Metal L_{III}-Edge Extended X-Ray Absorption Fine Structure of 5d Transition-metal Hexafluorides and Related Fluoroanions

Alan K. Brisdon,[a] **John H. Holloway,**[a] **Eric G. Hope,**[a] **William Levason,**[*,b] **J. Steven Ogden**[b] **and Ahmed K. Saad**[b]
[a] *Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK*
[b] *Department of Chemistry, University of Southampton, Southampton SO9 5NH, UK*

Metal L_{III}-edge extended X-ray absorption fine structure data have been collected for WF_6, ReF_6, OsF_6, IrF_6 and PtF_6 as solids at 10 K, and refined to give M–F bond lengths which lie in the range 1.81–1.83 Å. Similar data have been obtained for the related hexafluoroanions $K_2[MF_6]$ and $K[MF_6]$ (M = Os, Ir or Pt) as powdered solids at room temperature, which give M–F bond lengths of 1.92–1.93 and 1.88–1.91 Å respectively.

The hexafluorides of the later transition elements are rare examples of discrete molecular compounds in unusually high oxidation states and, in view of this, their spectroscopic and structural characterisation are of considerable importance. There is technological interest in some of these compounds, for example WF_6 and ReF_6 are used in chemical vapour deposition processes, and others are of potential interest in this area.[1] Although detailed spectroscopic and structural data have been obtained for the vapour-phase materials,[2,3] structural information on the solids is sparse.[4] The hexafluorides are volatile, highly corrosive and moisture sensitive, and in some cases of limited thermal stability, properties which have combined thus far to prevent single-crystal X-ray studies. X-Ray powder diffraction studies[5] have shown that they are dimorphic with a high-temperature cubic and a low-temperature orthorhombic form and, for WF_6, powder neutron diffraction studies have been reported for both forms.[6]

Here we report the application of the EXAFS (extended X-ray absorption fine structure) technique to these compounds. EXAFS is atom-centre specific, does not require single crystals, and can provide internuclear distances even for very unstable materials.[7] When combined with suitable spectroscopic data to establish the symmetry at the metal centre, this approach can produce an essentially complete local structural characterisation. In this paper we report data for the solid 5d hexafluorides, and for related fluoroanions $[MF_6]^{n-}$ (n = 1 or 2).

Experimental

Metal L_{III}-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 in transmission mode on station 9.2 using a double-crystal Si (220) monochromator, and on station 7.1 using an order-sorting Si (111) monochromator, in both cases offset to 50% of the rocking curve for harmonic rejection.

The hexafluorides were prepared as described previously,[2] and were manipulated in pre-fluorinated metal equipment. The EXAFS data were collected in transmission mode from the hexafluorides condensed on to 0.25 mm thick aluminium windows (Goodfellow Metals, 99.999%) at 10 K, using the cryostat described previously.[8] For the data collection on OsF_6 where volatile OsO_4 is a persistent contaminant,[2] the metal line and the cryostat were pre-treated with OsF_6 vapour before cool down.

The fluoroanions were prepared as the potassium salts, $K[OsF_6]$,[9] $K[IrF_6]$,[9] $K[PtF_6]$,[10] $K_2[OsF_6]$,[9] $K_2[IrF_6]$[9] and $K_2[PtF_6]$[11] by literature methods and their identities confirmed by comparison of their X-ray powder patterns and diffuse reflectance UV/VIS spectra with literature data.[12] The air- and moisture-stable and relatively unreactive solid hexafluorometalate(IV) samples were diluted with dry boron nitride, and mounted between Sellotape strips in 1 mm aluminium spacers. The readily hydrolysed $K[OsF_6]$, $K[IrF_6]$ and $K[PtF_6]$ were diluted with dry powdered LiF in a dry-box, and run in sealed FEP cells. The design of these cells is shown in Fig. 1.

