771. *The Magnetic Properties of the Quinquevalent Complex Fluorides of Molybdenum, Tungsten, and Rhenium.*

By G. B. HARGREAVES and R. D. PEACOCK.

The magnetic moments of the complex fluorides $MMoF_6$, MWF_6, and $MReF_6$ (where M is an alkali metal) have been measured over the temperature range 90—300° K.

APART from the complex fluorides recently prepared in these laboratories, no compound of quinquevalent molybdenum, tungsten, and rhenium is known which contains discrete AX_6^- ions, although salts such as K_2MoOCl_5 (where the complex ion includes two different ligands) are well established. Recent interest in the magnetic behaviour of " d " block transition-metal ions has now led us to study this aspect of the properties of our compounds.

The complex fluorides have the low magnetic moments to be expected for transition-metal ions of the second or third Periods in these electronic configurations; the spin-only value for the salts $MMoF_6$ and MWF_6 ($d\varepsilon_1$ configuration) is $\mu = 1\cdot73$ B.M., and for the salts $MReF_6$ ($d\varepsilon_2$) is $\mu = 2\cdot83$ B.M. None of the moments follows the simple relation $\chi_A \propto 1/T$ (where T is the absolute temperature), but $MMoF_6$ and $MReF_6$ fit the Curie–Weiss relationship $\chi_A \propto 1/(T + \theta)$ but with rather large positive values of the Curie constant (Fig. 1 and Table 1). The plot $1/\chi_A$ against T for the tungsten salts does not give a straight line; hence there is undoubted antiferromagnetism with Néel points over the range 110—140° K.

TABLE 1.

	θ	$\mu_{calc.}$ (300°)		θ	$\mu_{calc.}$ (300°)		θ	$\mu_{calc.}$ (300°)		θ	$\mu_{calc.}$ (300°)
$NaMoF_6$	218	1·66	$RbMoF_6$	158	1·75	$NaReF_6$	100	1·57	$RbReF_6$	50	1·56
$KMoF_6$	66	1·51	$CsMoF_6$	224	1·66	$KReF_6$	58	2·05	$CsReF_6$	35	1·53

The simple idea of the magnetic behaviour of the " d " block elements which relates paramagnetism directly to the number of unpaired spins, whilst specially useful for the first transition series, is of less value when applied to the second and third rows. In particular, difficulties usually arise with d^2 and d^4 complexes of the heaviest transition elements. For second- and third-row transition elements spin–orbit coupling, which depends largely on nuclear charge and hence on atomic number, has also to be taken into account. In this discussion we follow the views of Earnshaw, Figgis, Lewis, and Nyholm,[1] who have applied Kotani's theory [2] to the magnetic behaviour of ruthenium and osmium compounds. The theory predicts magnetic moments of gaseous ions subjected to a cubic crystal field, so that when it is applied to solids departures from ideal behaviour may be expected. Fig. 2 shows the experimental change of μ_{eff} with T for the three series of salts, together with " ideal " plots of μ_{eff} expected for various values of the spin–orbit coupling constant A. It is relevant to note that for $d\varepsilon_1$ and $d\varepsilon_2$ configurations large changes in the spin–orbit coupling constant cause only small changes in the magnetic moment.

The graphs show that Kotani's theory cannot be applied directly to our compounds. In the case of the tungsten salts this is obviously because there is antiferromagnetism, and the nature of the other experimental curves suggests that in these cases also Néel points exist at temperatures below those at which our measurements were made. The antiferromagnetic interaction in these compounds is not likely to be of the normal type such as occurs in a perovskite lattice ABO_3 and is presumably similar to that observed by Owen *et al.*[3] in K_2IrCl_6. One point, however, which does emerge from the graphs in

[1] Earnshaw. Figgis, Lewis, and Nyholm, *Nature*, 1957, **179**, 1121.
[2] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.
[3] Griffiths, Owen, and Ward, *Proc. Roy. Soc.*, 1953, **219**, A, 526.

all three series of compounds is the different behaviour of the potassium salts from that of the rest. This is particularly noticeable in the rhenium series, and it is relevant to call attention to the structures of the salts.

