanation. To obtain this we have used accepted values^{10,18} of Δ for octahedral hexa-aquo-complexes and have taken Δ for tetrahedral complexes as $\frac{4}{9}$ of this. Since we will be dealing with the ligand Cl^- rather than H_2O , one ought to take an even larger value. However, as comparative results only are required this seems justifiable. It is known that the corrected heats of hydration of the hexa-aquo-bivalent-metal ions increase steadily from Mn^{II} to Cu^{II} and then fall to zinc.^{28,10} These are shown in curve (1), which is obtained by subtracting the stabilisation energies from the experimental curve (2). Now let us assume that the corrected heats of formation of $[\text{MCl}_4]^{2-}$ fall on the straight line (3). For experimental reasons which emerge shortly we suggest that this curve is steeper than (1). On adding to this the (estimated) stabilisation energies we get curve (4). Now the separation between these two curves (2) and (4) is a ΔH value, but, since it is reasonable to assume that the ΔS value for the reaction $[\text{M}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^-, \text{aq} \rightleftharpoons [\text{MCl}_4]^{2-} + 6\text{H}_2\text{O}$ is approximately the same for all metals from Mn to Zn, the separation x can be used as a

²⁸ Holmes and McClure, *J. Chem. Phys.*, 1957, **26**, 1686.

comparative measure of ΔG . Now if curves (1) and (3) do converge as shown, then by ignoring first any C.F.S.E., a steadily increasing tendency to form $[\text{MCl}_4]^{2-}$ complexes as we pass from Mn to Zn can be explained. However, in passing from Co^{II} to Ni^{II} the enhanced tendency to form $[\text{NiCl}_4]^{2-}$ due to convergence of curves (1) and (3) must be weighed against the relative differences between the C.F.S.E. values for octa- and tetra-hedral co-ordination. For the various elements concerned these differences are roughly: Mn^{II} , 0; Fe^{II} , $12 - 8 = 4$; Co^{II} , $22 - 14 = 8$; Ni^{II} , $28.5 - 8.6 = 20$; Cu^{II} , $21 - 6 = 15$; Zn^{II} , 0. Thus the convergence in passing from Co^{II} to Ni^{II} has to be sufficient to outweigh a relative destabilisation of an *extra* 11 kcal. due to C.F.S.E. for Ni^{II} over and above the value for cobalt. It is suggested that this quantity causes the instability of $[\text{NiCl}_4]^{2-}$ in water relative to $[\text{CoCl}_4]^{2-}$. It must be emphasised, however, that this tells us nothing about the actual heat of formation of the $[\text{NiCl}_4]^{2-}$ ion which is clearly very stable in the absence of water. Some support for the proposal that curves (3) and (1) are convergent emerges from a study of the curves by Holmes and McClure²⁸ for the heats of formation of bi- and ter-valent hexahydrates. They show that the curve for ΔH of hydration of the latter is steeper than that for the former. It is suggested that curve (3) for the tetrahalides, like the curve for the trivalent hexahydrates, is steeper than (1) because there is greater covalent character in the metal-ligand bond than there is in the bivalent hydrates. This has been expressed in another way by Williams.²⁹ He points out that, as we pass across the transition series, *e.g.*, from $\text{Ti}^{2+} \rightarrow \text{Cu}^{2+}$, *i.e.*, as the polarising power of the cation increases, the tendency to complex with more easily polarised ligands increases. Thus H_2O is preferred to NH_3 at the beginning of the series but NH_3 to H_2O at the end.

The isolation of these regular tetrahedral $[\text{NiHal}_4]^{2-}$ complexes has emphasised the importance of covalent bonding in compounds of this type. It also shows that the tetrahedral arrangement is little affected by the presence of an asymmetric d_ϵ shell (*i.e.*, one which is not empty, half-full, or filled). This is in marked contrast to the well-known distortion which occurs in the sexicovalent complexes where an unsymmetrical d_γ shell causes marked deviation from a regular octahedral arrangement.

EXPERIMENTAL

Preparation.—All compounds were prepared by mixing the calculated amounts of the appropriate metal halide (not necessarily anhydrous) and arsonium or tetraethylammonium halide dissolved in ethyl alcohol. The products were recrystallised from ethyl alcohol except bis-(tetraethylammonium) tetrabromomanganese(II) for which methyl alcohol was used.

