682. *Studies in Co-ordination Chemistry. Part XIV.* The Magneto-chemistry of Simple and Complex Fluorides of Transition Metals.*

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The magnetic susceptibilities of the following compounds at 20° are reported for the first time: K_2TiF_6; K_2TiF_6,H_2O; VF_3; K_3VF_6; K_2CrF_5,H_2O; $KCrOF_4$; K_2MnF_5,H_2O; Li_3FeF_6; Na_3FeF_6; K_2FeF_5; $CsFeF_4$; $CuF_2,2H_2O$; TaF_3; RhF_4; Na_3RhF_7; PdF_3; PtF_4; K_2PtF_6; AuF_3; $AgAuF_4$. The susceptibilities of several other transition-metal fluorides have been redetermined and available data for all fluorine-containing transition-metal compounds have been assembled. The correlation of the observed magnetic moments with valency, structural chemistry, and bond type is discussed. Compounds of the first transition series, except when magnetically concentrated, show the number of unpaired electrons calculated for so-called "ionic" bonds on the assumption of maximum multiplicity. For the second and third transition series the compounds are diamagnetic when the number of electrons in the metal ion is even and paramagnetic, with a moment corresponding to only one unpaired electron, when the number of electrons is odd, showing that for these two series minimum multiplicity is the rule even for fluorides. Possible reasons for these observations are discussed.

In the development of the structural chemistry of transition-metal compounds, fluorides have occupied an important position, since the difference in magnetic properties between the strongly paramagnetic complex ions, such as $[FeF_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$, and the weakly paramagnetic complex ions, such as $[Fe(CN)_6]^{3-}$, is the key point in the division

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* Part XIII, preceding paper.

of bonds in ferric complexes into two types. The nature of these two types of binding has been much discussed, *e.g.*, by Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367; "Nature of the Chemical Bond," Cornell Univ. Press, 1939), Van Vleck ("Theory of Electric and Magnetic Susceptibilities," Oxford Univ. Press, 1932; *J. Chem. Phys.*, 1935, **3**, 807), Selwood ("Magnetochemistry," Interscience Publ. Corp., N.Y., 1943), Asmussen ("Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser," Copenhagen, 1944), and Burstall and Nyholm (Part XIII*). Here we adopt the view taken in Part XIII, that for octahedral bonds the essential distinction is between the use of $3d^24s4p^3$ hybrid orbitals ("covalent" bonds in Pauling's terminology) and $4s4p^34d^2$ hybrid orbitals ("ionic" bonds in Pauling's terminology). A more detailed theoretical discussion of the use of higher ($4d$) orbitals for σ- and π-bond formation in transition-metal complexes occurs in a forthcoming publication by Craig, Maccoll, Nyholm, Orgel, and Sutton (see also Orgel, *Nature*, 1951, **167**, 434).

It is well known that, in the first transition series, the more electronegative ligands (such as F, Cl, O) favour the use of higher orbitals, giving compounds with the maximum magnetic moments, whereas ligands containing atoms of lower electronegativity (*e.g.*, P, As, S) generally favour the use of lower-level bonding orbitals with maximum electron pairing. The fluorides of transition metals are especially interesting, since fluorine is particularly effective in producing higher oxidation states [*e.g.*, Co(IV), Ni(IV), Cu(III)] and in forming compounds with the most polar bonds. There is thus a greater likelihood of the metal being present as an ion, and maximum magnetic moments are therefore more likely to be found in fluorides than in any other compounds.

The comparative inaccessibility and instability of many fluorine-containing compounds have hitherto limited the range of such substances examined, and no general account of their magnetic properties is available. In the present investigation susceptibilities have been measured at or near 20° and the values corrected to this temperature, on the assumption that the Curie law is valid. The fact that the simple Curie law is not strictly obeyed by many, if not by most, substances is unimportant for this small correction, since temperature differences were only of the order of $\pm 5°$. The effect of wide variation in temperature or field strength has not been studied, but the mere demonstration of the presence or absence of unpaired electrons is often of great interest. It is intended to examine the magnetic behaviour of certain of the more magnetically concentrated compounds in more detail, with a view to determining values of Δ in the Curie–Weiss expression [molar susceptibility $\alpha \propto 1/(T + \Delta)$] and hence obtaining moments calculated on the basis of this Law. For many compounds of transition metals, Δ is large and, though μ is proportional only to $\sqrt{T + \Delta}$, we are not justified in discussing in this paper small differences between values of μ calculated on the Curie law and values for other compounds calculated on the Curie–Weiss law. This limitation of our general survey of moments at 20° has been stressed throughout the following discussion. Van Vleck (*op. cit.*, p. 304) has discussed the theoretical significance of Δ; since Δ is usually smaller in magnetically dilute compounds, it is suggested that exchange forces between paramagnetic atoms are at least partly responsible for it. However, the view that Δ is often due mainly to the influence of orbital angular momentum finds support in the fact that Δ is usually smaller for Mn(II) and Fe(III) salts that for most others; in these cases we are of course dealing with S states where the total orbital angular momentum is zero.

