Preparation and Properties of Alkali-metal Hexafluoromolybdates(IV)

By **Anthony J. Edwards** * and **Brian R. Steventon**, Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Alkali-metal hexafluoromolybdates(IV), $M_2[MoF_6]$ (M = Li, Na, Rb, or Cs), have been prepared by interaction of equivalent amounts of MoF_6 and MI in sulphur dioxide solution. The potassium salt has been obtained impure, mixed with hexafluoromolybdate(III). Unit-cell dimensions and magnetic susceptibilities of all the compounds have been measured, and i.r. and visible spectra in the case of caesium.

THE preparation of sodium hexafluoromolybdate(IV) by the interaction of molybdenum hexafluoride with a large excess of sodium iodide in sulphur dioxide solution has been briefly reported.[1] The crystal structure of the corresponding lithium salt [2] has also been determined, on a single fragment derived from the interaction of molybdenum trifluoride and lithium fluoride at elevated temperatures. (Presumably this compound resulted from some unexpected oxidation.) Attempts to extend the method used for the sodium salt to other alkali metals using excess of alkali-metal iodide led to reduction of MoF_6 to Mo^{III}. The syntheses have now been achieved by the interaction of weighed equivalent amounts of alkali-metal iodide and MoF_6 in sulphur dioxide solution.

EXPERIMENTAL

Molybdenum hexafluoride was prepared from the elements, freed from hydrogen fluoride by treatment with dry sodium fluoride, and stored in a Hoke stainless-steel cylinder. Alkali-metal iodides (B.D.H., AnalaR grade) were dried before use. Sulphur dioxide (B.D.H.) was passed over phosphorus pentaoxide before use.

Fluoromolybdates(IV).—A fused Pyrex-glass apparatus was used throughout, rigorously dried and with provision for the entry of air, dried over P_4O_{10}. Several unsuccessful attempts to prepare the potassium salt were made. Initially the technique reported [1] for the sodium salt was attempted.

(*a*) An excess of potassium iodide was treated with molybdenum hexafluoride in sulphur dioxide solution. The SO_2 and iodine were removed by pumping *in vacuo* and the sample was then washed with more SO_2 to remove the excess of KI. The buff product gave a complex *X*-ray powder photograph with a set of strong lines corresponding to a trigonal cell for potassium hexafluoromolybdate(IV), but with other weak lines corresponding [3] to potassium hexafluoromolybdate(III).

(*b*) A weighed quantity of dry KI was treated with excess of MoF_6 in sulphur dioxide solution to produce the fluoromolybdate(V).[4] The SO_2, excess of MoF_6, and iodine were removed by pumping *in vacuo*. A second quantity of KI, equal to the first, was added to the solid product under rigorously dry conditions, and more SO_2 was added. Iodine was released in the sulphur dioxide solution, but the buff solid product obtained after the removal of SO_2 and iodine gave a very complex *X*-ray powder photograph and the method was abandoned.

(*c*) A quantity of MoF_6 was distilled into a Pyrex bulb containing sodium fluoride and equipped with a break-seal. The weight of hexafluoride was determined and two equivalents of KI were transferred to the reaction flask. The iodide was treated with MoF_6 in sulphur dioxide solution. Iodine was released, and together with SO_2 was removed after *ca.* 1 h by warming, initially to room temperature and finally to 150 °C. An *X*-ray powder photograph of the product showed the presence of potassium hexafluoromolybdate(V) and KI, as well as some $K_2[MoF_6]$.

(*d*) The preparation was repeated, but the solution in SO_2 was stored in a deep-freeze unit at -25 °C for 10 d, maintaining the sulphur dioxide liquid. After removal of SO_2 and iodine, the product again showed the presence of unchanged KI, from an *X*-ray powder photograph.

(*e*) The successful preparations were achieved by following the procedure in (*c*), with a 2 : 1 ratio of alkali-metal iodide to MoF_6, up to the removal of SO_2 and iodine. A second quantity of SO_2 was then condensed on to the product and held at *ca.* -20 °C for *ca.* 2 h. More iodine was released and together with SO_2 was removed by heating as before. Further quantities of SO_2 were added and the above procedure repeated until virtually no iodine was released. This usually entailed at least six additions of the solvent. The iodine evolved was collected and estimated both by weighing and volumetrically, and recovery was always $>90\%$.

