Metal K-Edge Extended X-Ray Absorption Fine Structure Studies of MoF_6, RuF_6, RhF_6 and Related Fluoroanions

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Metal K-edge extended X-ray absorption fine structure data obtained for MoF_6, RuF_6 and RhF_6 as solids at 10 K have been refined to give *d*(M–F) = 1.81 (Mo), 1.83 (Ru) and 1.84 Å (Rh). Corresponding values for the powdered fluoroanions at room temperature are *ca.* 1.85 Å for $K[MF_6]$ (M = Ru or Rh) and 1.90–1.93 Å for $K_2[MF_6]$ (M = Ru, Rh or Pd). The value of *d*(Rh–Cl) in $Cs_2[RhCl_6]$ is 2.31 Å. The results are compared with previous data on the 5d analogues and with X-ray crystallographic data.

In a companion paper[1] we demonstrated that metal L_{III}-edge extended X-ray absorption fine structure (EXAFS) data could provide *d*(M–F) bond lengths for the volatile, moisture-sensitive and highly corrosive 5d hexafluorides MF_6 (M = W –Pt), and for related hexafluoroanions $[MF_6]^{n-}$. Here we report similar K-edge studies on the 4d analogues MoF_6, RuF_6 and RhF_6 (TcF_6 was unavailable for the present study due to its radioactivity), and on the fluoroanions $K[MF_6]$ (M = Ru or Rh) and $K_2[MF_6]$ (M = Ru, Rh or Pd). Ruthenium and rhodium hexafluorides are powerful oxidants, exceptionally corrosive, and thermally unstable at temperatures little above ambient,[2,3] properties which have thus far combined to prevent any detailed structural studies on these compounds, and which will almost certainly preclude electron diffraction studies in the vapour phase. However, the EXAFS technique is well suited to the study of such unstable materials. The potassium hexafluorometalates listed are, with the sole exception of $K_2[RuF_6]$, immediately decomposed by water, and have not been obtained in single crystalline form. As we demonstrated for the 5d analogues, the EXAFS data provide *d*(M–F) distances and, in favourable cases, distances to the neighbouring (non-bonded) fluorines and potassium ions.[1]

Experimental

Metal K-edge EXAFS data were collected at the Daresbury Synchrotron Radiation Source operating at 2 GeV (*ca.* 3.2×10^{-10} J) with an average current of 190 mA on station 9.2 using a double-crystal Si (220) monochromator, offset to 50% of the rocking curve for harmonic rejection. The EXAFS data were collected in transmission mode for MoF_6 or RuF_6 condensed onto 0.25 mm thick aluminium windows (Goodfellows Metals, 99.999%) at 10 K, using the cryostat described previously.[4] Owing to the limited amounts of sample, the data for RhF_6 were collected in the same apparatus, but in fluorescence mode. The EXAFS data treatment was similar to that described in previous papers[1,4,5] and utilized the programs PAXAS[6] and EXCURVE 90.[7] Several data sets were collected for each compound in *k* space (k = photoelectron wave vector/Å^{-1}), and averaged to improve the signal-to-noise ratio. The pre-edge background was removed by fitting the spectrum to a cubic polynomial, and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using polynomials, and the optimum function judged by minimizing the intensity of chemically insignificant shells at low *r* (*r* = radial distance from primary absorbing atom) in the Fourier transform. The data were multiplied by k^3 to compensate for the decreased intensity at higher *k*. Curve fitting used single scattering curved-wave theory with phase shifts and back-scattering factors calculated using the normal *ab initio* methods.[7] The fits discussed below are model data compared to the raw (background subtracted) EXAFS, and no Fourier filtering or smoothing has been applied.

Molybdenum hexafluoride was obtained from Matheson Chemical Co. and used as received. Ruthenium and rhodium hexafluorides were made by high-pressure fluorination of the corresponding pentafluorides.[2] After removal of excess of fluorine at low temperature, the autoclaves were filled to *ca.* 2 atm (*ca.* 2×10^5 Pa) pressure with dry nitrogen, and stored at −78 °C until required. (Samples were used within 5 d of synthesis.) The autoclave was connected to the cryostat by a prefluorinated metal tube, warmed to room temperature, and the MF_6 entrained in nitrogen sprayed on to the cold (10 K) window.

