

## UV–visible spectroscopic studies of group 8–10 metal trifluorides

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### Abstract

Diffuse reflectance UV–visible spectra (2000–200 nm/5000–50 000 cm<sup>-1</sup>) are reported for FeF<sub>3</sub>, CoF<sub>3</sub>, RuF<sub>3</sub>, RhF<sub>3</sub>, IrF<sub>3</sub> and PdF<sub>3</sub>. Assignments for the spectra are proposed and compared with literature data on related hexafluoroanions [MF<sub>6</sub>]<sup>n-</sup>. The spectrum of PdF<sub>3</sub> is consistent with the known mixed-valence Pd<sup>II</sup>[Pd<sup>IV</sup>F<sub>6</sub>] constitution of this material. © Elsevier Science S.A.

**Keywords:** UV–visible spectra; Transition metal; Trifluoride

### 1. Introduction

Detailed studies of the ultraviolet–visible spectra of transition metal fluorides and fluoroanions began with the work of Jorgensen in the 1950s [1]. Fluoride is a particularly suitable ligand for such studies, in that it supports a range of oxidation states for most metals, and its combination of high electronegativity and relatively weak ligand field means that in many cases the d–d bands will not be obscured by the more intense charge transfer bands. We have reported elsewhere UV–visible spectra of the metal hexafluorides MF<sub>6</sub> (M = Re, Ru, Os, Rh, Ir and Pt) isolated in nitrogen matrices at 10 K [2,3], and of the solid pentafluorides [MF<sub>5</sub>]<sub>4</sub> (M = Ru, Os, Rh, Ir and Pt) [4]. Data on transition metal hexafluoroanions [MF<sub>6</sub>]<sup>n-</sup> are collected in two reviews [5]. Apart from a limited study of the UV–visible spectrum of FeF<sub>3</sub> [6], data on metal trifluorides are unavailable. We have recently prepared a range of group 8–10 trifluorides as precursors for the synthesis of quaternary metal oxide–fluoride materials, and have taken the opportunity to record their UV–visible spectra which we report below.

