Synthesis and Characterisation of Iridium Carbonyl Fluorides

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Tetrairidium dodecacarbonyl reacted with XeF_2 in anhydrous HF solution at low temperatures *via* sequential fluorination yielding initially *fac*- and *mer*-$[IrF_3(CO)_3]$ and finally IrF_5. The novel 18-electron iridium carbonyl fluorides have been characterised by a combination of IR spectroscopy, ^{13}C, $^{13}C-\{^{19}F\}$ and ^{19}F NMR spectroscopies and extended X-ray absorption fine structure spectroscopy studies in HF solution.

The chemistry of organo-transition-metal fluoro complexes is relatively unexplored[1] even though on the basis of comparison with other soft metal–hard ligand combinations[2] potentially interesting synthetic chemistry may be anticipated for such systems. The principal factors contributing to this lack of study are (*i*) the view that the combination of a low-valent metal centre and a fluoride ion are inherently unstable, in spite of the considerable experimental evidence to the contrary when π-back-bonding ligands are also present, and (*ii*) the dearth of convenient ways to introduce fluoride. The recent applications of novel fluorinating agents, *e.g.* $(Me_2N)_3SSiF_2Me_3$,[3] Olah's reagent (py.*x*HF, py = pyridine)[4] and XeF_2,[5,6] to transition-metal systems may be expected to overcome these problems. Furthermore, definitive characterisation of many metal fluoride complexes is difficult in the absence of single-crystal X-ray data and only 26 such structures have been published so far.[1] The nature of some reported species is thus in doubt, *e.g.* the transition-metal carbonyl fluoride reported to have the formulation $[ReF_3(CO)_3]$[7] may be the species structurally identified as $[Re(CO)_6]^+[Re_2F_{11}]^-$.[8]

There is only one report of iridium carbonyl fluorides, the unusual and presumably polymeric iridium(II) $IrF_2(CO)_2$ and $IrF_2(CO)_3$, prepared by the carbonylation of IrF_5 and formulated on the basis of IR spectroscopy and elemental analysis.[9] Here we report the controlled fluorination of $[Ir_4(CO)_{12}]$ by XeF_2 in HF solution and identify a sequential fluorination *via* $[IrF_3(CO)_3]$ to IrF_5. A preliminary account of some of this work has been published.[10]

Experimental

Proton, ^{13}C and ^{19}F NMR spectroscopic studies were carried out on a Bruker AM300 spectrometer at 300.13, 75.47 and 282.41 MHz respectively and on a Varian VXR600S at the University of Edinburgh SERC Ultra-High Field NMR service at 600.0, 150.87 and 564.29 MHz respectively. Spectra were recorded on samples in 4 mm outside diameter FEP (perfluoroethylene–propylene co-polymer) NMR tubes held coaxially in 5 mm precision glass NMR tubes containing a small quantity of $[^2H_6]$acetone as lock substance. Proton and ^{13}C NMR spectra were referenced to external $SiMe_4$ and ^{19}F NMR spectra to external $CFCl_3$ using the high-frequency positive convention. Initial ^{19}F NMR spectra were recorded for *ca.* 400 scans between δ +200 and −600 using 125 000 Hz windows (*ca.* 7 Hz per point), acquisition times of 0.5 s without relaxation delays and pulse widths of 3 μs (28°). Higher-resolution spectra were recorded for narrower spectral widths dependent upon the experiment; typical data-point resolutions for 4000 scan acquisitions were *ca.* 1 Hz. Fourier transforms were carried out without exponential smoothing. Typical ^{13}C NMR spectra were recorded for *ca.* 10 000 scans using 20 000 Hz windows (*ca.* 1 Hz per point), acquisition times of 0.4 s with 0.8 s relaxation delays and pulse widths of 2 μs (30°). Fourier transforms were carried out with Lorentzian line broadening (1 Hz). IR spectra were recorded using a Digilab FTS40 on samples as dry powders between KBr discs, and Raman spectra as powdered samples in passivated thin-walled glass capillaries at −196 °C in an unsilvered glass Dewar on a modified Coderg T800 Raman spectrometer using the 488 nm excitation of an Ar^+ laser (model 52, Coherent Radiation Laboratories). Iridium L_{III}-edge extended X-ray absorption fine structure spectra (EXAFS) 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 7:1 using an order sorting Si(111) monochromator, offset to 50% of the rocking curve for harmonic rejection. The EXAFS data were collected in transmission mode for HF solutions (*ca.* 0.01 mol dm^{-3}) in heat-flattened (*ca.* 1 mm solution thickness) 4 mm outside diameter sealed FEP reaction tubes and for solid samples, diluted by boron nitride and mounted between Sellotape strips in 1 mm aluminium spacers. The EXAFS data treatment utilised the programs EX[11] and EXCURVE 90.[12] Several data sets were collected for each sample in *k* space (*k* = photoelectron wavevector/$Å^{-1}$), and averaged to improve the signal-to-noise ratio. The pre-edge background was removed by fitting the spectrum to a quadratic polynomial, and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using a fifth-order polynomial, and the optimum function judged by minimising the intensity of chemically insignificant shells at low *r* (*r* = radial distance from the 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 multiple scattering curved-wave theory with phase shifts and back-scattering factors calculated using normal *ab initio* methods.[13] The fits discussed below are for model data compared to raw (background-subtracted) EXAFS, and no Fourier filtering or smoothing has been applied.