Orange, unstable $K[RhF_6]$ was made from RhF_5 and KF in anhydrous HF,[8] and the other hexafluorometalates were made as potassium salts by literature methods: $K[RuF_6]$,[9] $K_2[RuF_6]$,[9] $K_2[RhF_6]$[10] and $K_2[PdF_6]$.[11] The green caesium hexachlororhodate(IV) $Cs_2[RhCl_6]$ was made as described by Feldman *et al.*[12] The identities of the fluoroanions were confirmed by comparison of their X-ray powder patterns and UV/VIS spectra with literature data.[13] Samples of the reactive and moisture-sensitive $K[RuF_6]$, $K[RhF_6]$, $K_2[RhF_6]$ and $K_2[PdF_6]$ were diluted with dry LiF in a dry-box, and run in the Teflon-FEP cells described elsewhere.[1] The less-reactive $K_2[RuF_6]$ and $Cs_2[RhCl_6]$ were diluted with dry BN, and run between Sellotape strips in 1 mm aluminium spacers.

Results and Discussion

Hexafluorides.—X-Ray powder diffraction studies on solid MoF_6 have shown it to be dimorphic with a body-centred cubic (b.c.c.) structure above 263 °C, and an orthorhombic structure below this temperature.[14] Powder neutron diffraction studies[15] gave *d*(Mo–F) as 1.802(14) Å for the former and 1.81 Å (average) for the latter, whilst electron diffraction data[16] on the vapour gave a value of 1.82 Å. The molybdenum K-edge EXAFS data, obtained from solid MoF_6 at 10 K, refined to *d*(Mo–F) = 1.81 Å in excellent agreement with the neutron diffraction data. As shown previously for the 5d analogues,[1] a weak feature at *ca.* 3.5 Å in the Fourier transform corresponds with back scattering by the fluorine atoms in neighbouring molecules. The data in this case are adequately reproduced by a two-shell fit.

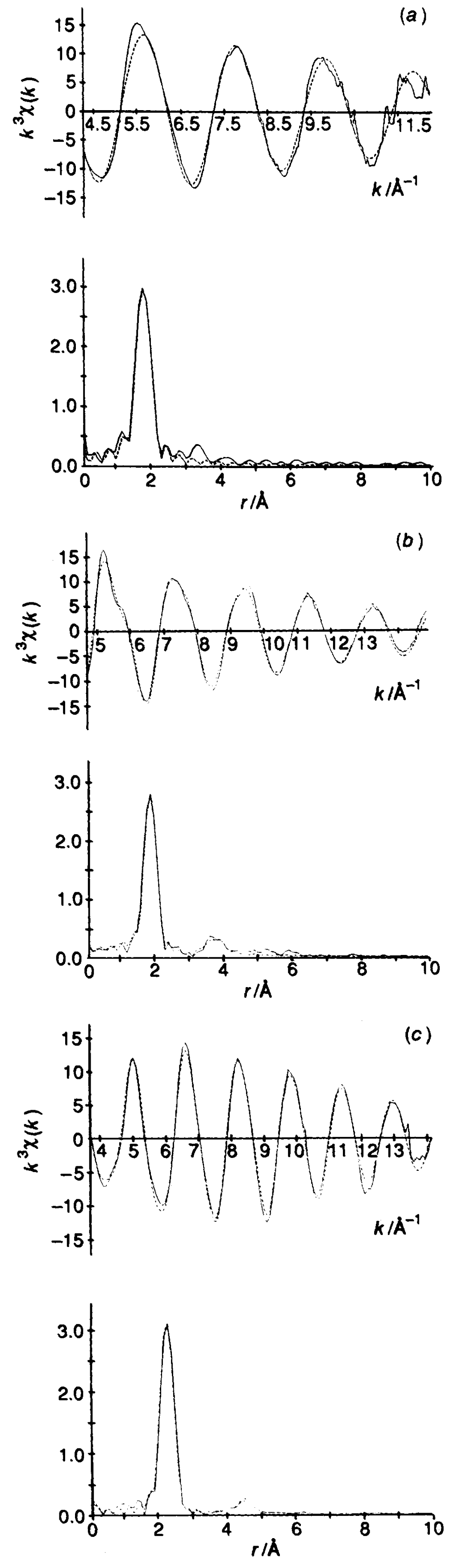

Fig. 1 The background-subtracted EXAFS (upper: ——, experimental × k^3; – – –, curved-wave theory × k^3) and the corresponding Fourier transforms (lower: ——, experimental; – – –, theoretical) for (*a*) RuF_6, (*b*) $K_2[RuF_6]$ and (*c*) $Cs_2[RhCl_6]$