The purity of all samples has been checked by at least partial analysis for the essential constituents. Corrections have been made for atomic diamagnetism (except that of the paramagnetic atom itself) in all instances. Except where special mention is made in the Experimental section (*e.g.*, for CoF_3) no paramagnetic corrections for impurities have been made. Previous work (*e.g.*, Woolf and Emeléus, *J.*, 1949, 2865; Sharpe, *J.*, 1950, 3444) has shown that, although substances prepared in bromine trifluoride are seldom quite pure, the degree of impurity is not such as would appreciably affect the values quoted for the magnetic moments. The importance in this work of analysis for a sufficient number of elements to justify the magnetic moment claimed is all too frequently overlooked, and for that reason any moments which are reported in the literature without a satisfactory accompanying analysis should be accepted with reserve.

The results of the experimental work in this investigation are given in Table 1; all values for μ are believed to be accurate to within $\pm 0{\cdot}1$ B.M. or less. In Table 2 are shown all the moments of the transition-metal fluorides which have so far been reported. Owing partly to their greater ease of preparation and partly to the greater interest previously attaching to them, results for fluorides of metals of the first transition series are more numerous than for the other two. It is convenient to discuss the results for individual elements in turn before arriving at some more general conclusions.

TABLE 1.

	Compound	$\chi_g^{20°}$, $\times 10^{-6}$	$\chi_M^{20°}$, $\times 10^{-6}$	Diamagnetic corrn., $\times 10^{-6}$	$\chi_M^{20°}$, $\times 10^{-6}$ (corr.).	μ
1	K_2TiF_6	$-0{\cdot}28$				Diamagnetic
2	K_2TiF_6,H_2O	$-0{\cdot}18$				Diamagnetic
3	VF_3	2·53	2,730	27	2,757	2·55
4	K_3VF_6	11·3	3,200	99	3,300	2·79
5	K_2CrF_5,H_2O	24·6	5,980	86	6,066	3·79
6	$KCrOF_4$	6·90	1,262	46	1,308	1·76
7	MnF_3	91·4	10,240	27	10,270	4·94
8	K_2MnF_5,H_2O	18·6	4,575	86	4,661	3·32
9	Li_3FeF_6	75·2	14,400	58	14,460	5·87
10	Na_3FeF_6	62·5	14,920	75	14,995	5·95
11	$(NH_4)_3FeF_6$	63·3	14,180	94	14,274	5·80
12	K_2FeF_5	43·9	10,020	76	10,100	4·87
13	$CsFeF_4$	36·0	9,680	91	9,770	4·79
14	CoF_3	16·4	1,900	27	1,927	2·1
15	$CuF_2,2H_2O$	11·35	1,560	39	1,600	1·94
16	TaF_3	3·3	795	27	822	1·4
17	RhF_4	2·8	500	36	536	1·1
18	Na_3RhF_7	3·92	1,195	84	1,279	1·74
19	PdF_3	10·8	1,760	27	1,787	2·05
20	PtF_4	1·68	455	36	491	1·1
21	K_2PtF_6	$-0{\cdot}21$				Diamagnetic
22	AuF_3	0·30	74	27	101	0·5
23	$AgAuF_4$	—				Diamagnetic

The diamagnetism of potassium fluorotitanate, thorium tetrafluoride, potassium hexafluorotantalate, and the hexafluorides of molybdenum, tungsten, and uranium is expected and calls for no special comment. The values for europous fluoride, and for uranium tetrafluoride and plutonium trifluoride, have been discussed by Selwood (*loc. cit.*) and Dawson (*loc. cit.*) respectively. For tantalum trifluoride the observed moment of 1·4 B.M. is far below that expected for a Ta^{3+} ion if maximum multiplicity were operative; then the moment should be similar to that of the V^{3+} ion; the environment of the Ta^{3+} ion in TaF_3 (Jack and Gutmann, *Acta Cryst.*, 1951, **4**, 244) differs little from that of the V^{3+} ion in VF_3 (*idem, ibid.*, p. 246), but, since magnetic measurements have been made only at 20° and no data are available for other compounds of lower oxidation states of tantalum, it is difficult to make any deduction from this result. The following discussion is therefore restricted to elements in the first transition series, the platinum metals, silver, and gold.