The cubic sodium salts and the rhombohedral rubidium and cæsium salts undoubtedly

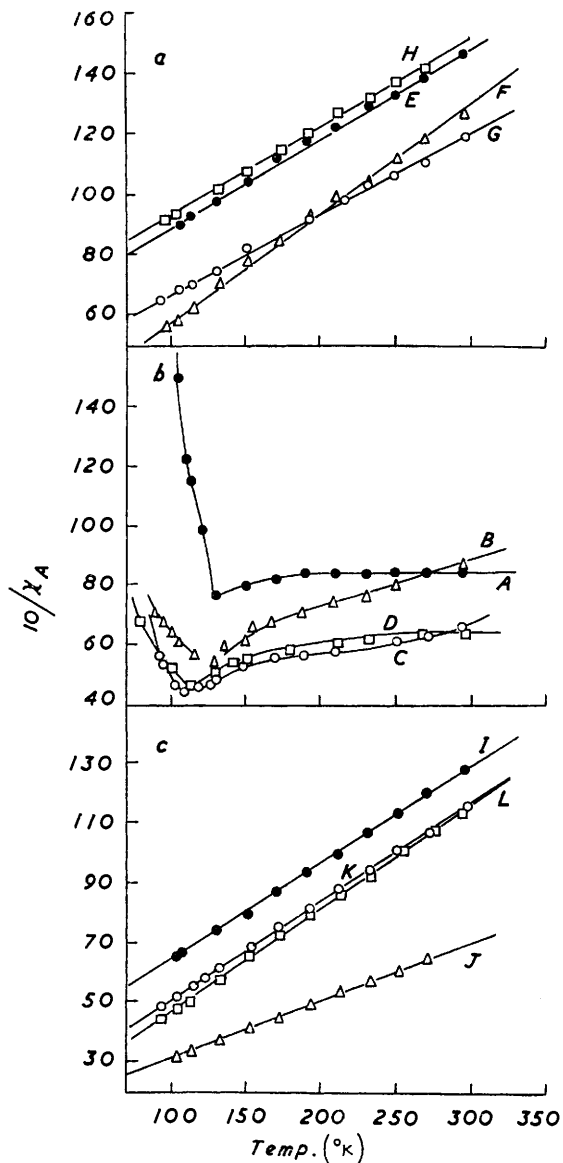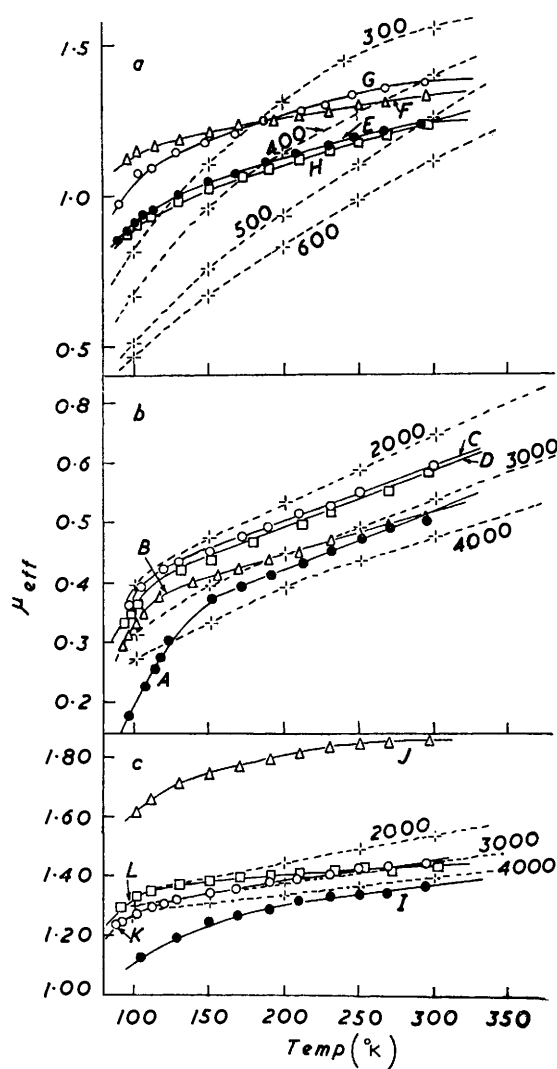FIG. 1. *Plots of $1/\chi_A$ against absolute temperature.*

FIG. 2. *Plots of μ_{eff} against absolute temperature.*

a, $XMoF_6$ series; *b*, XWF_6 series; *c*, $XReF_6$ series. For individual compounds, see Table 2. Broken lines are theoretical curves calculated on the basis of values of A as marked thereon.

contain discrete AF_6^- (A = Mo, W, Re) octahedra with a single A–F distance.[5,6] But the potassium salts are tetragonally distorted, and a recent determination [4] of the structure

[4] Bode and Döhren, *Acta Cryst.*, 1958, **11**, 80.
[5] Hargreaves and Peacock, *J.*, 1957, 4212; Peacock, *J.*, 1957, 467.
[6] For the rhombohedral $KOsF_6$ structure see Hepworth, Jack, and Westland, *J. Inorg. Nucl. Chem.*, 1956, **2**, 79.

of $KNbF_6$, which is isostructural with our salts, has shown that in each NbF_6^- octahedron there are two shorter Nb–F distances and four longer ones. The difference between them is slight (~ 0.02 Å) and would not account for the differences in magnetic behaviour between the potassium salts and the rest if Kotani's theory alone were taken into account. However, a tetragonal distortion would also affect antiferromagnetic interaction, and could therefore have a disproportionately large effect on the magnetic moment.