Ruthenium and rhodium hexafluorides have limited thermal stability, and our previous spectroscopic studies[2] revealed that some decomposition to lower fluorides often accompanies their transport in high vacuum at ambient temperatures. This decomposition is largely eliminated if they are entrained in an inert gas such as nitrogen or argon, and the samples from which the EXAFS data were collected were carried in nitrogen (which has a lower mass absorption for X-rays than does argon). The mixture was condensed onto the window at 10 K, with the estimated $N_2:MF_6$ ratios >50:1. Although this dilution is much lower than that normally used in matrix-isolation studies, it ensured that the MF_6 molecules in the deposited solid are mostly surrounded by nitrogen, and thus only single-shell fits are given for these two compounds. The broad, weak features at *ca.* 3.5–4.5 Å in the Fourier transforms probably arise from the nitrogen cage but, although addition of such a shell to the model produces reductions in the fit index and *R* factor, it is not well defined, as might be expected for a disordered matrix composed of light back scatterers. The inevitable result of using only the single-shell fit is somewhat poorer modelling of the EXAFS, particularly at low *k*, and higher *R* factors and fit indices. However, there is no effect upon the precision of *d*(M–F), which is the main parameter of interest. The refined *d*(Ru–F) and *d*(Rh–F) and parameters are given in Table 1, and an example of the EXAFS and Fourier transform are shown in Fig. 1. The bond lengths of 1.83 and 1.84 Å respectively are the only data on these two compounds in any phase, but can be compared with *d*(M–F) in solid OsF_6 and IrF_6, which are 1.82 Å.[1] A similar comparison of the EXAFS-determined M–F bond lengths in MoF_6 (1.81 Å) and WF_6 (1.82 Å)[1] shows, as expected, that the corresponding 4d and 5d compounds have effectively identical *d*(M–F), within the normal precision of first-shell measurements (±0.02 Å).

Halogeno-anions.—The structure of $K_2[RuF_6]$ belongs to the trigonal $K_2[GeF_6]$ type,[10] and the treatment of the EXAFS data follows that previously applied[1] to the isostructural $K_2[PtF_6]$. Here, shells were added in succession as required for the lattice type, each shell being iterated, and the best fits tested for statistical significance.[17] The three-shell model (6F, 6K, 6F) (Table 2) passed the statistical significance tests, although the potassium shell has a high Debye–Waller factor (0.046). Addition of further shells, which would correspond to 2Ru (shell 4) and 12F (shell 5), was unsatisfactory in that the shell radii merged on iteration, and the fit cited in Table 2 is for the three-shell model. The Rh K-edge data on $K_2[RhF_6]$ refined to give a satisfactory first-shell distance but, although further features between *ca.* 3.5 and 5 Å are evident in the Fourier transform, addition of two further shells corresponding to 6K and 6F back scatterers was less satisfactory in that the shell radii merged on iteration to *ca.* 3.9 Å, although the reductions in fit index and *R* were, however, significant. Similarly for $K_2[PdF_6]$ the data refined to give a first-shell [*d*(Pd–F)] distance of 1.90 Å, but the radii of shells 2 and 3 again merged on iteration to *ca.* 3.8 Å. The bonded Pd–F distance determined in the present study is in excellent agreement with that reported in $[XeF_5]_2[PdF_6]$ of 1.893 Å (average).[18]

Rhodium K-edge data were also collected on $Cs_2[RhCl_6]$, which is the only known salt containing the hexachlororhodate(IV) ion. This complex is precipitated as a green powder from oxidation of $[RhCl_6]^{3-}$ and CsCl in aqueous solution with Cl_2 and Ce^{4+},[12] and reduces to Rh^{III} immediately when redissolved in water. Hence, it cannot be obtained in single-crystal form, although powder diffraction has identified it as having the $K_2[PtCl_6]$ lattice.[19] A good fit to the experimental data was obtained with a two-shell model (6Cl, 8Cs) which placed *d*(Rh–Cl) = 2.31 Å, which can be compared to 2.344(4) Å in $K_3[RhCl_6]$[20] and 2.309 Å in $K_2[PdCl_6]$.[21] The Fourier transform (Fig. 1) shows no other significant shells.