Vanadium.—Only compounds of the tervalent state are available for study and for all of these except VF_3 the moment is close to that calculated for the spin-only value for two unpaired electrons (2·83 B.M.). The moment of VF_3 is noticeably lower than that calculated for VCl_3 from the Curie–Weiss law [2·85 B.M. (Starr, Bitter, and Kaufman, *Phys. Review*, 1940, **58**, 977; Starr, *ibid.*, p. 984)]; presumably this is caused by the magnetic concentration, but in the absence of data for various temperatures calculation of Δ and application of the Curie–Weiss law are not possible. For vanadium alum between 3° K and 293° K it has been shown by Handel and Siegert (*Physica*, 1937, **4**, 871) that the Weiss law is obeyed, μ being 2·62 B.M. It should be mentioned that, since a V^{3+} ion contains only two 3*d* electrons (both unpaired), there are three vacant 3*d* orbitals available for bond formation. Magnetic moments would therefore provide no basis for distinguishing between "ionic" and "covalent" bonds, since both types of binding would give the same moment (Pauling, *op. cit.*). When two 3*d* orbitals are available without promotion of

TABLE 2. *Magnetic moments at 20° (ref. in parentheses).*

	K_2TiF_6 0·0 (1)	VF_3 2·55 (1)	CrF_3 3·9 (3)	MnF_2 5·73 (4, 11)	FeF_2 5·59 (6)	CoF_2 4·60 (8, 10)	NiF_2 2·85 (8, 11)	CuF_2 1·57 (8, 11)
	K_2TiF_6,H_2O 0·0 (1)	K_3VF_6 2·79 (1)	K_2CrF_5,H_2O 3·79 (1)	MnF_3 4·94 (1) 4·91 (21)	FeF_3 — (4)	CoF_3 2·46 (8) 2·1 (1)		
		$(NH_4)_3VF_6$ 2·79 (2)		K_2MnF_5,H_2O 3·32 (1)	Li_3FeF_6 5·87 (1)		K_2NiF_6 0·0 (9)	$CuF_2,2H_2O$ 1·94 (1)
		K_2VF_5,H_2O 2·74 (2)	$KCrOF_4$ 1·76 (1)		Na_3FeF_6 5·95 (1)	K_3CoF_6 4·26 (5)		
		$(NH_4)VF_4,2H_2O$ 2·77 (2)		K_2MnF_6 3·86 (5)	$(NH_4)_3FeF_6$ 5·88 (7) 5·80 (1)	$Co(NH_3)_6F_3$ 0·0 (2)		K_3CuF_6 2·8 (9)
		$VF_3,3H_2O$ 2·79 (2)			K_2FeF_5 4·87 (1)	$Co(NH_3)_3F_3$ 0·0 (19)		
					$(NH_4)_2FeF_5,H_2O$ 5·91 (7)			
					$FeF_3,3H_2O$ 4·25 (7)			
					$CsFeF_4$ 4·79 (1)			
			MoF_6 0·0 (12)			RhF_4 1·1 (1)	PdF_3 2·05 (1)	AgF_2 1·0 (17, 18)
						Na_3RhF_7 1·74 (1)		
EuF_2 7·4 (15)		TaF_3 1·4 (1)	WF_6 0·0 (12)				PtF_4 1·1 (1)	AuF_3 0·5 (1)
		$KTaF_6$ 0·0 (16)					K_2PtF_6 0·0 (1, 20)	$AgAuF_4$ 0·0 (1)
	ThF_4 0·0 (13)		UF_4 2·92 (13)					
			UF_6 0·0 (12)					
			PuF_3 1·25 (14)					