### 2. Results and discussion

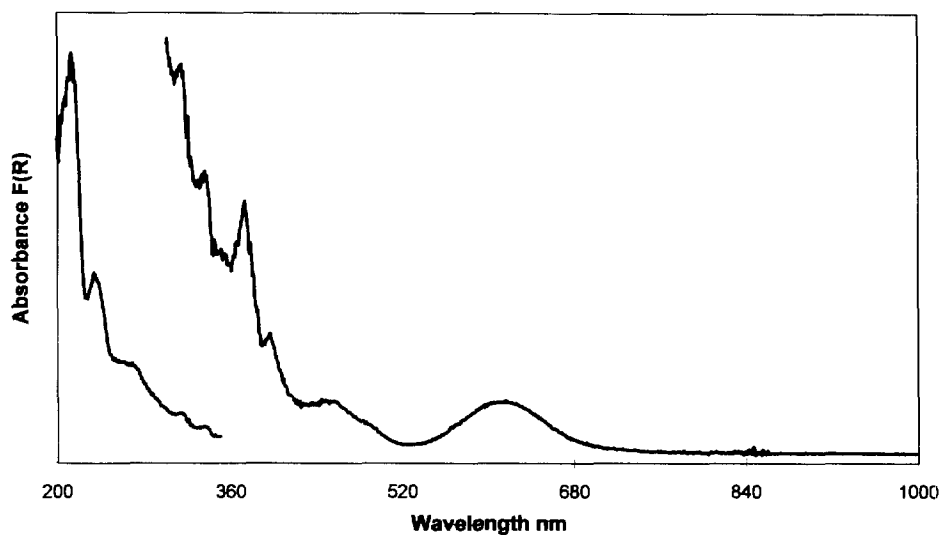
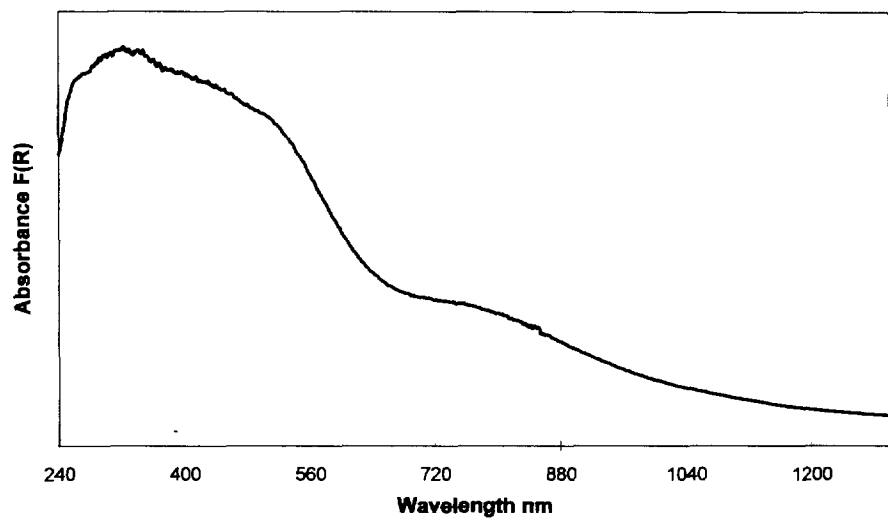
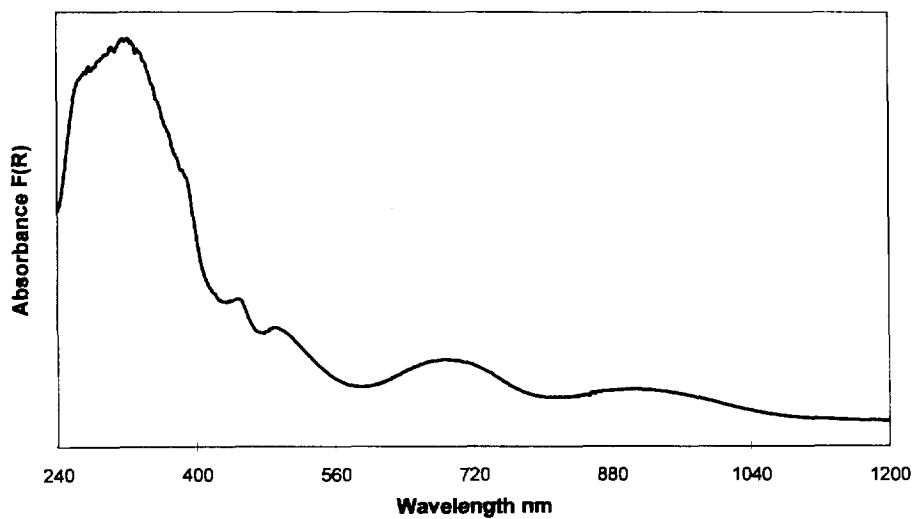
The spectra were recorded from powdered solids, both neat and diluted with dry NaF, over the energy range 5000–50 000 cm<sup>-1</sup>, by diffuse reflectance and using the Kubelka–Munk function to offset the effect of particle size on scattering at