Nickel Compounds.—*Bis(triphenylmethylarsonium) tetrachloronickelate*(II), blue hygroscopic needles (Found: C, 53.9; H, 4.4; Cl, 16.6; Ni, 6.9. $\text{C}_{38}\text{H}_{36}\text{Cl}_4\text{As}_2\text{Ni}$ requires C, 54.1; H, 4.3; Cl, 16.8; Ni, 7.0%). *Bis(tetraethylammonium) tetrachloronickelate*(II), blue deliquescent needles (Found: C, 41.8; H, 8.9; Cl, 30.7; Ni, 12.9. $\text{C}_{16}\text{H}_{40}\text{N}_2\text{Cl}_4\text{Ni}$ requires C, 41.7; H, 8.7; Cl, 30.8; Ni, 12.7%). *Bis(tetraethylammonium) tetrabromonickelate*(II), blue deliquescent needles (Found: C, 30.1; H, 6.5; N, 4.6; Br, 49.8. $\text{C}_{16}\text{H}_{40}\text{N}_2\text{Br}_4\text{Ni}$ requires C, 30.1; H, 6.3; N, 4.4; Br, 50.0%). *Bis(triphenylmethylarsonium) tetraiodonickelate*(II), red leaflets from hot ethyl alcohol but dissociated when the mixture was cooled; it was therefore filtered from the mother liquor while still warm; the crystals are hygroscopic (Found: C, 37.1; H, 3.5; I, 42.0. $\text{C}_{38}\text{H}_{36}\text{I}_4\text{As}_2\text{Ni}$ requires C, 37.75; H, 3.0; I, 42.1%).

Cobalt Compounds.—*Bis(triphenylmethylarsonium) tetrachlorocobaltate*(II), blue needles (Found: C, 54.2; H, 4.7; Cl, 16.6; Co, 6.7. $\text{C}_{38}\text{H}_{36}\text{Cl}_4\text{As}_2\text{Co}$ requires C, 54.1; H, 4.3; Cl, 16.8; Co, 7.0%). *Bis(triphenylmethylarsonium) tetrabromocobaltate*(II), blue needles (Found: C, 44.4; H, 3.8; Co, 5.5. $\text{C}_{38}\text{H}_{36}\text{Br}_4\text{As}_2\text{Co}$ requires C, 44.7; H, 3.55; Co, 5.8%). *Bis(triphenylmethylarsonium) tetraiodocobaltate*(II), green leaflets (Found: C, 37.8; H, 3.2. $\text{C}_{38}\text{H}_{36}\text{I}_4\text{As}_2\text{Co}$ requires C, 37.75; H, 3.0%).

Manganese Compounds.—*Bis(triphenylmethylarsonium) tetrachloromanganate*(II), very pale green, deliquescent needles (Found: C, 53.9; H, 4.5; Cl, 16.6. $\text{C}_{38}\text{H}_{36}\text{Cl}_4\text{As}_2\text{Mn}$ requires C, 54.4; H, 4.3; Cl, 16.9%). *Bis(tetraethylammonium) tetrachloromanganate*(II), very pale green needles (Found: C, 42.3; H, 8.8; N, 6.5. $\text{C}_{16}\text{H}_{40}\text{N}_2\text{Cl}_4\text{Mn}$ requires C, 42.0; H, 8.8; N, 6.1%).

²⁹ Williams, *J. Roy. Inst. Chem.*, 1959, 234.

Bis(triphenylmethylarsonium) tetrabromomanganate(II), pale green, deliquescent needles (Found: C, 44.8; H, 4.0. $C_{38}H_{36}Br_4As_2Mn$ requires C, 44.9; H, 3.6%). *Bis(tetraethylammonium) tetrabromomanganate(II)*, pale green needles (Found: C, 30.9; H, 6.2; N, 4.4. $C_{16}H_{40}N_2Br_4Mn$ requires C, 30.2; H, 6.35; N, 4.4%). *Bis(triphenylmethylarsonium) tetraiodomanganate(II)*, cream leaflets which when dry slowly decompose and finally become brown owing to formation of iodine (Found: C, 38.1; H, 3.3. $C_{38}H_{36}I_4As_2Mn$ requires C, 37.9; H, 3.0%).

Zinc Compounds.—*Bis(triphenylmethylarsonium) tetrachlorozincate(II)*, white needles (Found: C, 53.7; H, 4.5; Cl, 16.4. $C_{38}H_{36}Cl_4As_2Zn$ requires C, 53.7; H, 4.3; Cl, 16.7%). *Bis(triphenylmethylarsonium) tetrabromozincate(II)*, white needles (Found: C, 44.3; H, 4.0. $C_{38}H_{36}Br_4As_2Zn$ requires C, 44.4; H, 3.5%). *Bis(triphenylmethylarsonium) tetraiodozincate(II)*, white leaflets (Found: C, 38.0; H, 3.5. $C_{38}H_{36}I_4As_2Zn$ requires C, 37.55; H, 3.0%).

Copper Compounds.—*Bis(triphenylmethylarsonium) tetrachlorocuprate(II)*, yellow needles (Found: C, 54.0; H, 4.4; Cl, 16.4. $C_{38}H_{36}Cl_4As_2Cu$ requires C, 53.8; H, 4.3; Cl, 16.7%). *Bis(triphenylmethylarsonium) tetrabromocuprate(II)*, purple needles (Found: C, 44.3; H, 3.7. $C_{38}H_{36}Br_4As_2Cu$ requires C, 44.5; H, 3.5%).

Absorption spectra were obtained with a Unicam SP.500 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method.³⁰

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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³⁰ Figgis and Nyholm, *J.*, 1959, 331.