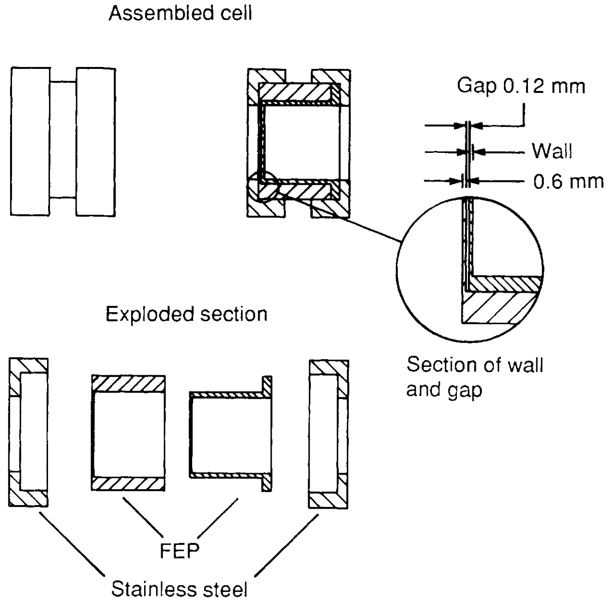

Fig. 1 Cell for collection of EXAFS data on the fluoroanions

The EXAFS data treatment was similar to that described in previous papers[7,8] and utilised the programs PAXAS[13] and EXCURVE.[14,15] Several data sets were collected for each compound in k space, 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 minimising the intensity of chemically insignificant shells at low r in the