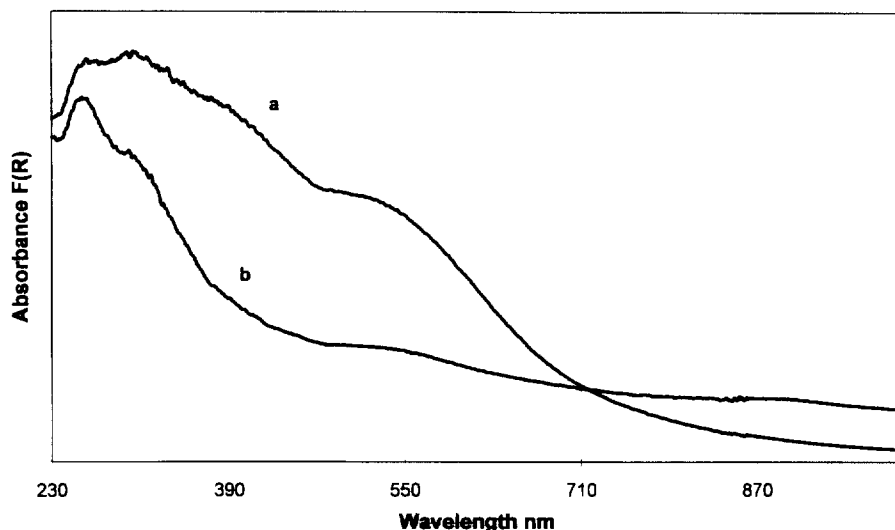
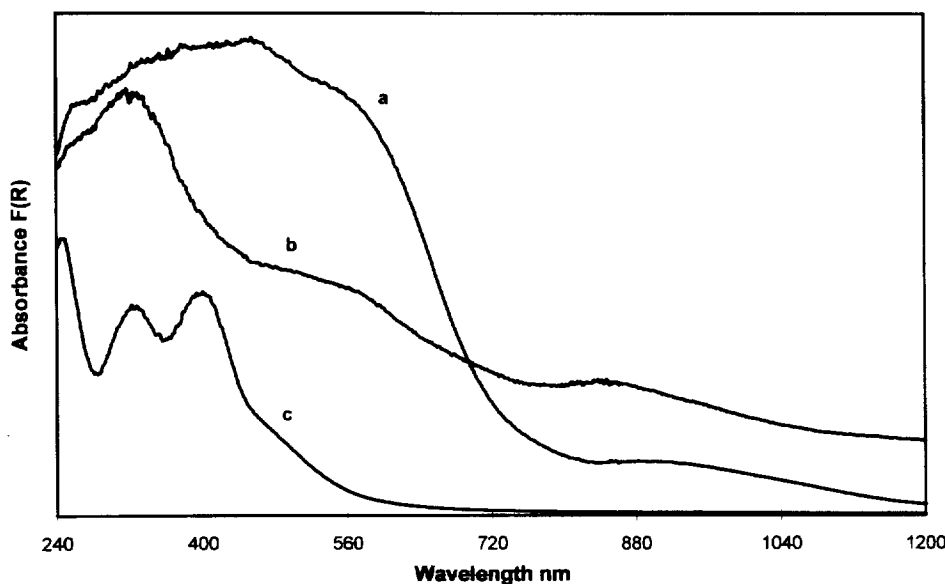
high energies. Comparison of the spectra of corresponding MF<sub>3</sub> and [MF<sub>6</sub>]<sup>3-</sup> (where available) [5] show, as expected, considerable similarities, but it is notable that in the spectra of the trifluorides the bands are generally broader, and the resolution correspondingly poorer. The structures of FeF<sub>3</sub>, CoF<sub>3</sub>, RuF<sub>3</sub>, RhF<sub>3</sub> and IrF<sub>3</sub> are rhombohedral (R $\bar{3}$ c) with the metal in an MF<sub>6</sub> environment [7]. Palladium trifluoride ‘PdF<sub>3</sub>’, in contrast, is a mixed valence Pd<sup>II</sup>[Pd<sup>IV</sup>F<sub>6</sub>] substance with the LiSbF<sub>6</sub> structure containing Pd<sup>IV</sup>–F<sub>6</sub> (1.90 Å) and Pd<sup>II</sup>–F<sub>6</sub> (2.17 Å) octahedra [8]. The diffuse reflectance spectra are shown in Figs. 1–5 and the band maxima and proposed assignments are presented in Tables 1 and 2. It is convenient to discuss each of the spectra in turn.