All preparative manipulations were carried out on a metal vacuum line with facilities to connect Teflon and FEP reaction vessels. Xenon difluoride was prepared by the static fluorination of xenon gas under UV irradiation at room temperature.[14] Hydrogen fluoride (Fluorochem) was purified by vacuum transfer, dried by repetitive fluorination at room temperature and stored in Kel-F tubes over dry BiF_5.[15] Approximately 15% ^{13}CO enriched $[Ir_4(CO)_{12}]$ was prepared by stirring a solution of $[Ir_4(CO)_{12}]$ (1 g, 0.9 mmol) (Aldrich) in tetrahydrofuran (thf) (50 cm^3) for approximately 2 w at 60 °C under 1 atm (101 325 Pa) of 99.5% ^{13}CO [MSD isotopes (Cambrian Gases)].[16] Weighed samples of $[Ir_4(CO)_{12}]$ and

XeF_2 were loaded, in a dry-box (< 10 ppm H_2O), into pre-fluorinated FEP reactors (4 mm outside diameter, 0.5 mm wall thickness) fitted with poly(tetrafluoroethylene) valves (Production Techniques). After evacuation on the vacuum line, HF (*ca.* 0.3 cm^3) was condensed into the reaction tube at −196 °C. The HF was allowed to melt, when reaction ensued as evidenced by gas evolution. The reaction was controlled by judicious cooling in a solid CO_2–acetone bath and venting of the xenon gas generated. After the reaction was complete, the reaction mixture was warmed cautiously to room temperature, left to stand at room temperature overnight to ensure complete reaction and then either heat-sealed as described previously[17] for NMR studies, or the HF solvent was removed *in vacuo* to leave solid samples which were manipulated in a dry-box for IR spectroscopy, EXAFS and further NMR studies.

Results and Discussion

Tetrairidium dodecacarbonyl was found to be insufficiently soluble in simple halocarbons to allow an investigation of its fluorination in these solvents, however, we have shown that it dissolves in anhydrous HF overnight at room temperature to give a pale yellow solution containing a single species, $[H_2Ir_4(CO)_{12}]^{2+}$.[18]

Xenon difluoride readily fluorinates $[Ir_4(CO)_{12}]$ in HF solution at *ca.* −40 °C with the liberation of xenon; in HF solution, XeF_2 forms an $F–Xe^{\delta+}\cdots F\cdots H–F^{\delta-}$ adduct which is an aggressive fluorinating agent.[19] Ratios of XeF_2: $[Ir_4(CO)_{12}]$ of 1:1 through to 30:1 were investigated. At low ratios, unreacted $[H_2Ir_4(CO)_{12}]^{2+}$ is observed in both the ^1H and ^{13}C NMR spectra. Above the 6:1 ratio, COF_2 is observed in the ^{19}F NMR spectra and in the gas-phase IR spectra of the gases vented from the reaction mixture. At very high ratios, the ^{19}F NMR signal due to HF broadened significantly, due to the generation of paramagnetic species. Iridium L_{III}-edge EXAFS studies on these solutions showed a single Ir–F fluorine distance comparable to that observed previously for solid $[IrF_6]^-$ salts.[20] Removal of the HF left a yellow solid which was characterised as $[XeF][IrF_6]$ by comparison with the literature IR and Raman spectroscopic data.[21] The complex $[Ir_4(CO)_{12}]$ is, therefore, oxidatively fluorinated by XeF_2 to IrF_5, which, in the presence of excess of XeF_2, forms the previously reported iridium(v) salt. This is a new synthetic route to the binary fluoride, which is not unexpected since XeF_2 has been shown to fluorinate iridium metal to form IrF_5 in HF solution.[22] However, the requirement for large quantities of expensive XeF_2 is unlikely to make it a route of choice for the preparation of IrF_5.