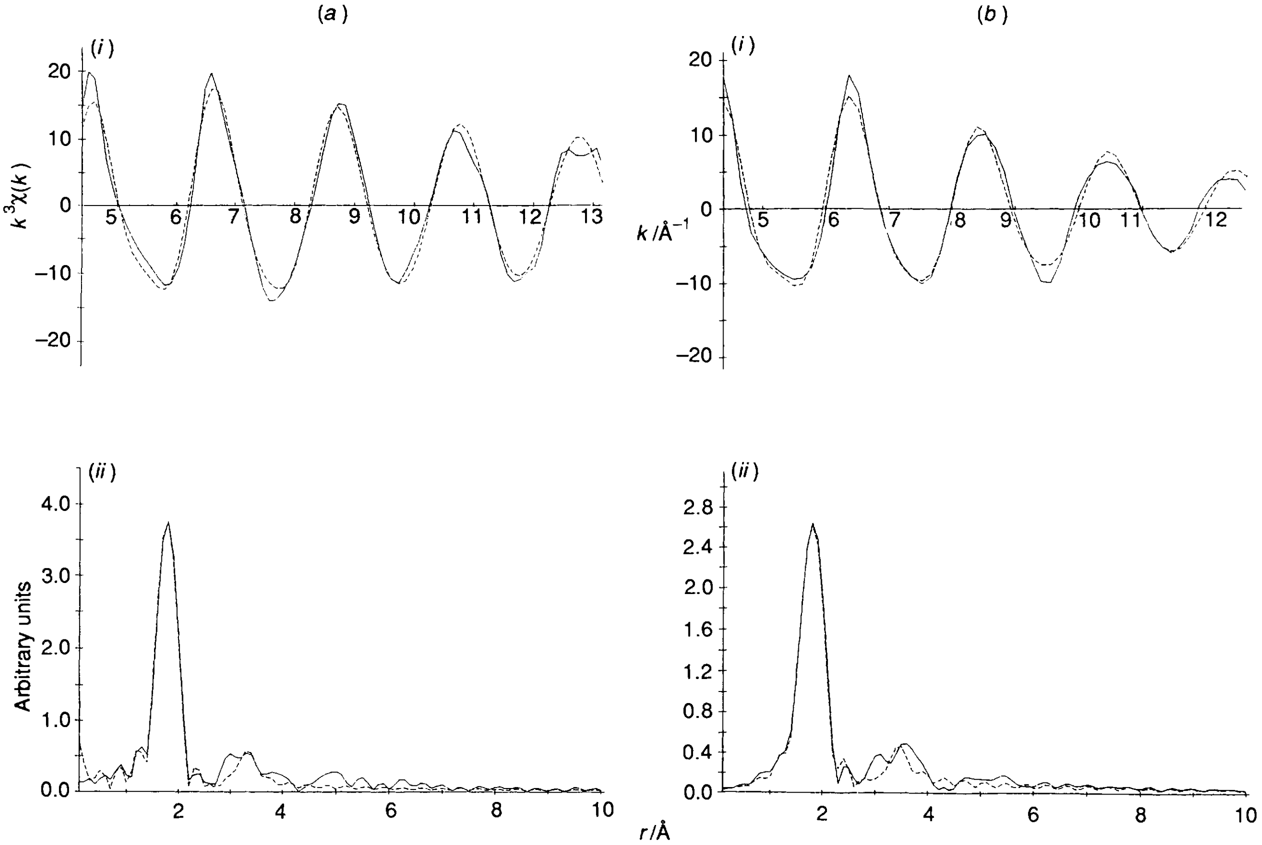

Fig. 2 Background-subtracted EXAFS (*i*) (——, experimental × k^3; – – –, curved-wave theory × k'^3) and the Fourier transforms (*ii*) (——, experimental; – – –, theoretical) for (*a*) WF$_6$ and (*b*) PtF$_6$; k is the photoelectron wave vector and r is the radial distance from the absorbing atom

Fourier transform. Curve fitting using single-scattering curved-wave theory with phase shifts and back-scattering factors calculated using the normal *ab initio* methods.[14]

Results

Hexafluorides.—Samples of the five 5d hexafluorides were condensed from the vapour phase onto a 0.25 mm thick aluminium window mounted in a high-vacuum shroud and cooled to 10 K.[8] Transmission EXAFS data were collected out to $k = 15$ Å^{-1} (k = photoelectron wave vector) beyond the edge, but due to poor signal/noise at high k the data were usually truncated at $k = 13$. Several data sets on each compound were averaged, and the data multiplied by k^3 to compensate for the fall-off in intensity at higher k. No smoothing or Fourier filtering was applied, and the fits discussed below were all compared with the averaged raw (background subtracted) EXAFS data. The data were initially modelled to a single shell of six fluorine atoms at *ca.* r = 1.9 Å. However, examination of the Fourier transforms revealed that all contained broad features at *ca.* 3.5 Å, and sometimes weaker features at higher r (r = radial distance from absorbing atom/Å). The neutron powder data[6] on the body-centred cubic phase of WF$_6$ showed that the W ··· W separation is *ca.* 5.46 Å with W ··· F$_{\text{non-bonded}}$ at *ca.* 3.6 Å. The orthorhombic phase has a smaller molar volume and hence tighter packing. Since the samples from which EXAFS data were collected were condensed from the gas phase at very low temperatures, the solids are likely to be disordered. Modelling of the EXAFS data was attempted using two (6F, 8F) and three (6F, 8F, 8M)* shell models, the extra shells being added stepwise, iterated in the usual way, and the best fits tested for statistical significance.[16,17] For all five hexafluorides the addition of the second shell resulted in significant decreases in the fit index and R factor and resulted in d(M ··· F$_{\text{non-bonded}}$) of *ca.* 3.3 Å. The addition of a third shell corresponding to back scattering by the next metal centres failed the statistical significance tests,[16,17] except in the case of ReF$_6$ d(Re ··· Re 4.9 Å) where it just passed the tests. The bonded M–F distances were invariant within the normal precision (±0.01 Å) upon the addition of the extra shells. Refined data for the two-shell fits are given in Table 1, and Fig. 2 shows representative examples of the background-subtracted EXAFS and the Fourier transforms.

Direct comparisons are possible only with the neutron diffraction data on solid WF$_6$,[6] from which d(W–F) was deduced as 1.829(20) Å for the cubic phase and as 1.81 Å (mean) for the orthorhombic form. These distances are in excellent agreement with the result (1.82 Å) from the present EXAFS data on the solid at 10 K. Since the solids consist of MF$_6$ molecules packed together,[4,5] comparison of the dimensions with those of the gas-phase molecules are expected to show minimal differences. Electron diffraction on WF$_6$ vapour gave d(W–F) (r_g) 1.833(8) Å.[18] For ReF$_6$,[19] OsF$_6$ [18] and IrF$_6$,[18] electron diffraction (r_e) results gave d(M–F) 1.832(4), 1.831(8) and 1.830(8) Å respectively, which are similarly in excellent agreement with the EXAFS data on the solids (Table 1). Although subsequent analyses found no evidence for significant OsO$_4$ impurity in the OsF$_6$ data, for completeness osmium L$_{\text{III}}$-edge EXAFS data were also collected for solid OsO$_4$, and refined to d(Os–O) 1.69 Å which can be compared with the X-ray crystallographic result[20] of 1.697 Å (mean).