(1) Present work. (2) Asmussen, *loc. cit.* (3) Bizette and Tsai, *Compt. rend.*, 1940, **211**, 252. (4) *Idem, ibid.*, 1939, **209**, 205. (5) Grey, *J. Amer. Chem. Soc.*, 1946, **68**, 605. (6) Bizette and Tsai, *Compt. rend.*, 1941, **212**, 119. (7) Feytis, *ibid.*, 1911, **152**, 710. (8) Henkel and Klemm, *Z. anorg. Chem.*, 1935, **222**, 73. (9) Klemm, personal communication; Hoppe, *Angew. Chem.*, 1950, **62**, 339. (10) de Haas, Schultz, and Koothaus, *Physica*, 1939, **6**, 481. (11) *Idem, ibid.*, 1940, **7**, 57. (12) Henkel and Klemm, *Z. anorg. Chem.*, 1935, **222**, 70. (13) Dawson, *J.*, 1951, 2889; 1952, 1185. (14) Dawson, Mandleberg, and Davies, *J.*, 1951, 2047. (15) Klemm and Döll, *Z. anorg. Chem.*, 1939, **241**, 233. (16) Bose and Bhar, *Z. Physik*, 1928, **48**, 716. (17) Ruff, Giese, and Hartmann, *Z. anorg. Chem.*, 1934, **219**, 146. (18) Gruner and Klemm, *Naturwiss.*, 1937, **25**, 59. (19) Cartledge, quoted by Pauling, *loc. cit.*, p. 117. (20) D. P. Mellor, personal communication. (21) Klemm and Krose, *Z. anorg. Chem.*, 1947, **253**, 226.

electrons, however, it is difficult to find any justification for suggesting the use of *4d* orbitals for hybrid-bond formation; that all compounds of V(III), Cr(III), and Mn(IV) should show similar magnetic properties then follows as a matter of course.

Chromium.—Bizette and Tsai (*loc. cit.*) give μ 3·9 at 20° for CrF_3 (calculated from their graph); Starr, Bitter, and Kaufman (*loc. cit.*) and Starr (*loc. cit.*) report the same value for $CrCl_3$ at 25°. Tervalent chromium with configuration d^3 has two vacant $3d$ orbitals and the binding is probably $3d^24s4p^3$, since there is no reason to suppose otherwise. The complex K_2CrF_5,H_2O, like all other tervalent chromium complexes, has a moment corresponding well with three unpaired electrons.

The moment of $KCrOF_4$ corresponds closely with one unpaired electron and is analogous to those of Rb_2CrOCl_5 (μ = 1·80 B.M.) and Cs_2CrOCl_5 (μ = 1·84 B.M.), both results being reported by Asmussen (*loc. cit.*); this is the moment expected for Cr(V). The crystal structure is unknown and there is at present no evidence for discrete $CrOF_4^-$ ions.

Manganese.—(*a*) Mn(II). Like manganous chloride (Starr, Bitter, and Kaufman, *loc. cit.*; Starr, *loc. cit.*), manganous sulphate (Asmussen, *loc. cit.*), and many complexes of Mn(II), MnF_2 has approximately the value of μ for 5 unpaired electrons. Only the complex cyanide $K_4Mn(CN)_6,3H_2O$, for which Asmussen (*loc. cit.*) reports 2·13 B.M. (see also Goldenberg, *Trans. Faraday Soc.*, 1940, **36**, 847) differs from this. The reluctance of Mn(II) to form complexes in which electron pairing occurs is very well known; possible reasons for this have been discussed in Part XIII.

(*b*) Mn(III). The moment of MnF_3 is in reasonable agreement with that calculated for four unpaired electrons. This is the only stable anhydrous salt of tervalent manganese, but many complexes are known for which μ is 4·9—5·0 B.M. These presumably utilise higher octahedral $4s4p^34d^2$ orbitals. For the tervalent complex cyanide $K_3Mn(CN)_6$ moments of 3·18 B.M. (Asmussen, *loc. cit.*) and 3·64 B.M. (Biltz, *Z. anorg. Chem.*, 1928, **170**, 161) are reported; as in the bivalent complex cyanide, the binding is clearly $3d^24s4p^3$, there being two unpaired electrons. The difference between the experimental results of the two workers is serious but does not affect this conclusion. We have observed a reduction of moment with K_2MnF_5,H_2O which is entirely unexpected and this compound is being further investigated. Goldenberg (*loc. cit.*) reports μ 0·6 B.M. for a compound which he tentatively formulated as $K_3Mn_2(CN)_9,4KOH$, but his analytical data for both Mn and CN differ considerably from the calculated figures and no evidence for the KOH is quoted in the paper. Until the formula is more satisfactorily established the moment cannot be interpreted.

(*c*) Mn(IV). Grey (*loc. cit.*) reports μ 3·86 for K_2MnF_6, in good agreement with the spin-only value for three unpaired electrons, but again the magnetic data are not diagnostic of the bond type. Similar values are quoted by Asmussen (*loc. cit.*) for many other quadrivalent manganese compounds. For the complex $KMnF_5$ (which cannot be obtained pure) we found μ 4·3 B.M. This value is rather higher than the spin-only value and even some contamination with Mn(III) would not completely account for the high moment. The structure of this salt is unknown and the excess in the moment may arise from an incompletely quenched orbital contribution.