Once an XeF_2: $[Ir_4(CO)_{12}]$ ratio of 6:1 is reached, all the NMR signals due to the $[H_2Ir_4(CO)_{12}]^{2+}$ cation disappear, and, at 25 °C, the ^{19}F NMR spectrum is dominated by three broad, unresolved, peaks at *ca.* δ −310, −338 and −476. On cooling the system to −78 °C, these resolve into a singlet, triplet and doublet respectively, the latter two exhibiting mutual $^2J_{FF}$ coupling of 75 Hz. Undoubtedly the system is slowly exchanging at room temperature, but we are unable to determine the coalescence point because HF rapidly attacks our NMR tubes above room temperature. The peaks at δ −310 and −338 are in a region of the spectrum characteristic of F_{trans}–CO[23] while the peak at δ −476 occurs in a region characteristic of F_{trans}–F.[24] We therefore assign these peaks to the 18-electron *fac*- and *mer*-$[IrF_3(CO)_3]$ species. Carbon-13 NMR spectra at 25 °C and −78 °C support this assignment. The predominant peak at *ca.* δ 131 is a broad unresolved multiplet with two additional features at δ 130.7 and 141.6 which appear to be doublets of triplets (Table 1). Assignment of these signals to *fac*- and *mer*-$[IrF_3(CO)_3]$ was aided by recording selective ^{13}C-{^{19}F} NMR spectra (Fig. 1) at the SERC Ultra-high-field NMR Centre. Irradiation at the ^{19}F NMR peak at δ −476 removed the triplet couplings on the ^{13}C NMR peaks at δ 130.7 and 141.6 while irradiation at δ −338 removed the doublet couplings on the same peaks. These resonances are therefore assigned to the CO_{trans}–F and CO_{trans}–CO in *mer*-$[IrF_3(CO)_3]$. Irradiation at δ −310 collapsed the multiplet at *ca.* δ 131 to a sharp singlet at δ 131.3, and this resonance is therefore assigned to CO_{trans}–F in *fac*-$[IrF_3(CO)_3]$. The ^{13}C NMR spectrum for the *fac* isomer is expected to be an AXX'_2 system, and the broad multiplet may be simulated using the coupling constants given in Table 1. The ^{13}C NMR spectrum occasionally shows an additional sharp carbonyl singlet at the unusually high field of δ 165 which appears to correlate with a weak signal at δ −438 in the ^{19}F NMR spectrum. The ^{13}C resonance is very temperature dependent. On cooling it broadens and, at −80 °C, close to the freezing point of HF, the resonance disappears into the baseline. We have been unable to obtain spectra at lower temperatures, but the appearance of these peaks only with a slight deficit of XeF_2 (< 6:1 ratio), their unusual chemical shifts and extreme fluxionality suggests a five-co-ordinate cationic iridium(III) species, possibly $[IrF_2(CO)_3]^+$ in solution.