The very moisture-sensitive $K[RuF_6]$ and $K[RhF_6]$ belong to the rhombohedral $K[OsF_6]$ structure type ($R\bar{3}$).[13] The low

Table 1 EXAFS data for the hexafluorides

Compound	d(M–F)/Å	$2\sigma^{2\,a}$/Å^2	d(M $\cdots$ F)^b/Å	$2\sigma^2$/Å^2	Fit index^c	R^d
MoF_6^{e}	1.809(1)	0.002(02)	3.554(9)	0.019(2)	4.28	12.94
RuF_6^{f}	1.824(2)	0.004(02)	—	—	6.50	17.50
RhF_6^{f}	1.838(2)	0.005(02)	—	—	5.88	17.98

[a] $2\sigma^2$ = Debye–Waller factor. Standard deviations in parentheses. Note that the systematic errors in bond distances arising from the data collection and analysis procedures are *ca.* ±0.02 Å for well defined co-ordination shells. [b] Metal to nearest non-bonded F. [c] Fit index = $\Sigma_i[(\chi^T - \chi^E)k_i^3]^2$. [d] $R = [\int(\chi^T - \chi^E)k^3 dk/\int\chi^E k^3 dk] \times 100\%$. [e] Two-shell fit (6F, 8F). The solids are likely to be disordered[2] and the 8F (shell two) occupation number is the idealized value. [f] One-shell fit as discussed in the text.

Table 2 EXAFS data for the halogeno-anions

Salt	d(M–F)^a/Å	$2\sigma^2$/Å^2	Fit index	R
$K_2[RuF_6]$^{b}	1.916(1)	0.005(01)	1.64	11.68
$K_2[RhF_6]$^{c}	1.934(2)	0.002(03)	1.00	17.85
$K_2[PdF_6]$^{c}	1.896(2)	0.004(03)	5.87	19.81
$Cs_2[RhCl_6]$^{d}	2.313(1)	0.007(01)	1.60	11.13
$K[RuF_6]$^{c}	1.845(2)	0.005(02)	5.99	19.90
$K[RhF_6]$^{c}	1.855(2)	0.007(02)	3.53	17.53

[a] See footnotes to Table 1. [b] Three-shell (6F, 6K, 6F) fit: Ru $\cdots$ K = 3.454(10) Å, $2\sigma^2$ = 0.046(3) Å^2; Ru $\cdots$ F = 3.811(9) Å, $2\sigma^2$ = 0.022(2) Å^2. [c] Single-shell (6F) fit. [d] d(Rh–Cl), two-shell fit (6Cl, 8Cs): d(Rh $\cdots$ Cs) = 4.267(10) Å, $2\sigma^2$ = 0.034(2) Å^2.

symmetry of this lattice caused problems in our previous study[1] of the 5d analogues in that the shells predicted in order of increasing distance are 6F, 2K, 6F, 6F, 6F, with shells 2 and 3 and 4 and 5 lying only *ca.* 0.1 Å apart. In the present cases, the first-shell fits gave d(Ru–F) and d(Rh–F) of *ca.* 1.85 Å (Table 2), but the 2K and 6F (shells 2 and 3) merged on iteration. For $K[RuF_6]$ a 'second' shell of '8F' (corresponding to the merged 2K + 6F shells) gave statistically significant reductions in the fit index and R factor, but for $K[RhF_6]$ the Fourier transform of the experimental data showed no significant features beyond the first shell. The data given in Table 2 are for the single-shell fits for both compounds. There are no single-crystal X-ray data for alkali-metal compounds of $[RuF_6]^-$ or $[RhF_6]^-$, but the powder diffraction data place d[Ru(Rh)–F] in the range 1.82–1.89 Å, depending upon the positioning of the fluorines within the cell.[22] Single-crystal X-ray data are available for $[XeF_5][RuF_6]$,[23] $[ClO_2][RuF_6]$[24] and $[ClF_2][RuF_6]$,[24] giving average d(Ru–F) values of 1.85, 1.84 and 1.82 Å respectively, although in all three there are short anion–cation contacts which distort the octahedron.