---

* It is likely that the solids are disordered as a result of the rapid condensation at 10 K. The occupation numbers of the second and third shells are idealised values. The fits were not sensitive to small variations in the occupation numbers.

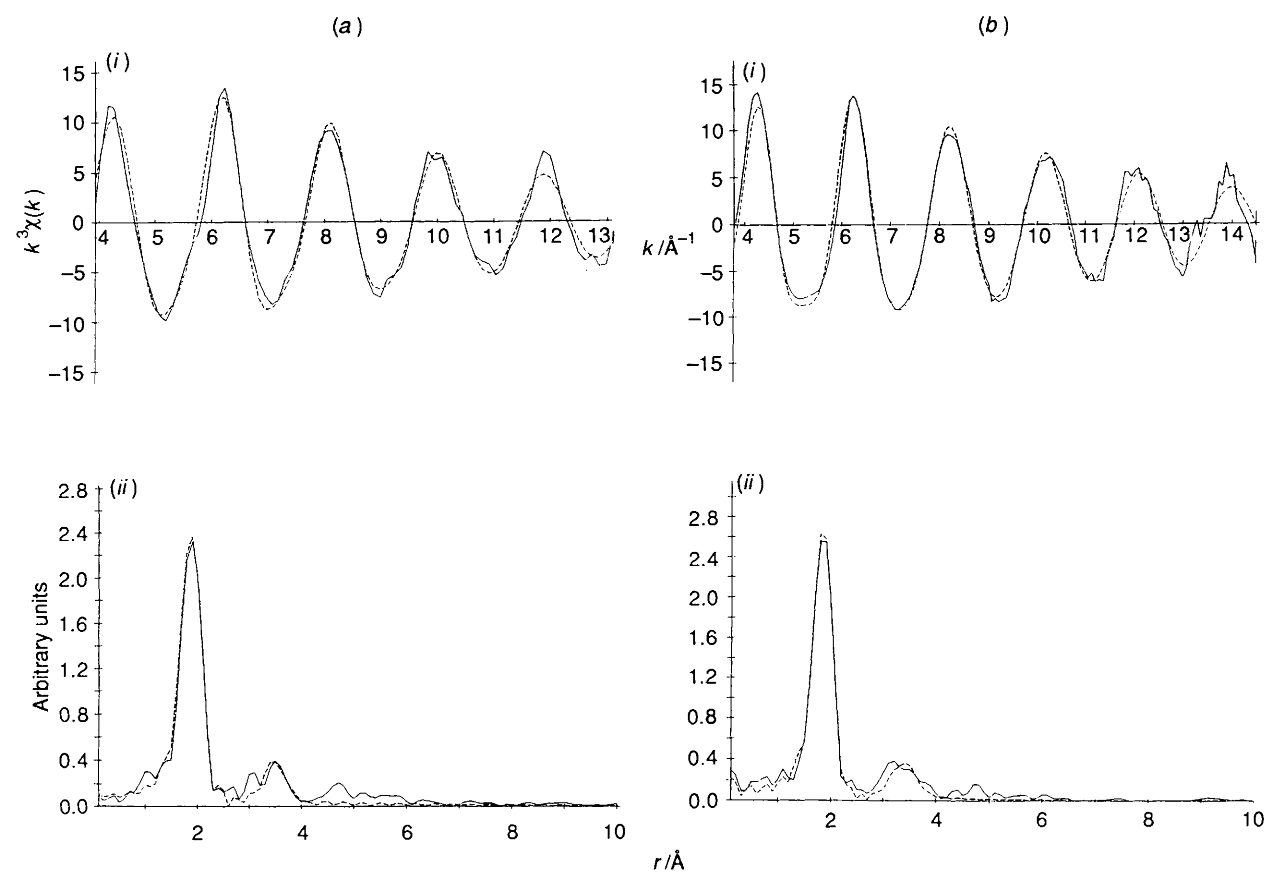

Fig. 3 Background-subtracted EXAFS (*i*) and the Fourier transforms (*ii*) for (*a*) $K_2[OsF_6]$ and (*b*) $K[PtF_6]$. Key as in Fig. 2

Table 1 EXAFS data for the hexafluorides[a]