#### 2.1. FeF<sub>3</sub>

The ground state is high spin d<sup>5</sup>, and thus all d–d bands observed (Table 1) are forbidden sextet–quartet transitions (sextet–doublet transitions are expected to be of very low intensity and the transitions to the quartet states account for all the observed features). Fitting to the appropriate Tanabe–Sugano diagram leads to 10Dq = 13 900 cm<sup>-1</sup> and B = 840 cm<sup>-1</sup>, which compare relatively poorly with the literature values [6] (10Dq = 11 100 cm<sup>-1</sup>, B = 830 cm<sup>-1</sup>), but are in better agreement with the values derived from [FeF<sub>6</sub>]<sup>3-</sup> (10Dq = 13 000 cm<sup>-1</sup>, B = 800 cm<sup>-1</sup>) [9]. The intense feature at 46 750 cm<sup>-1</sup> must be a F(π) → Fe(t<sub>2g</sub>) charge transfer band. Adopting the optical electronegativity model [10], E<sub>max</sub> = 30 000{χ optt(F) – χ optt(Fe)} + 8D/3, and using Allen et al.’s value [9] for χ optt(Fe<sup>III</sup>) of 2.9 and D = 7B, we predict the first allowed charge transfer band at ca. 45 700

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Fig. 1. Diffuse reflectance spectrum of FeF<sub>3</sub>.Fig. 2. Diffuse reflectance spectrum of RuF<sub>3</sub>.Fig. 3. Diffuse reflectance spectrum of CoF<sub>3</sub>.

Fig. 4. Diffuse reflectance spectra of (a) RhF<sub>3</sub> and (b) IrF<sub>3</sub>.Fig. 5. Diffuse reflectance spectra of (a) Pd[PdF<sub>6</sub>], (b) PdF<sub>2</sub> and (c) Cs<sub>2</sub>PdF<sub>6</sub>.

cm<sup>-1</sup>, clearly a reasonable fit. It is difficult to judge the intensity of the feature at 42 550 cm<sup>-1</sup> which from its energy could be either the <sup>6</sup>T<sub>2g</sub> → <sup>4</sup>A<sub>2g</sub> or a parity forbidden charge transfer band. The latter is more likely.

### 2.2. RuF<sub>3</sub>

The spectrum of RuF<sub>3</sub> consists of several broad absorptions (Fig. 2) with ill-defined maxima and as a result the assignments in Table 1 are tentative. For a low-spin d<sup>5</sup> ion in an octahedral field the ground state is <sup>2</sup>T<sub>2g</sub>. The weak broad features at ca. 9500 and ca. 13 500 cm<sup>-1</sup> are plausibly assigned to the spin-forbidden transitions to low lying quartet states. The more intense overlapping bands between ca. 20 200 and ca. 37 000 cm<sup>-1</sup> are spin-allowed transitions, and as expected no charge transfer bands are present before the instrument cut-off at 50 000 cm<sup>-1</sup>. Since the spin-allowed

bands are not clearly defined, the derived values of 10Dq (22 500 cm<sup>-1</sup>) and B (570 cm<sup>-1</sup>) are subject to some error, although they are in fact similar to those derived by Allen et al. [11] from [RuF<sub>6</sub>]<sup>3-</sup>.

### 2.3. CoF<sub>3</sub>

Cobalt(III) fluoride is a rare example of high spin d<sup>6</sup> cobalt(III) and hence the ground state is <sup>5</sup>T<sub>2g</sub> and only one spin allowed transition to <sup>5</sup>E<sub>g</sub> is expected. However as can be seen from Fig. 3, two bands of similar intensity are present at 10 940 and 14 460 cm<sup>-1</sup>, in addition to weaker sharp features assignable as quintet–triplet bands. Similar features are seen in the spectra of [CoF<sub>6</sub>]<sup>3-</sup> salts [9,12], and we follow Allen et al. [9] in assigning both features to a Jahn–Teller split <sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub> transition, since the alternative assignment of the 10 940 cm<sup>-1</sup> feature as <sup>5</sup>T<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> leaving the