Iron.—(*a*) Fe(II). The value for FeF_2 is close to that of $FeCl_2$, for which μ is 5·59 B.M. (Starr, Bitter, and Kaufman, *loc. cit.*); the values for magnetically dilute ferrous compounds range from 5·0 to 5·6 B.M. [*e.g.*, $FeSO_4,(NH_4)_2SO_4,6H_2O$ has μ 5·55 B.M.] The behaviour is thus characteristic of the Fe^{2+} ion and must, as with bivalent cobalt complexes, arise from a large orbital contribution.

(*b*) Fe(III). Ferric fluoride shows field strength dependence at both 20° and −183°; hence moments are meaningless. The moments of several complex fluoroferrates have been measured at 20° and these yield interesting results. Some slight indication of field strength dependence was obtained for the more concentrated compounds, but of greater interest is the departure from the spin-only value (observed with the hexafluoroferrates) when tetra- and penta-fluoroferrates are formed. As the size of the alkali metal cation increases, the atomic ratio F : Fe decreases and a decrease in moment is observed. This decrease in moment as the magnetic concentration increases is most interesting and it is proposed to follow this problem by an investigation of crystal structures of complexes such as K_2FeF_5 and $CsFeF_4$ and of their variation of magnetic susceptibility with temperature. We have discarded the value of μ 5·2 B.M. for Na_3FeF_6 reported by Welo (*Phil. Mag.*, 1928, **6**, 496) since his analytical figures do not agree with the above formula.

Cobalt.—(*a*) Co(II). The moment of CoF_2 (4·60 B.M.) is much higher than that calculated for three unpaired electrons, but this behaviour is quite general for compounds of bivalent cobalt. The value of μ generally increases as we pass from tetrahedral to octahedral Co(II) complexes owing to the greater contribution to the moment. This experimental observation covering a wide range of compounds (Kanekar and Nyholm, unpublished work) can be predicted theoretically from calculations on the effect of various crystalline fields on the size of the moment (Bose, *Indian J. Phys.*, 1948, **22**, 76, 195, 483, and earlier references quoted therein). The value of the orbital contribution in tetrahedral complexes is also quite sensitive to changes in the electronegativity of the attached groups. Calculated on the Curie law, the value of μ for CoF_2 increases steadily with temperature from 90° K to 293° K (Henkel and Klemm, *loc. cit.*) and the figure quoted for 20° C has therefore probably not reached its limiting value. Since Δ is not constant it is impossible to calculate the value of μ from the Curie–Weiss law.

(*b*) Co(III). The value reported by Henkel and Klemm for CoF_3 has been confirmed. For this compound there is also temperature dependence at least up to 293° K, but the Curie–Weiss law is not obeyed, and hence the limiting value of μ is certainly greater than 2·5 B.M. According to Gutmann and Jack (*loc. cit.*), CoF_3 is probably isomorphous with VF_3, each cobalt atom having six octahedrally arranged fluorine atoms as nearest neighbours. Tervalent cobalt is d^6; if the bonds were $3d^24s4p^3$ the complexes would be diamagnetic (as in the complex ammines) but the use of " ionic " or $4s4p^34d^2$ bonds with maximum multiplicity requires a moment of 4·90 B.M., there being four unpaired electrons. The value reported by Grey (*loc. cit.*) for the blue complex salt K_3CoF_6, which was prepared by Mitchell (Thesis, Univ. Buffalo, 1940) by treating $Co_2F_6,7H_2O$ with potassium fluoride in aqueous hydrofluoric acid, is rather less than this, but it certainly shows that the binding is not $3d^24s4p^3$ and is more consistent with $4s4p^34d^2$ hybrid orbitals. This fluoride thus differs from all other Co(III) complex ions, including even the $Co(H_2O)_6^{2+}$ ion, for which Asmussen (*loc. cit.*) and Barkworth (Thesis, London, 1937) report $\mu < 0·5$ B.M. (even this small moment is probably due to traces of cobaltous salt). Thus, with the exception of the compounds K_3CoF_6 and $CoCl_3,2Et_3P$ (Jensen, unpublished work) for both of which μ indicates four unpaired electrons, tervalent cobalt in its complex compounds resembles metals of the second and third transition series much more than those of the first.

Nickel.—(*a*) Ni(II). The moment of NiF_2 is also temperature dependent from 90° K to 293° K (Henkel and Klemm, *loc. cit.*); the value at 293° K corresponds to two unpaired electrons. Since, however, Ni(II) compounds usually have moments of the order of 3·1—3·3 B.M. it seems that some reduction of moment owing to magnetic concentration has occurred.