The fluoromolybdates(IV) are light brown to buff crystalline powders (Found: Cs, 54.9; F, 23.9; Mo, 19.4. $Cs_2[MoF_6]$ requires Cs, 55.9; F, 24.0; Mo, 20.2%. Found: F, 28.5; Mo, 24.5. $Rb_2[MoF_6]$ requires F, 29.9; Mo, 25.2%.

---

[1] A. J. Edwards and R. D. Peacock, *Chem. and Ind.*, 1960, 1441.

[2] G. Brunton, *Mat. Res. Bull.*, 1971, **6**, 555.

[3] R. D. Peacock, *Progr. Inorg. Chem.*, 1960, **2**, 193; L. M. Toth, G. D. Brunton, and P. G. Smith, *Inorg. Chem.*, 1969, **8**, 2694.

[4] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1957, 4212.

Found: F, 43.9; Mo, 36.4. $Na_2[MoF_6]$ requires F, 44.5; Mo, 37.5%. Found: F, 42.1; Mo, 39.6. $Li_2[MoF_6]$ requires F, 50.9; Mo, 42.9%). The identity of the compounds was confirmed by *X*-ray powder crystallography. Considerable difficulty was experienced in the analysis of the lithium salt, which was much more reactive than the others, and the low results may be due to losing sample during dissolution in water or possibly to some co-ordinated sulphur dioxide. The other salts only slowly decomposed in contact with the atmosphere, that of caesium appearing particularly stable.

As reported previously [1] the sodium salt could be prepared by the interaction of excess of sodium iodide with MoF_6 and subsequent removal of the unchanged iodide, by washing with SO_2 and finally ethanol. The present procedure was found to be more controllable and to give more consistent preparations.

Potassium Hexafluoromolybdate(IV).—Attempts to prepare this salt pure were unsuccessful. The procedure outlined above resulted in evolution of 97% of the iodine expected and an acceptable analysis (Found: F, 38.6; Mo, 30.8. $K_2[MoF_6]$ requires F, 39.6; Mo, 33.3%). However, the *X*-ray powder photograph of this product showed reasonably strong lines other than those ascribed to $K_2[MoF_6]$, and the magnetic susceptibility was different from that of the other salts.

Since some hexafluoromolybdate(III) had been produced in our attempted preparations, we treated MoF_6 with a very large excess of KI in sulphur dioxide solution, and kept the mixture at −25 °C for 4 d. On removal of liberated iodine and the excess of KI, by washing with SO_2, an *X*-ray powder photograph showed strong lines corresponding [3] to the hexafluoromolybdate(III), although other lines were also present.

These results implied that $[MoF_6]^{2-}$ was rather easily reduced to $[MoF_6]^{3-}$ for the potassium salt and the preparation was therefore attempted using a 2 : 1 ratio of potassium bromide to MoF_6. When no more bromine was evolved, SO_2 was removed and the product was examined using *X*-ray crystallography. The photograph showed the presence of large amounts of KBr and the molybdate(V) salt.

Analysis.—The sample was treated with water and gave a deep red solution which was promptly made alkaline with sodium hydroxide solution and treated with dilute hydrogen peroxide solution (5 cm³) to oxidize molybdenum. Molybdenum was estimated as the oxine complex, and fluorine volumetrically by the Volhard method after precipitation as lead chloride fluoride. Caesium was determined gravimetrically as the tetraphenylborate.

Magnetic measurements were made on a Gouy balance as previously described [5] over the range 90—290 K. Absorption spectra were obtained on a Unicam SP 800 spectrophotometer fitted with a reflectance attachment, and/or a Perkin-Elmer 337 instrument. *X*-ray powder photographs were taken on a Hilger and Watts 19-cm camera using filtered Cu-K_α radiation.