Conclusion

The K-edge EXAFS data reported above further demonstrate the ability of this technique to provide local structural information on solids such as $K[MF_6]$, presently obtained only in powder form, and for thermally unstable or reactive molecules such as RuF_6 or RhF_6 it currently offers the best approach. The reliability of the bond lengths obtained for such compounds can be viewed with some confidence from the excellent agreement with other data for more stable analogues, such as MoF_6.

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References

1 A. K. Brisdon, J. H. Holloway, E. G. Hope, W. Levason, J. S. Ogden and A. K. Saad, *J. Chem. Soc., Dalton Trans.*, 1992, 139.

2 A. K. Brisdon, P. J. Jones, W. Levason, J. S. Ogden, J. H. Holloway, E. G. Hope and G. Stanger, *J. Chem. Soc., Dalton Trans.*, 1990, 715.

3 R. C. Burns and T. A. O'Donnell, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1613.

4 I. R. Beattie, N. Binsted, W. Levason, J. S. Ogden, M. D. Spicer and N. A. Young, *High Temp. Sci.*, 1990, **26**, 71.

5 W. Levason, J. S. Ogden, M. D. Spicer and N. A. Young, *J. Am. Chem. Soc.*, 1990, **112**, 1019.

6 PAXAS, N. Binsted, University of Southampton, 1988.

7 EXCURVE, S. J. Gurman, N. Binsted and I. Ross, *J. Phys. C.*, 1984, **17**, 143; 1986, **19**, 1845; EXCURVE 90, N. Binsted, S. J. Gurman and J. W. Campbell, SERC Daresbury Laboratory program, 1990.

8 A. K. Brisdon, J. H. Holloway, E. G. Hope and W. Levason, *Polyhedron*, in the press.

9 M. A. Hepworth, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.*, 1954, 1197.

10 A. G. Sharpe, *J. Chem. Soc.*, 1950, 3444.

11 A. G. Sharpe, *J. Chem. Soc.*, 1950, 197.

12 I. Feldman, R. S. Nyholm and E. Watton, *J. Chem. Soc.*, 1965, 4724.

13 D. Babel, *Struct. Bonding (Berlin)*, 1967, **3**, 1; G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, 1974, **19**, 105.

14 S. Siegel and D. A. Northrop, *Inorg. Chem.*, 1966, **5**, 2187.

15 J. H. Levy, J. C. Taylor and P. W. Wilson, *Acta Crystallogr., Sect. B*, 1975, **31**, 398; J. H. Levy, P. L. Sanger, J. C. Taylor and P. W. Wilson, *Acta Crystallogr., Sect. B*, 1975, **31**, 1065.

16 H. M. Seip and R. Seip, *Acta Chem. Scand.*, 1966, **20**, 2698.

17 R. W. Joyner, K. J. Martin and P. Meehan, *J. Phys. C*, 1987, **20**, 4005.

18 K. Leary, D. H. Templeton, A. Zalkin and N. Bartlett, *Inorg. Chem.*, 1973, **12**, 1726.

19 F. P. Dwyer, R. S. Nyholm and L. E. Rogers, *Proc. R. Soc. New South Wales*, 1947, **81**, 267.

20 P. J. Cresswell, J. E. Ferguson, B. R. Penfold and D. E. Scaife, *J. Chem. Soc., Dalton Trans.*, 1972, 254.

21 H. Takazawa, S. Ohba and Y. Saito, *Acta Crystallogr., Sect. B*, 1988, **44**, 580.

22 W. Wilhelm and R. Hoppe, *J. Inorg. Nucl. Chem. (Suppl.)*, 1976, 113.

23 N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell and A. Zalkin, *Inorg. Chem.*, 1973, **12**, 1717.

24 R. Bougon, W. V. Cicha, M. Lance, L. Meublat, M. Nierlich and J. Vigner, *Inorg. Chem.*, 1991, **30**, 102.

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