Table 1  
UV-visible spectra of FeF<sub>3</sub>, RuF<sub>3</sub>, CoF<sub>3</sub>, RhF<sub>3</sub> and IrF<sub>3</sub><sup>a</sup>

FeF <sub>3</sub>			RuF <sub>3</sub>			CoF <sub>3</sub>		
<i>E</i> <sub>max</sub> (nm)	<i>E</i> <sub>max</sub> (cm <sup>-1</sup> )	Assignment	<i>E</i> <sub>max</sub> (nm)	<i>E</i> <sub>max</sub> (cm <sup>-1</sup> )	Assignment	<i>E</i> <sub>max</sub> (nm)	<i>E</i> <sub>max</sub> (cm <sup>-1</sup> )	Assignment
613	16 300	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	1053	9 500sh	<sup>2</sup> T <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub>	1285	7 780	<sup>5</sup> T <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub>
454	22 000	<sup>4</sup> T <sub>2g</sub>	740	13 500sh	<sup>4</sup> T <sub>2g</sub>	914, } 692 }	10 940, } 14 460 }	<sup>5</sup> E <sub>g</sub>
398	25 100	<sup>4</sup> A <sub>1g</sub>	495	20 200	<sup>2</sup> A <sub>2g</sub> , <sup>2</sup> T <sub>1g</sub> , <sup>2</sup> T <sub>2g</sub>	492	20 325	<sup>3</sup> T <sub>2g</sub> , <sup>3</sup> T <sub>1g</sub>
374	26 750	<sup>4</sup> E <sub>g</sub>	380	26 300br	<sup>2</sup> E <sub>g</sub> , <sup>2</sup> T <sub>1g</sub> , <sup>2</sup> T <sub>2g</sub>	451	22 125	<sup>3</sup> T <sub>1g</sub> , <sup>3</sup> E <sub>g</sub>
338	29 600	<sup>4</sup> T <sub>2g</sub>	323	31 000	<sup>2</sup> A <sub>1g</sub>	372	26 880	<sup>3</sup> T <sub>2g</sub>
314	31 850	<sup>4</sup> E <sub>g</sub>	270	37 000sh	<sup>2</sup> E <sub>g</sub>	315	31 650	F(π) → Co(t <sub>2g</sub> ) <sup>b</sup>
270	37 050	<sup>4</sup> T <sub>1g</sub>				276	36 230	F(π) → Co(t <sub>2g</sub> )
235	42 550	F(π) → Fe(t <sub>2g</sub> ) <sup>b</sup>						
214	46 750	F(π) → Fe(t <sub>2g</sub> )						
RhF <sub>3</sub>			IrF <sub>3</sub>					
671	14 900br	<sup>1</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub>	500	20 000br	<sup>1</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub>			
473	21 150	<sup>1</sup> T <sub>1g</sub>	300	33 330	<sup>1</sup> T <sub>1g</sub>			
364	27 500	<sup>1</sup> T <sub>2g</sub>	256	39 060	<sup>1</sup> T <sub>2g</sub>			
286	35 000sh	<sup>1</sup> T <sub>2g</sub>						

<sup>a</sup> Diffuse reflectance spectra 5000–50 000 cm<sup>-1</sup>, *E*<sub>max</sub> ± 50 cm<sup>-1</sup>.

<sup>b</sup> Parity forbidden charge transfer band.