The ^{13}C and ^{19}F NMR data obtained can be compared with those of the neutral *cis*-$[IrF_2X(CO)(PEt_3)_2]$ (X = F, Cl, Br or I)[24] and $[IrFCl(NSF_2)(CO)(PPh_3)_2]$,[25] and the cationic $[IrF(COF)(CO)_2L_2]^+$ (L = PMe_3, PEt_3, PMe_2Ph, PEt_2Ph or $PEtPh_2$) and $[IrF(CO)_3L_2]^{2+}$ (L = PEt_3 and PPh_3)[26,27] all of which contain F_{trans}–CO on iridium(III). For *mer*- and *fac*-$[IrF_3(CO)_3]$ the ^{19}F NMR resonances for F_{trans}–CO (δ −310 and −338) fall in the range δ −289 to −338 observed for the neutral species while the sequential shift to lower frequencies for

Table 1 Carbon-13 and ^{19}F NMR data[a] for iridium carbonyl fluorides

	^{13}C	^{19}F
fac-$[IrF_3(CO)_3]$[b]	131.0[c]	−310
mer-$[IrF_3(CO)_3]$[b]	130.7 (80,2)[d]	−338 (75)[e]
	141.6 (7,7)[d]	−476 (75)[e]

[a] Shifts in ppm relative to external $SiMe_4$ or $CFCl_3$. Coupling constants in Hz in parentheses. [b] Recorded at −78 °C. [c] AXX'_2 System, simulated with coupling constants of *trans*-$^2J_{FC}$ = 84, *cis*-$^2J_{FC}$ = 5, $^2J_{FF}$ = 120, see text. [d] $^2J_{FC}$. [e] $^2J_{FF}$.

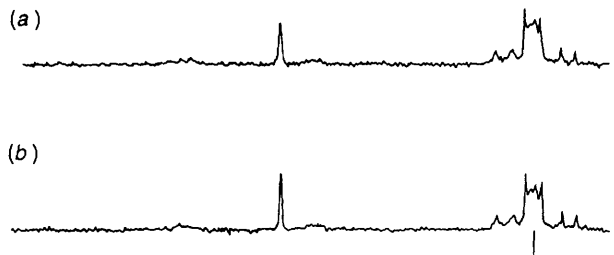

Fig. 1 150.87 MHz ^{13}C NMR Spectra of the iridium carbonyl fluorides: fluorine-coupled spectrum (*a*) and spectrum ^{19}F selectively decoupled at δ −476 (*b*), −338 (*c*) and δ −310 (*d*)

cationic complexes δ −382 to −394 and −429 to −456 supports our assignments. Carbon-13 NMR data have only previously been reported for $[IrF(COF)(CO)_2(PEt_3)_2]^+$ and $[IrF(CO)_3L_2]^{2+}$ (L = PEt_3 or PPh_3)[26,27] which show a low frequency shift with increasing cationic charge (δ 151 to 142 and 143 for CO_{trans}–F; δ 163 to 154 and 153 for CO_{trans}–CO respectively). This trend is, however, not continued for the neutral *mer*- and *fac*-$[IrF_3(CO)_3]$ (CO_{trans}–F δ 131; CO_{trans}–CO δ 142) suggesting that in these neutral complexes the carbonyl ligands have unusual electronic properties (see below).

Removal of the solvent from the 6:1 ratio sample leaves a pale yellow, very moisture-sensitive, solid which, when redissolved in HF, shows only the ^{13}C and ^{19}F NMR signals due to the *fac* isomer, suggesting that this isomer has greater thermodynamic stability than the *mer* isomer. We note that all the NMR data described above have been recorded on solutions containing both isomers which had been left to stand at room temperature overnight for safety reasons. However, when spectra were recorded immediately after reaction, the peaks assigned to the *mer* isomer are significantly more intense indicating that this isomer is kinetically favoured. The NMR signals due to the *fac* isomer grow with time confirming its thermodynamic stability, as expected from bonding considerations.[28]

The pale yellow solid obtained on removal of the solvent immediately turns black in the presence of dry Nujol or perfluorodecalin, precluding all attempts to obtain spectra in these media, but dry powder-IR spectra showed two bands, assignable as ν(C–O), at 2213 and 2165 cm^{-1} as expected for *fac*-$[IrF_3(CO)_3]$. The weighted average of these resonances occurs at higher frequency than that reported for the other iridium(III) carbonyl fluoride complexes (2022–2137 cm^{-1})[25–27] and also at higher frequency than that of free carbon monoxide.[29] High ν(CO) IR frequencies, reported previously for $[M(CO)]^+$ complexes (M = Cu, Ag or Au)[30,31] and $[Hg(CO)_2]^{2+}$,[32] have been attributed to σ-donation of the slightly antibonding 5σ lone pair on CO to the metal with little or no π-back donation from the metal to the carbonyl. The strongly electron-withdrawing fluoride ligands in *fac*-$[IrF_3(CO)_3]$ must therefore be effectively removing electron density from the d^6 Ir^{III} metal centre, significantly increasing the σ-acceptor ability of the metal,[31] and influencing the electronic properties of the carbonyl ligands as indicated by the ^{13}C NMR data. These IR bands actually correlate well with the prominent vibrations reported[9] for both '$IrF_2(CO)_3$' and '$IrF_2(CO)_2$', suggesting that *fac*-$[IrF_3(CO)_3]$ may be the correct formulation for the majority of the yellow solid obtained by the carbonylation of IrF_5.