Compound	d(M–F)/Å	$2\sigma^{2\,b}$/Å^2	d(M $\cdots$ F)[c]/Å	$2\sigma^2$/Å^2	f.i.[d]	R[e]
WF_6	1.821(2)	0.002(02)	3.28(1)	0.019(3)	5.71	15.4
ReF_6[f]	1.812(1)	0.002(01)	3.27(06)	0.021(2)	3.49	14.0
OsF_6	1.816(3)	0.006(04)	3.29(2)	0.023(4)	7.59	22.2
IrF_6	1.822(2)	0.005(02)	3.30(07)	0.022(2)	5.01	15.5
PtF_6	1.839(3)	0.007(03)	3.36(1)	0.022(3)	3.77	14.9

[a] 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 first co-ordination shells and *ca.* ±0.04 Å for subsequent shells. Data for two-shell fit (6F, 8F). [b] Debye–Waller factor. [c] Metal to nearest non-bonded F. [d] Fit index $\Sigma_i[(\chi^T - \chi^E)k_i^3]^2$. [e] $R = [\int(\chi^T - \chi^E)k^3 dk / \int\chi^E k^3 dk] \times 100\%$. [f] Three-shell fit gave third shell of 8M at 4.92(1) Å, $2\sigma^2$ 0.028(3) Å^2.

Table 2 Comparison of XRD and EXAFS data for $K_2[PtF_6]$

Shell	d(XRD)*/Å	d(EXAFS)/Å	$2\sigma^2$/Å^2
6F	1.89	1.922(1)	0.007(01)
6K	3.54	3.527(5)	0.018(1)
6F	3.79	3.599(7)	0.008(2)
2Pt	4.60	4.576(11)	0.010(2)
12F	4.67	4.342(14)	0.042(5)
6K	4.78	4.682(11)	0.027(3)

* Calculated with the CRAD program.

Fluoroanions.—X-Ray powder-diffraction (XRD) studies show[12] that the $K_2[MF_6]$ (M = Os, Ir or Pt) salts have the trigonal $K_2[GeF_6]$ lattice ($P\bar{3}m1$), and initial fits of the EXAFS data on these compounds were again developed using a single shell of six fluorines. However, in addition to the major feature at *ca.* 1.92 Å, the Fourier transforms from all three compounds showed further weaker features between 3 and 5 Å (Fig. 3). Based upon the X-ray powder data for $K_2[PtF_6]$ the radial distances for shells out to *ca.* 5 Å from the platinum centre were calculated,† and the results are given in Table 2. Further shells were added to the theoretical EXAFS model for $K_2[PtF_6]$ with the occupation numbers fixed consistent with the $K_2[GeF_6]$ structure, each shell being iterated and the best fit tested for significance in the usual way. The results of this procedure are compared with those from the X-ray powder data in Table 2. Good fits were obtained with the three-shell model (R = 18.3%) but, although stepwise addition of subsequent shells (2Pt, 12F, 6K) led to statistically significant falls in the R factor, the shells were not clearly discriminated in the EXAFS, as evidenced by high Debye–Waller factors, and the merging of the shell radii on refinement. This is hardly surprising since the XRD data indicate that these three shells are spread over only 0.2 Å. Very similar results were obtained for $K_2[OsF_6]$ and $K_2[IrF_6]$, and the reported fits were terminated at three shells. The d(M–F) distances are given in Table 3.

---

† These calculations were carried out by Dr. M. Webster using the CRAD program available in the Daresbury program library.

Table 3 EXAFS data for fluoroanions

Salt	d(M–F)[a]/ Å	$2\sigma^{2\,b}$/Å^2	f.i.[b]	R[b]
$K[OsF_6]$	1.882(2)	0.009(03)	3.15	18.8
$K[IrF_6]$	1.910(2)	0.007(02)	1.74	15.8
$K[PtF_6]$	1.886(2)	0.006(02)	3.03	16.4
$K_2[OsF_6]$	1.927(2)	0.007(03)	2.69	16.0
$K_2[IrF_6]$	1.928(2)	0.006(02)	5.11	18.8
$K_2[PtF_6]$	1.921(2)	0.007(02)	4.53	18.3

[a] Parameters quoted for two-shell fit for $K[MF_6]$ and three-shell fit for $K_2[MF_6]$ (see text). [b] Terms defined in Table 1.