14 460 cm<sup>-1</sup> band as the spin-allowed transition seems unacceptable on grounds of their relative intensities. On this basis the assignments of the other bands listed in Table 1 are straightforward leading to 10*Dq* = 12 680 cm<sup>-1</sup>, *B* = 760 cm<sup>-1</sup> (cf K<sub>3</sub>[CoF<sub>6</sub>] 10*Dq* = 14 100 cm<sup>-1</sup>, *B* = 765 cm<sup>-1</sup> [9]; other [CoF<sub>6</sub>]<sup>3-</sup> salts have 10*Dq* ca. 13 100 cm<sup>-1</sup> [12]). The lowest energy charge transfer transition is predicted by *E*<sub>max</sub> = 30 000{χ optt(F) - χ optt(Co<sup>III</sup>)} + 2*D*, and, with χ optt(Co<sup>III</sup>) = 3.0, we calculate *E*<sub>max</sub> as 37 650 cm<sup>-1</sup>. Observed bands at 31 650 and 36 230 cm<sup>-1</sup> are thus assignable as parity forbidden and allowed charge transfer bands respectively.

#### 2.4. RhF<sub>3</sub>

Salmon-coloured rhodium trifluoride samples were made by fluorination of RhCl<sub>3</sub> or RhI<sub>3</sub>, the spectra from the products of the two preparations proving to be identical. The two main features are clearly the spin allowed <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub>, <sup>1</sup>T<sub>2g</sub> respectively, leading to 10*Dq* = 22 100, *B* = 400 cm<sup>-1</sup>. The tail to low energy exhibits a slight inflection at ca. 14 900 cm<sup>-1</sup> possibly the spin-forbidden transition to <sup>3</sup>T<sub>1g</sub>. There is also a band at ca. 35 000 cm<sup>-1</sup> for which the assignment is unclear. A similar band in the spectrum of [RhF<sub>6</sub>]<sup>3-</sup> was suggested [13] to be the two electron transition <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> (t<sub>2g</sub><sup>4</sup> e<sub>g</sub><sup>2</sup>), and this is the most likely assignment, since from the energy of the lowest energy charge transfer band in [RhCl<sub>6</sub>]<sup>3-</sup> at 39 200 cm<sup>-1</sup> [14], no F(π) → Rh(e<sub>g</sub>) band is expected in the region examined.

#### 2.5. IrF<sub>3</sub>

Samples of light brown IrF<sub>3</sub> were prepared by SF<sub>4</sub> reduction of IrF<sub>5</sub> in a bomb. The assignment of the UV-visible spectrum of the IrF<sub>3</sub> (t<sub>2g</sub><sup>6</sup>) is straightforward (Table 1) showing the expected two spin-allowed transitions, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub>, <sup>1</sup>T<sub>2g</sub> respectively, and a weak feature of ill-defined maximum at ca. 20 000 cm<sup>-1</sup> which is the spin-forbidden <sup>1</sup>A<sub>1g</sub> → <sup>3</sup>T<sub>1g</sub> transition. The <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> peak is asymmetric with shoulders evident of the low energy side. These are probably due to the effect of spin-orbit coupling which is substantial in the 5d elements (ζ for 5d elements may be 3000–4000 cm<sup>-1</sup>) [5], although they are too ill-defined for any attempt at fitting to be worthwhile. The analysis of the spectral data produced 10*Dq* = 33 150 and *B* = 375 cm<sup>-1</sup>. The fluoroanion [IrF<sub>6</sub>]<sup>3-</sup> is unknown, but comparison with the 10*Dq* value derived for [IrCl<sub>6</sub>]<sup>3-</sup> (22 750 cm<sup>-1</sup>) [15] shows the ligand field splitting in IrF<sub>3</sub> is rather higher than expected, although similar to that in the isoelectronic [PtF<sub>6</sub>]<sup>2-</sup> [5].