Table 2 Iridium L_{III}-edge EXAFS data[a] for *fac*-$[IrF_3(CO)_3]$

Shell	*d*(EXAFS)/Å	$2\sigma^2$/Å^2 [b]
3F	1.92(0.006)	0.012(0.001)
3C	2.03(0.008)	0.007(0.001)
3O	3.04(0.004)	0.013(0.001)
5F	3.39(0.007)	0.011(0.002)
4F	3.56(0.008)	0.010(0.002)

[a] Standard deviations in parentheses. Note that the systematic errors in bond lengths arising from the data collection and analysis procedures are *ca.* ±0.02 for the first two co-ordination shells and *ca.* ±0.04 Å for subsequent shells. Fit index = $\Sigma_i[(\chi^T - \chi^E)k_i^3]^2$ = 0.744 where χ is the energy recorded as a function of *k*. $R = [\int(\chi^T - \chi^E)k^3dk/\int\chi^E k^3 dk] = 16.2\%$. [b] Debye–Waller factor.

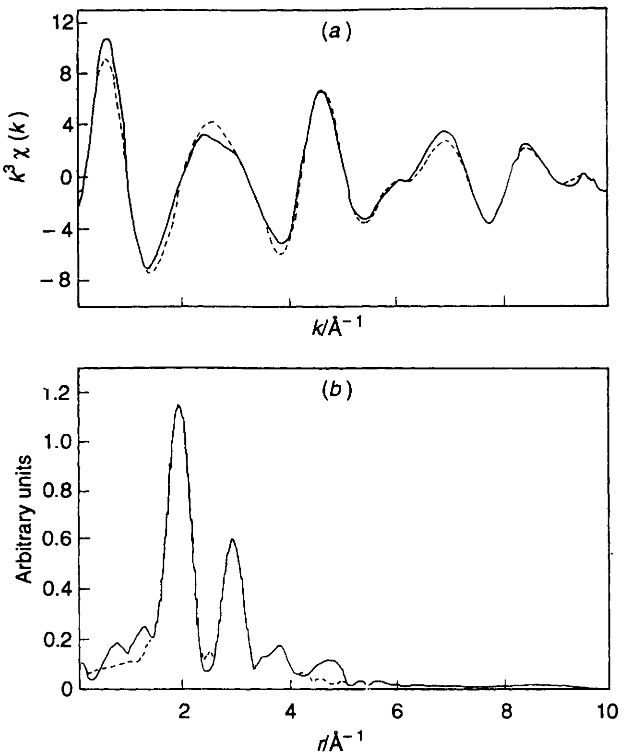

Fig. 2 Background-subtracted EXAFS (*a*) (—, experimental × k^3; - - - -, curved-wave theory × k'^3) and the Fourier transform spectrum (*b*) (—, experimental; - - - -, theoretical) for *fac*-$[IrF_3(CO)_3]$; *k* is the photoelectron wave vector and *r* is the radial distance from the absorbing atom