(*b*) Ni(IV). The complex K_2NiF_6 is of great interest as showing a resemblance between nickel in its highest valency state and the platinum metals (cf. K_2PtF_6). Diamagnetism in the Ni(IV) complex, $[NiCl_2 (diarsine)_2][ClO_4]_2$ (Part IX, *J.*, 1951, 2602), is not surprising, since the ditertiary arsine is a donor of low electronegativity and favours the use of the $3d$ orbitals for binding. The failure to observe paramagnetism in K_2NiF_6, however, shows that Ni(IV) in its complex fluoride has even greater capacity for covalent bond formation using $3d^24s4p^3$ orbitals than the isoelectronic Co(III).

Copper.—(*a*) Cu(II). No complex fluoride is known. The structure of $CuF_2,2H_2O$ is unknown but if it is similar to that of $CuCl_2,2H_2O$ the four bonds are co-planar. This requires dsp^2 bonds; these might be $3d4s4p^2$, involving the promotion of an electron to a higher ($4p$) orbital, or, more probably, $4s4p^24d$ orbitals as originally suggested by Huggins (*J. Chem. Phys.*, 1937, **5**, 527). Strong support for the latter view is found on theoretical grounds (Craig, Maccoll, Nyholm, Orgel, and Sutton, unpublished work) and it overcomes the objection that if an electron is promoted its removal by oxidation should be facilitated. Such ready oxidation of square Cu(II) complexes is, of course, not observed.

(*b*) Cu(III). The moment of K_3CuF_6 indicates two unpaired electrons; the use of $3d^24s4p^3$ orbitals would necessitate the most improbable promotion of two unpaired electrons, but the use of $4s4p^34d^2$ hybrid orbitals leaves these two unpaired electrons in the $3d$ shell. This makes the reasonable assumption that the CuF_6^{3-} ion is octahedral.

Silver.—The moment of AgF_2 is notably low in comparison with those of Ag(II) complexes, which have values of μ corresponding closely with that required for one unpaired electron. The reason for this is as yet unknown.

The Platinum Metals.—These elements are noted for their tendency to form diamagnetic complexes, but paramagnetism has been reported in a few instances. Ruthenium trichloride (Cabrera and Fahlenbrach, *Anal. Fis. Quim.*, 1934, **32**, 1045; *Ann. Physik*, 1934, **21**, 832) has μ 2·09 B.M., and similar values are reported for many Ru(III) complexes (Gleu and Breuel, *Z. anorg. Chem.*, 1938, **237**, 326, 335, 350). For K_2RuCl_6, μ is 2·83 B.M. (Groves, Thesis, London, 1941); here there are clearly two unpaired electrons as required for $4d^25s5p^3$ octahedral orbitals. Groves also reported μ 1·4 B.M., an unexpectedly low value, for K_2OsCl_6. For Ir(IV), isoelectronic with Ru(III), Bose and Bhar (*Z. Physik*, 1928, **48**, 716) gave μ 1·9 B.M. for $IrCl_4$. Whether or not Hund's maximum multiplicity principle is generally valid, paramagnetism is, of course, to be expected in any compound in which the number of electrons on the metal is odd, *e.g.*, for compounds of Ru(III), Os(III), Rh(II), Rh(IV), Ir(II), Ir(IV), Pd(III), and Pt(III).

The complex Na_3RhF_7 is the first rhodium compound to show the moment required for one unpaired electron. The moment for the magnetically more concentrated simple fluoride is smaller, but its temperature dependence has not been measured. Palladium trifluoride, like many Ni(III) complexes (NiF_3 has not been described), has a moment corresponding to a single unpaired electron; the physical characteristics of palladium trifluoride suggest an ionic structure, though previous claims for the isomorphism of PdF_3 and CoF_3 have been questioned by Gutmann and Jack (*loc. cit.*). The diamagnetism of both K_2NiF_6 and K_2PtF_6 is entirely in accord with the assumption that octahedral complexes using $3d^24s4p^3$ and $5d^26s6p^3$ bonds are formed. The octahedral arrangement of the PtF_6^{2-} ion has already been established by *X*-ray crystallography (Mellor and Stephenson, *Austral. J. Sci. Res.*, 1951, **4**, *A*, 406). It is also interesting to note that Lander (*Acta Cryst.*, 1951, **4**, 148) and Lander and Wooten (*J. Amer. Chem. Soc.*, 1951, **73**, 2452) have prepared the complex $BaNiO_3$ and have shown that the Ni(IV) atom is octahedrally co-ordinated, the very weak paramagnetism of this compound being attributed to a small amount of dissociation.