RESULTS AND DISCUSSION

The reduction of molybdenum hexafluoride by iodide ion occurs in a stepwise manner to produce hexafluoromolybdates-(V), -(IV), and -(III) under appropriate conditions. The use of excess of hexafluoride results in very rapid formation of the molybdate(V) ion.[4] When two equivalents of iodide ion are used an equilibrium appears to be established between the molybdate-(V) and -(IV) ions. This is supported by the incomplete formation of

$$2[MoF_6]^- + 2\,I^- \rightleftharpoons 2[MoF_6]^{2-} + I_2$$

the molybdate(IV) salt after a very long reaction time. Removal of the iodine displaces the reaction to the right and virtually complete formation of $[MoF_6]^{2-}$ can be achieved by the technique involving successive applications of SO_2 followed by removal of the iodine produced.

The failure to prepare a pure sample of the potassium salt is surprising since the method was successful for the other alkali metals. The observation of lines corresponding to the molybdate(III) salt [3] on powder photographs of products from the potassium salt suggests that further reduction takes place more easily in this case, although there is no obvious reason for this. Replacement of iodide by bromide ion, to provide a less powerful reducing agent, gave only formation of the molybdate(V) salt, so that bromide ion is too weak a reducing agent even for the second stage of the reduction.

The unit-cell dimensions of the fluoromolybdates(IV) given in Table 1 are very similar to those of the corresponding technetium, rhenium, and zirconium compounds [6] for the rubidium and caesium salts. The sodium salt was previously reported [1] to be cubic a_0 = 10.00 Å, but it was later suggested [7] that the compound is isostructural with the α form of disodium hexafluorouranate(IV), with an orthorhombic cell having a_0 = 5.76, b_0 = 4.48, and c_0 = 10.48 Å. The agreement between observed and calculated sin²θ values is, however, rather poorer for this cell than for the original, and the true symmetry appears to be monoclinic, with the compound isostructural [8] with sodium hexafluorostannate(IV). Although accurate cell parameters cannot be deduced from the powder photograph, due to multiple overlapping of lines, sin²θ values calculated from the parameters of the tin salt give very good agreement with observed values. It has previously been observed [7] that the orthorhombic cell can be related to the monoclinic cell, and this is also the case for the original cubic cell.

TABLE 1

Unit-cell sizes of hexafluoromolybdates(IV), $M_2[MoF_6]$

		Length/Å			Angle (°)
M	Crystal system	a_0	b_0	c_0	β
Li	Hexagonal	4.93		4.55	
Na	Monoclinic	11.3	5.1	5.1	117
K	Trigonal	5.84		4.63	
Rb	Trigonal	6.02		4.78	
Cs	Trigonal	6.27		4.98	

The unit-cell dimensions for the lithium salt are quite different from those reported by Brunton,[2] and the

---

[5] B. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 331.

[6] J. H. Canterford and R. Colton, 'Halides of the Second and Third Row Transition Metals,' Wiley–Interscience, London, New York, 1968.

[7] D. H. Brown, K. R. Dixon, R. D. W. Kemmitt, and D. W. A. Sharp, *J. Chem. Soc.*, 1965, 1559.

[8] C. Hebecker, H. G. von Schnering, and R. Hoppe, *Naturwiss.*, 1966, **53**, 154.

powder photograph could not be indexed on the basis of his tetragonal unit cell. Since the reaction conditions were completely different in the two preparations, the two unit cells may correspond to different polymorphs. The unit cell reported here is very similar to those of the lithium hexafluorometallates(IV) of tin,[9] lead,[9] and zirconium.[10]

The trigonal cell, indexed from the powder photograph of the impure potassium salt, is very similar to the trigonal cells of the corresponding technetium and rhenium salts.[6] Potassium hexafluorozirconate(IV) has an orthorhombic cell,[11] with a change in structure from the isolated octahedra of the trigonal compounds to a polymeric anion containing eight-co-ordinate zirconium. The difficulty in obtaining a pure sample of $K_2[MoF_6]$ may be due to a tendency towards formation of the eight-co-ordinate arrangement.