All attempts to grow crystals suitable for structural characterisation have been unsuccessful. However, we have obtained reliable M–F bond length data using EXAFS,[20] and so we have investigated the purified *fac*-$[IrF_3(CO)_3]$ in HF solution by EXAFS. In the absence of structurally characterised iridium(III) fluoride complexes as model compounds, the reliability of the data collection and treatment was confirmed by the collection and analysis of iridium L_{III}-edge EXAFS data on $[Ir_4(CO)_{12}]$. The results are in satisfactory agreement with the data from the highly disordered single crystal X-ray analysis;[33] Ir–C 1.90, Ir–Ir 2.61 and Ir–O 3.03 Å *cf.* averages of 1.87, 2.69 and 3.01 Å respectively. Data for *fac*-$[IrF_3(CO)_3]$ in HF solution were acquired on samples used previously for the ^{19}F and ^{13}C NMR experiments by heat-flattening the top ends of the 4 mm FEP NMR tubes with the HF solutions frozen in liquid nitrogen. (**CAUTION**: Too much pressure during heat-flattening can cause the FEP tubes to split releasing anhydrous HF.) On melting, the solutions were readily transferred into the flattened cells by inversion and transmission EXAFS data recorded. Data were collected out to $k = 16$ Å^{-1} (k = photoelectron wave vector) beyond the edge, but due to poor signal-to-noise at high *k*, the data were truncated at $k = 13$ Å^{-1} Five data sets were collected, averaged, and the data multiplied by k^3 to compensate for drop-off in intensity at higher *k*. No smoothing or Fourier filtering was applied and the fits discussed below are all compared with the averaged raw (background-subtracted) EXAFS data (Fig. 2). The data were initially modelled to three shells of three fluorine atoms at r = *ca.* 1.92 Å, 3 carbons at r = *ca.* 2.03 Å and three oxygens at r = *ca.* 3.04 Å using localised C_{3v} symmetry and a fixed Ir–C–O of 180° for multiple scattering (Table 2). Each shell was added stepwise, iterated in the usual way, and the best fits tested for statistical significance.[34] Even though the first two shells occur at very similar positions, the correlations between the refined parameters were well within acceptable limits, *i.e.* < 0.7. Examination of the Fourier transforms revealed additional weak broad features around 3.5 Å. We have shown[35] that octahedral fluorides (*e.g.* IrF_6) in anhydrous HF solution show hydrogen-bonded HF solvation shells, with occupation numbers of six back-scattering fluorine atoms, at between 3.36 and 3.38 Å. Therefore, further modelling of the EXAFS data was attempted using four (3F, 3C, 3O, 5F) and five (3F, 3C, 3O, 5F, 4F) shell models, the extra shells being added stepwise, iterated in the usual way, and the best fits tested for statistical significance.[34] Significant decreases in the fit-index and R factor resulted, while the bonded Ir–F and Ir–C distances were invariant within the normal precision (±0.01 Å), giving *d*(Ir–F · · · H–F) of *ca.* 3.4 and 3.6 Å (Fig. 2). No attempt was made to refine the occupation numbers for these weak shells at the limit of the reliability of the EXAFS technique, but we note the similarity between the Debye-Waller factors for these shells and those obtained for the non-bonded HF solvation shells for the metal hexafluorides in anhydrous HF.[35]

Our inability to obtain single crystals of *fac*-$[IrF_3(CO)_3]$ is not surprising since there have been very few crystallographic determinations for iridium fluorides, iridium carbonyls or transition-metal carbonyl fluorides. The Ir^{III}–F bond length obtained by EXAFS for *fac*-$[IrF_3(CO)_3]$ of 1.92 Å is reasonable when compared with the Ir^{VI}–F, Ir^{V}–F and Ir^{IV}–F bond lengths of 1.83, 1.91 and 1.93 Å respectively, obtained by electron diffraction for IrF_6[36] and solid-state EXAFS for $[IrF_6]^{n-}$.[20] This Ir–F bond length is, however, slightly shorter than the previously reported Ir^{III}–F bond lengths of 1.998 and 2.089 Å in $[IrF(COF)(CO)(PEt_3)_2]^+$[26] and $[IrClF(NSF_2)(CO)(PPh_3)_2]$.[25] The Ir–C bond length (2.03 Å) is unusually long and the C–O bond length (1.01 Å) unusually short by comparison with most metal-bound carbonyl ligands.[37] This is also in firm agreement with the unusually high ν(CO) frequencies, and the ^{19}F and ^{13}C NMR data assigned to *fac*-$[IrF_3(CO)_3]$ and confirms the unusual ligand co-ordination in this molecule. Finally, we note that the non-bonded distances associated with HF solvation are slightly longer than those observed for HF solvation of the binary transition-metal fluorides,[35] the variation mirroring the differences in the M^{III}–F and M^{VI}–F bond lengths.

Acknowledgements

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