Crystallographic data on these hexafluorometalates(IV) are very limited: the powder diffraction data[12,21] suggest d(M–F) values of *ca.* 1.89 Å, whilst single-crystal studies[22,23] on $M'_2[PtF_6]$ (M′ = K, Rb or Cs) have reported bond lengths of 1.91–1.92 Å. For this series of hexafluoroanions, the metal-edge EXAFS data give reliable d(M–F) distances, and clear evidence for the neighbouring K and F shells, although this is no doubt helped by the high-symmetry structure which results in reasonable numbers (six) of back-scattering atoms in each of shells two and three.

For the hexafluorometalates(V), which have rhombohedral cells ($R\bar{3}$),[12,24] the initial attempts to treat the EXAFS data in the same manner as for $[MF_6]^{2-}$ were less successful. The EXAFS data for $K[OsF_6]$, $K[IrF_6]$ and $K[PtF_6]$ were initially fitted by a single-shell model, and refined to yield a d(M–F) of *ca.* 1.89 Å, but further shells could not be added satisfactorily. Our inability to fit further shells and the discrepancy between the bond lengths deduced from the EXAFS and that reported from the X-ray powder data for $K[OsF_6]$ (see below) raised questions about the data quality. New samples of the complexes were prepared and the EXAFS data recollected. However, refinement of these data sets gave results which were effectively identical with those obtained initially. For the rhombohedral $K[OsF_6]$ structure, the X-ray powder data placed shells at the following distances from the Os centre: 6F, 1.82; 2K, 3.74; 6F, 3.85; 6F, 4.34; 6F, 4.47 Å. Our EXAFS data refined to place shell 1 at 1.89 Å, but attempts to fit shells 2 (2K) and 3 (6F) failed, the shell radii merging on iteration. Clearly the EXAFS cannot distinguish back scattering for 2K and 6F atoms only 0.1 Å apart. A better fit, which passed the usual statistical significance tests, was achieved using a shell of 8 'F' atoms as shell 2. Addition of further shells failed to produce significant reductions in the R factor or fit index. For the lower-symmetry $K[OsF_6]$ structure the EXAFS data treatment was terminated at the two-shell fit. The best-fit data are listed in Table 3.

The d(M–F) values of 1.88–1.91 Å deduced in the present work are in rather poor agreement with that (1.82 Å) derived[24] from the X-ray powder study for $K[OsF_6]$. The origin of the discrepancies between the d(M–F) distances in these compounds deduced by the XRD and the EXAFS techniques is not clear. For the rhombohedral cell of the $K[OsF_6]$ structure the Os (0,0,0) and K $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ positions are unequivocal, but positioning the fluorides is less clearcut.[25] As the EXAFS data for the MF_6 and $K_2[MF_6]$ gave bond lengths in excellent agreement with those determined by other techniques, it seems unlikely that the discrepancies arise from errors in the phase shifts used or from the data treatment, whilst the reproducibility of the results from different samples (above) suggests that sample decomposition or purity is not the problem. The alkali-metal hexafluorometalates(V) have not thus far been obtained as single crystals, but the average d(Pt–F) distances in the anions in $[O_2][PtF_6]$ and $[XeF_5][PtF_6]$ are given as 1.82(3) and 1.89(5) Å respectively.[26,27] However, in these latter compounds the anions are distorted by the significant interaction with the cations.

The data in Table 3 show a clear trend of decreasing d(M–F) with increasing metal oxidation state from *ca.* 1.92 Å in $[MF_6]^{2-}$, to *ca.* 1.89 Å in $[MF_6]^{-}$, and *ca.* 1.83 Å in the neutral MF_6. Data for other platinum metal halogenoanions, although limited, are consistent with these trends, for example a contraction of *ca.* $\leqslant 0.06$ Å is observed between $[OsCl_6]^{2-}$ and $[OsCl_6]^{-}$,[28] and between $[RuCl_6]^{3-}$ and $[RuCl_6]^{2-}$.[29]

Discussion

This study has shown that the EXAFS technique can provide bond-length information for molecular fluorides and fluoroanions, without the need to produce single crystals. In favourable cases some information about the distances of neighbouring molecules or ions is also obtained. For the more volatile compounds data collection was carried out at low temperatures, with the samples deposited directly from the vapour phase on to a suitable cold window. Involatile solids, even if very moisture sensitive, can be handled in sealed fluoroplastic cells, and this approach can be readily extended to thermally unstable solids, using the same fluoroplastic cells at low temperatures. In a related study[30] we have shown that the metal-edge EXAFS data can resolve M–F from M=O in oxide fluorides such as MnO_3F.