#### 2.6. PdF<sub>3</sub>

Although early work assumed that PdF<sub>3</sub> was analogous to the other platinum metal trifluorides [7], it was subsequently established that the constitution is Pd<sup>II</sup>[Pd<sup>IV</sup>F<sub>6</sub>], and a neutron diffraction study revealed both palladium centres were in octahedral fluoride environments with Pd<sup>II</sup>-F = 2.17 Å and Pd<sup>IV</sup>-F = 1.90 Å [8]. Thus it belongs in Class II in the Robin and Day scheme [16], i.e. the palladium centres are in similar but structurally distinguishable sites. A Class II material should show the spectroscopic fingerprints of the constituent

Table 2  
UV-visible spectra of palladium fluorides<sup>a</sup>

PdF <sub>2</sub>			PdF <sub>3</sub>		[PdF <sub>6</sub> ] <sup>2-</sup> <sup>b</sup>	
<i>E</i> <sub>max</sub> (nm)	<i>E</i> <sub>max</sub> (cm <sup>-1</sup> )	Assignment	<i>E</i> <sub>max</sub> (nm)	<i>E</i> <sub>max</sub> (cm <sup>-1</sup> )	<i>E</i> <sub>max</sub> (nm)	<i>E</i> <sub>max</sub> (cm <sup>-1</sup> )
1220	8 200br	<sup>3</sup> A <sub>2g</sub> → <sup>1</sup> E <sub>g</sub>	909	11 000	469	21 300sh
847	11 800	<sup>3</sup> T <sub>2g</sub>	519	19 250	400	25 000
560	17 850	<sup>3</sup> T <sub>1g</sub>	410	24 400	323	31 000
313	31 950	<sup>3</sup> T <sub>1g</sub> (P)	312	32 050	250	40 000
266	37 600sh	<sup>1</sup> E <sub>g</sub> , <sup>1</sup> T <sub>2g</sub>	250	40 000		

<sup>a</sup> Diffuse reflectance spectra 5000–50 000 cm<sup>-1</sup>, *E*<sub>max</sub> ± 50 cm<sup>-1</sup>.

<sup>b</sup> A detailed assignment for this spectrum is in Ref. [18].

ions at similar energies to those in single valence analogues and one or more intervalence charge transfer bands. In Fig. 5 are shown the spectra of ‘‘PdF<sub>3</sub>’’ and of the single valence analogues PdF<sub>2</sub> and Cs<sub>2</sub>[PdF<sub>6</sub>]. The rutile form of palladium difluoride is a rare example of six-coordinate palladium(II) with a slightly distorted PdF<sub>6</sub> octahedron (2 × 2.17, 4 × 2.15 Å) [17]. No splitting of the main bands was evident in the diffuse reflectance spectrum of PdF<sub>2</sub>, and it was analysed assuming O<sub>h</sub> symmetry yielding 10Dq = 11 800 cm<sup>-1</sup> and B = 600 cm<sup>-1</sup>. The spectrum of [PdF<sub>6</sub>]<sup>2-</sup> has been reported previously [18]. Although the spectrum of ‘‘PdF<sub>3</sub>’’ is not well resolved, the weak low energy feature at ca. 11 000 cm<sup>-1</sup> corresponds to the <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> transition of the Pd(II) centre, and the overlapping features > ca. 25 000 cm<sup>-1</sup> will contain contributions from both metal centres. The strong feature(s) in the region 19 000–24 000 cm<sup>-1</sup> is/are the intervalence CT band(s). The UV-visible spectrum is thus consistent with the mixed valence formulation established structurally and by PES spectroscopy [19].

### 3. Experimental

Spectra were obtained from both neat samples and samples diluted with dry NaF on a Perkin Elmer Lambda 19 using the diffuse reflectance attachment. Data were recorded using the Kubelka–Munk function available in the PECS software. Finely powdered samples were loaded in a glove box (water < 1 ppm) into a Teflon cell. The latter was constructed from a Teflon block (4 cm × 3.6 cm × 0.3 cm) into the face of which a rectangular depression (2 cm × 1 cm) approx. 0.1 cm deep was cut. The powdered sample was packed into this depression, covered with a demountable quartz window sealed around the edges with fluorocarbon grease.