<div align="center">EXPERIMENTAL</div>

Quinquevalent Complex Fluorides.—The salts were prepared as described previously [5] and, except for KWF_6 (Found: W, 53·3. Calc.: W, 54·6), all analyses, carried out as before, gave the same figures.

<div align="center">TABLE 2.   Corrected molar susceptibilities (temperatures in °K).</div>

<div align="center">MWF$_6$ Series $d\varepsilon_1$</div>

NaWF$_6$ (A)		KWF$_6$ (B)		RbWF$_6$ (C)		CsWF$_6$ (D)	
Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$
294·2	112·8	294·2	108·2	294·2	142·4	295·0	145·8
270·0	112·8	269·0	117·3	271·3	147·6	267·5	145·8
250·0	112·8	249·7	117·3	249·5	152·8	230·5	148·6
229·5	112·8	230·7	124·0	230·0	152·8	210·5	151·4
210·0	112·8	208·2	126·3	209·3	160·6	149·8	165·5
189·8	112·8	188·5	133·1	188·5	153·3	139·5	168·3
169·5	115·4	167·6	137·6	169·5	165·9	128·5	176·7
150·0	118·0	154·4	139·8	148·5	173·7	120·6	176·7
130·0	123·3	149·8	151·1	128·8	186·7	111·5	196·4
120·0	96·9	136·0	153·4	127·0	189·4	99·5	173·89
116·8	83·6	128·5	169·1	117	194·6	90·8	165·5
110·0	78·3	115·0	160·2	108	202·4		
105·0	65·1	104·0	151·1	102·8	194·6		
94·3	43·9	90	130·8	95	171·1		
				90	168·5		

<div align="center">MMoF$_6$ Series $d\varepsilon_1$</div>

NaMoF$_6$ (E)		KMoF$_6$ (F)		RbMoF$_6$ (G)		CsMoF$_6$ (H)	
Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$
295·0	681·1	294·4	792·0	294·6	841·4	294·0	680·5
268·3	722·1	268·5	840·8	267·8	908·5	268·4	704·8
258·6	748·5	249·5	892·1	248·0	943·1	248·8	731·5
230·3	768·8	230·5	942·6	230·0	969·6	231·0	756·0
209·3	815·7	209·0	1008	214·3	1014	210·0	787·5
189·3	847·9	190·8	1074	189·8	1090	190·0	823·9
169·2	888·7	170·5	1171	169·0	1124	171·8	870·1
150·3	955·9	149·5	1279	149·0	1213	149·0	928·5
129·3	1017	130·5	1413	128·8	1340	130·0	977·2
112·5	1070	112·8	1581	112·0	1425	111·0	1062
105·4	1104	101·0	1710	103	1455	101·3	1069
93·3	1082	95·5	1746	90·0	1502	94·3	1089
88	1099						

<div align="center">MReF$_6$ Series $d\varepsilon_2$</div>

NaReF$_6$ (I)		KReF$_6$ (J)		RbReF$_6$ (K)		CsReF$_6$ (L)	
Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$	Temp.	$10^6\chi_A$
294·2	792·7	295·4	1444	295·1	884·6	295·2	881·2
269·0	844·2	268·8	1585	269·5	952·3	269·5	940·4
250·0	894·3	250·0	1699	249·4	1015	250·8	1011
230·0	950·7	230·5	1818	229·8	1082	231·0	1088
210·0	1024	210·5	1943	209·4	1163	210·0	1177
190·3	1086	189·5	2106	190·3	1257	190·0	1283
169·5	1170	170·4	2279	169·2	1357	170·0	1408
149·5	1284	150·0	2507	150·8	1487	150·0	1567
129·3	1368	129·5	2783	129·3	1681	130·0	1787
104·0	1527	110·8	3087	120·0	1771	110·0	2054
102·5	1555	101·0	3232	112·0	1865	101·3	2166
				101·5	2000	90·0	2309
				90·8	2130		
				89·0	2135		

Magnetic Measurements.—These were made over the temperature range 90—300° K by the Gouy method. The apparatus was similar to that described by Figgis and Nyholm.[7] Since the salts are unstable in air, the powdered specimens were introduced into Pyrex magnetic tubes (whose diamagnetism had previously been determined) under vacuum. Results are shown in Table 2.

⁷ Figgis and Nyholm, *J.*, in the press.