Finally, the moment of the gold complexes calls for comment. The small moment of AuF_3 may be ignored. In passing it should be mentioned that a value of χ_g for $AuCl_3$ of $+0{\cdot}43 \times 10^{-6}$ is quoted in "International Critical Tables;" this figure has been erroneously transcribed from Meyer (*Ann. Physik*, 1899, **69**, 236) and should read $-0{\cdot}43 \times 10^{-6}$. In its physical properties auric fluoride differs notably from the other halides of gold; if it contains an Au^{3+} ion, the configuration for which would be $5d^8$, all of the electrons must be paired. Structures based on AuF_4 or AuF_6 squares or octahedra are also possible, however, and at present the structure is unknown. For the AuF_4^- ion the diamagnetism is in complete accord with the formation of covalent $5d6s6p^2$ bonds with the square arrangement found throughout the stereochemistry of complexes of tervalent gold.

The most important conclusion from this survey is that the previously observed differences in magnetic behaviour between the first and the later transition series exist also amongst the fluorides. Although these compounds might reasonably be expected to be the most likely to show maximum spin, in no instance are moments observed in the later series as high as those of analogous compounds of elements in the first transition series. Three possible explanations are suggested by Van Vleck (*loc. cit.*): (*a*) that the Hund theory of maximum multiplicity is not obeyed; (*b*) that the reduction is due to magnetic concentration; and (*c*) that the ions are not monatomic, *i.e.*, that metal–metal bonds are formed. Of these, (*c*) is known to be incorrect for K_2PtF_6 and many complex chlorides of the platinum metals; (*b*) is doubtless important in certain cases (cf. Dawson, *loc. cit.*), but it cannot account for the observed diamagnetism of both magnetically concentrated and magnetically dilute compounds; and it appears that (*a*) is the most likely general explanation of the smaller moments observed with these heavier elements.

This review emphasises the need for further experimental investigations along three main lines : the preparation of simple and complex fluorides of many of the heavier elements, especially those for which no values at all appear in Table 2; for many of the key substances mentioned, a thorough study of the temperature and field-strength dependence of susceptibility; more extensive *X*-ray crystallographic study of many of the substances mentioned, since until this is done interpretation of results is practically impossible. We are at present pursuing the second of these studies.

EXPERIMENTAL

Potassium Fluorotitanate.—The monohydrate, prepared from the iron-free dioxide according to Marchetti (*Z. anorg. Chem.*, 1895, **10**, 66), was dehydrated at 120°. Titanium was determined by decomposition with concentrated sulphuric acid and precipitation of the dioxide with ammonia (Found : Ti, 20·0. Calc. for K_2TiF_6 : Ti, 20·0%).

Vanadium Trifluoride.—This was prepared and analysed by Dr. V. Gutmann (Emeléus and Gutmann, *J.*, 1949, 2979). Another determination of vanadium was made by decomposition with sulphuric and nitric acids, reduction with sulphurous acid, and titration with permanganate (Found : V, 48·0. Calc. for VF_3 : V, 47·2%).

Potassium Hexafluorovanadate(III).—Vanadium pentoxide (5 g.) and potassium iodide (30 g.) were heated with hydrofluoric acid on a steam-bath until most of the liberated iodine had volatilised; after addition of a further 5 g. of potassium iodide (to ensure completion of reduction to tervalent vanadium), the green sparingly soluble deposit was washed with water, acetone, and ether. The *compound* was analysed as above (Found : V, 18·6. K_3VF_6 requires V, 18·4%).

Tantalum Trifluoride.—This was prepared and analysed by Dr. V. Gutmann (Emuléus and Gutmann, *J.*, 1950, 2115). In the absence of any knowledge of the determination of tervalent tantalum, the complete stability of the substance towards water appeared to guarantee its freedom from fluoride or oxyfluoride of Ta(V).

Potassium Pentafluorochromate(III) *Monohydrate.*—This was prepared according to Christensen (*J. pr. Chem.*, 1887, **35**, 161); chromium was determined iodometrically after oxidation to chromate by persulphate (Found : Cr, 21·6. Calc. for K_2CrF_5,H_2O : Cr, 21·4%).

Potassium Tetrafluoro-oxychromate(V).—Preparation and analysis were by Sharpe and Woolf's methods (*J.*, 1951, 798) (Found : Cr, 28·2. Calc. for $KCrOF_4$: Cr, 28·4%).