In summary, EXAFS is a valuable method for obtaining d(M–F) distances in highly reactive, volatile or thermally unstable fluorides, which are exceptionally difficult to obtain in single-crystalline form suitable for conventional X-ray crystallographic studies. Similarly it can provide first, and in favourable cases neighbouring, shell distances in fluoroanions. Many fluoroanions are obtained as powders and, for the hydrolytically unstable ones, single crystals are often obtainable only by prolonged annealing at high temperature and pressure.[31] The latter method is very time consuming and the success rate low.

Acknowledgements

We thank the SERC for support and the Director of the Daresbury Laboratory for the provision of facilities. We also thank Dr. M. Webster for the CRAD calculations and for discussion.

References

1 D. T. Meshri, in *Fluorine The First Hundred Years*, eds. R. E. Banks, D. W. A. Sharp and J. C. Tatlow, Elsevier, Amsterdam, 1986, p. 195.

2 J. H. Holloway, G. Stanger, E. G. Hope, W. Levason and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 1341.

3 B. Weinstock and G. L. Goodman, *Adv. Chem. Phys.*, 1965, **9**, 165.

4 A. J. Edwards, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 83.

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

6 J. H. Levy, J. C. Taylor and P. W. Wilson, *J. Solid State Chem.*, 1975, **15**, 360; *J. Less-Common Met.*, 1976, **45**, 155.

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

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

9 M. A. Hepworth, P. L. Robinson and G. J. Westland, *J. Chem. Soc.*, 1954, 4269.

10 N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 1962, 5253.

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

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

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

14 EXCURVE, S. J. Gurman, N. Binsted and I. Ross, *J. Phys. C.*, 1984, **17**, 143; 1986, **19**, 1845.

15 N. Binsted, S. J. Gurman and J. W. Campbell, EXCURVE 90, SERC Daresbury Laboratory Program, 1990.

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

17 N. Binsted, S. L. Cook, J. Evans, G. N. Greaves and R. J. Price, *J. Am. Chem. Soc.*, 1987, **109**, 3667.

18 M. Kimura, V. Schomaker, D. W. Smith and B. Weinstock, *J. Chem. Phys.*, 1968, **48**, 4001.

19 E. J. Jacob and L. S. Bartell, *J. Chem. Phys.*, 1970, **53**, 223.

20 B. Krebs and K. Haase, *Acta Crystallogr., Sect. B*, 1976, **32**, 1334.

21 M. A. Hepworth, P. L. Robinson and G. J. Westland, *J. Chem. Soc.*, 1958, 611.

22 D. P. Mellor and N. C. Stevenson, *Aust. J. Chem.*, 1951, **4**, 406.

23 L. Grosse and R. Hoppe, *Naturwissenschaften*, 1982, **69**, 447.

24 M. A. Hepworth and G. J. Westland, *J. Inorg. Nucl. Chem.*, 1956, **2**, 79.

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

26 N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 1964, 619; J. A. Ibers and W. C. Hamilton, *J. Chem. Phys.*, 1966, **44**, 1748.

27 N. Bartlett, F. Einstein, D. F. Stewart and J. Trotter, *J. Chem. Soc. A*, 1967, 1190.

28 B. Krebs, G. Henkel, M. Dartmann, W. Preetz and M. Bruns, *Z. Naturforsch., Teil B*, 1984, **39**, 843.

29 T. E. Hopkins, A. Zalkin, D. H. Templeton and M. G. Adamson, *Inorg. Chem.*, 1969, **8**, 2421; J. P. Deloume, R. Faure and G. Thomas-David, *Acta Crystallogr., Sect. B*, 1979, **35**, 558.

30 W. Levason, J. S. Ogden, A. K. Saad, N. A. Young, A. K. Brisdon, P. Holliman, J. H. Holloway and E. G. Hope, *J. Fluorine Chem.*, 1991, **53**, 43.

31 R. Hoppe, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 63.

Received 22*nd July* 1991; *Paper* 1/03711K