Several samples of each fluoride were prepared, their identity confirmed by PXRD, and the UV-visible spectra checked for consistency.

Anhydrous FeF<sub>3</sub> was a commercial sample (Aldrich), CoF<sub>3</sub> was made by fluorination of CoF<sub>2</sub> (400 °C/3 atm), RuF<sub>3</sub> by SF<sub>4</sub> reduction of RuF<sub>5</sub> [20], and RhF<sub>3</sub> by fluorination of either RhCl<sub>3</sub> or RhI<sub>3</sub> (400 °C/1 atm). IrF<sub>3</sub> and PdF<sub>2</sub>

were prepared by SF<sub>4</sub> reduction of IrF<sub>5</sub> and PdF<sub>3</sub> respectively and the preparations will be described elsewhere [21]. PdF<sub>3</sub> was made by fluorination of PdCl<sub>2</sub> (300 °C/2 atm), and Cs<sub>2</sub>[PdF<sub>6</sub>] by reaction of Cs<sub>2</sub>[PdCl<sub>6</sub>] with BrF<sub>3</sub> [22].

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### References

- [1] C.K. Jorgensen, Prog. Inorg. Chem. 12 (1970) 101.
- [2] J.H. Holloway, G. Stanger, E.G. Hope, W. Levason, J.S. Ogden, J. Chem. Soc. Dalton Trans. (1988) 1341.
- [3] A.K. Brisdon, P.J. Jones, W. Levason, J.S. Ogden, J.H. Holloway, E.G. Hope, G. Stanger, J. Chem. Soc. Dalton Trans. (1990) 715.
- [4] E.G. Hope, Polyhedron 12 (1993) 2977.
- [5] G.C. Allen, K.D. Warren, Struct. Bond. (Berlin) 9 (1971) 49; 19 (1974) 105.
- [6] I.W. Breman, A.M.A. Verwey, S. Balt, Spectrochim. Acta A 24 (1968) 1623.
- [7] A.J. Edwards, Adv. Inorg. Chem. Radiochem. 27 (1983) 83.
- [8] A. Tressaud, M. Wintenberger, N. Bartlett, P. Hagenmuller, C.R. Acad. Sci. Ser. C 282 (1976) 1069.
- [9] G.C. Allen, G.A.M. El-Sharkawy, K.D. Warren, Inorg. Chem. 10 (1971) 2538.
- [10] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd edn., Elsevier, New York, 1984.
- [11] G.C. Allen, G.A.M. El-Sharkawy, K.D. Warren, Inorg. Chem. 12 (1973) 2231.
- [12] F.A. Cotton, D. Meyers, J. Am. Chem. Soc. 82 (1960) 5023.
- [13] H.H. Schmidtke, Z. Phys. Chem. 40 (1964) 96.
- [14] C.K. Jorgensen, Mol. Phys. 2 (1959) 309.
- [15] K.A. Schröder, J. Chem. Phys. 37 (1962) 2553.
- [16] M. Robin, P. Day, Adv. Inorg. Chem. Radiochem. 10 (1966) 247.
- [17] N. Bartlett, R. Maitland, Acta Crystallogr. 11 (1958) 7; B.G. Müller, R. Hoppe, Mater. Res. Bull. 16 (1981) 207.
- [18] D.H. Brown, D.R. Russell, D.W.A. Sharp, J. Chem. Soc. A. (1966) 18.
- [19] A. Tressaud, S. Khairoun, H. Touhara, N. Watanabe, Z. Anorg. Allg. Chem. 540/541 (1986) 291.
- [20] W.J. Casteel, A.P. Wilkinson, H. Borrmann, R.E. Stefass, N. Bartlett, Inorg. Chem. 31 (1992) 3124.
- [21] A.L. Hector, W. Levason, M.T. Weller, manuscript in preparation.
- [22] A.G. Sharpe, J. Chem. Soc. (1953) 197.