Manganese Trifluoride.—Preparation from manganous iodate and bromine trifluoride (Sharpe and Woolf, *loc. cit.*), followed by removal of the solvent at 220°, gave the purple-red trifluoride (Found : Mn, 50·0. Calc. for MnF_3 : Mn, 49·2%).

Potassium Pentafluoromanganite(IV).—The product from interaction of potassium permanganate and bromine trifluoride (Sharpe and Woolf, *loc. cit.*) was heated to constant weight at 180° and analysed as described previously (Found : Mn, 30·5; F, 46·8; Br, 1·8. Calc. for $KMnF_5$: Mn, 29·1; F, 50·2%).

Potassium Pentafluoromanganite(III) *Monohydrate.*—This compound, prepared according to Müller and Koppe (*Z. anorg. Chem.*, 1910, **68**, 160), was analysed by decomposition with sodium carbonate, ignition of the insoluble residue to Mn_3O_4, and precipitation of fluoride from the filtrate as calcium fluoride (Found : Mn, 22·4; F, 39·2. Calc. for K_2MnF_5,H_2O : Mn, 22·4; F, 38·6%).

Fluoroferrates.—Lithium, sodium, and ammonium hexafluoroferrate(III), potassium pentafluoroferrate(III), and *cæsium tetrafluoroferrate*(III) were obtained from mixtures of the metal chlorides and hydrofluoric acid. Iron was determined gravimetrically after decomposition of the complexes by hot concentrated sulphuric acid [Found, for the Li salt : Fe, 28·6. Calc. for Li_3FeF_6 : Fe, 29·2. Found, for the Na salt : Fe, 23·9. Calc. for Na_3FeF_6 : Fe, 23·5. Found, for the NH_4 salt : Fe, 25·5. Calc. for $(NH_4)_3FeF_6$: Fe, 25·0. Found, for the K salt : Fe, 24·3. Calc. for K_2FeF_5 : Fe, 24·4. Found, for the Cs salt : Fe, 20·9. $CsFeF_4$ requires Fe, 20·9%].

Cobalt Trifluoride.—Cobaltous fluoride was fluorinated by elemental fluorine according to Ruff and Ascher (*Z. anorg. Chem.*, 1929, **183**, 193), to a mixture shown by iodometric determination to contain 88% of CoF_3. Fluorine was determined by decomposition with sodium carbonate solution and precipitation as calcium fluoride (Found : F, 47·8. Calc. for 88% CoF_3 + 12% CoF_2 : F, 47·4%). We thank Dr. E. G. Walaschewski for this preparation. The susceptibility was corrected for the presence of 12% of CoF_2.

Cupric Fluoride Dihydrate.—The commercial product was recrystallised from dilute hydrofluoric acid, and the copper content determined iodometrically (Found : Cu, 46·4. Calc. for $CuF_2,2H_2O$: Cu, 46·2%).

Compounds of Platinum Metals.—Rhodium tetrafluoride (Found: Rh, 53·8; Br, 3·0. Calc. for RhF_4: Rh, 57·4; Br, 0%), palladium trifluoride (Found: Pd, 64·3. Calc. for PdF_3: Pd, 65·2%), platinum tetrafluoride (Found: Pt, 74·0. Calc. for PtF_4: Pt, 72·0%), sodium heptafluororhodate(IV) (Found: Rh, 33·2. Calc. for Na_3RhF_7: Rh, 33·7%), and potassium hexafluoroplatinate (Found: Pt, 19·9. Calc. for K_2PtF_6: Pt, 20·1%) were prepared and analysed as described previously (Sharpe, *J.*, 1950, 3444). Qualitative analysis showed the freedom of the compounds from contamination by iron, cobalt, or nickel.

Auric Fluoride and Silver Tetrafluoroaurate.—These were obtained and analysed according to Sharpe (*J.*, 1949, 2901) (Found: Au, 78·7. Calc. for AuF_3: Au, 78·4%) (Found: Au, 51·3. Calc. for $AgAuF_4$: Au, 51·7%).

Magnetic Measurements.—The Gouy method was used. For details see Part III (*J.*, 1950, 851).

The loan of compounds of precious metals by Messrs. Johnson, Matthey and Company, Limited, is gratefully acknowledged. The authors are also indebted to Professor W. Klemm, Dr. J. T. Grey, and Dr. G. H. Cartledge for most helpful communications on unpublished or inaccessible work.

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[*Received, May 2nd,* 1952.]