The magnetic-susceptibility behaviour (Table 2) is very similar to that [12] of the isoelectronic hexafluorotechnetates(V), varying with temperature according to the Curie–Weiss law, with θ ranging from 60 to 100 °C. The room-temperature magnetic moments are similar, especially those for the sodium and rubidium salts (2.3 B.M.),* and are less than the spin-only value for a d^2 configuration. The lower values for the lithium and caesium salts may reflect the difficulty of packing the sample tubes.

The reflectance spectrum of the caesium salt showed an extremely broad absorption over the range 13 000—31 000 cm^{-1}. No definite peaks could be distinguished, unlike the hexafluorotechnetates(V) where the peaks in the same region were resolvable. The i.r. spectrum of the caesium salt showed absorptions at 540 and 255 cm^{-1}. These can be assigned to ν_3 and ν_4 respectively. A comparison can be made with molybdenum hexafluoride [13] and with the [14] hexafluoromolybdate(V) ion where ν_3 is at 741 and 635 cm^{-1} respectively. The decrease in frequency throughout the series is in line with the increase in Mo–F distance with decreasing oxidation state for molybdenum and with increasing overall negative charge. The ν_4 frequencies for MoF_6 at 262 cm^{-1} and for $[MoF_6]^-$ at 250 cm^{-1} are very similar and reflect the different character of this mode compared with ν_3. No Raman data are available and hence no comparisons of ν_1 can be made.

TABLE 2

Magnetic susceptibilities of hexafluoromolybdates(IV)

$Li_2[MoF_6]$

T/K	$10^6\chi_A$/ c.g.s. units	$\mu_{eff.}$/B.M.
293	1 819	2.07
274	1 914	2.05
244	2 097	2.03
185	2 588	1.96
164	2 813	1.93
143	3 090	1.89
123	3 445	1.85
103	3 901	1.80

θ = 66°

$Na_2[MoF_6]$

T/K	$10^6\chi_A$/ c.g.s. units	$\mu_{eff.}$/B.M.
294	2 288	2.33
274	2 397	2.30
244	2 615	2.27
224	2 812	2.25
204	3 013	2.22
185	3 237	2.19
164	3 510	2.16
143	3 842	2.10
123	4 246	2.05
103	4 709	1.98

θ = 73°

$Rb_2[MoF_6]$

T/K	$10^6\chi_A$/ c.g.s. units	$\mu_{eff.}$/B.M.
293	2 267	2.32
275	2 382	2.30
245	2 608	2.27
224	2 808	2.24
203	3 034	2.22
185	3 266	2.20
164	3 566	2.17
143	3 944	2.13
123	4 302	2.07
103	4 865	2.01
98	5 038	1.99

θ = 63°

$Cs_2[MoF_6]$

T/K	$10^6\chi_A$/ c.g.s. units	$\mu_{eff.}$/B.M.
295	1 872	2.11
275	1 961	2.09
245	2 121	2.05
224	2 245	2.01
205	2 396	1.99
185	2 560	1.95
164	2 747	1.91
144	2 986	1.86
123	3 270	1.80
103	3 594	1.73
95	3 753	1.70

θ = 99°

We thank the S.R.C. for financial assistance (to B. R. S.), and I.C.I. Ltd. (Mond Division) for the gift of a fluorine cell.

[7/552 *Received*, 29*th March*, 1977]

---

* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[9] C. Hebecker and R. Hoppe, *Naturwiss.*, 1966, **53**, 106.

[10] R. Hoppe and W. Dahne, *Naturwiss.*, 1960, **47**, 397.

[11] H. Bode and G. Teufer, *Acta Cryst.*, 1956, **9**, 929.

[12] D. Hugill and R. D. Peacock, *J. Chem. Soc.* (*A*), 1966, 1339.

[13] B. Weinstock and G. L. Goodman, *Adv. Chem. Phys.*, 1965, **9**, 169.

[14] A. Beuter and W. Sawodny, *Z. anorg. Chem.*, 1976, **427**, 37.