

UV–Vis spectroscopic studies of fluorides and fluoroanions of silver(III) and gold(III) and (V)

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Abstract

Diffuse reflectance UV–Vis spectra (2000–200 nm/5000–50 000 cm⁻¹) are reported for AgF₃, AuF₃, [AgF₄]⁻, [AuF₄]⁻ and [AuF₆]⁻ and assignments proposed. © 1997 Elsevier Science S.A.

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1. Introduction

UV–Vis spectra have been reported and assigned for many transition metal fluoroanions [1]. We have reported elsewhere UV–Vis spectra of the metal hexafluorides MF₆ (M = Re, Ru, Os, Rh, Ir and Pt) isolated in nitrogen matrices at 10 K [2,3], of the solid pentafluorides [MF₅]₄ (M = Ru, Os, Rh, Ir and Pt) [4], and recently of the group VIII–X trifluorides [5]. A range of fluorides and fluoroanions of the group XI metals are known [6], but the UV–Vis spectra have been reported only for [CuF₆]³⁻, [AgF₆]³⁻ and [AgF₄]²⁻ [7,8]. We report below the spectra of other examples and propose assignments for the major features.

2. Results and discussion

It is convenient to discuss the compounds in turn.

2.1. Cs[AuF₆]

The reddish–orange caesium salt prepared by fluorination of Cs[AuF₄] (3 atm/350°C) has the LiSbF₆ (R3⁻) structure with a regular octahedral [AuF₆]⁻ anion [9]. The diffuse reflectance spectrum (Fig. 1) shows a weak shoulder at ca. 25 650 cm⁻¹ which can be assigned to the spin-forbidden transition ¹A_{1g} → ³T_{1g}, and stronger bands at 33 780, 39 060 and 41 320 cm⁻¹. The first two of these are the spin-allowed

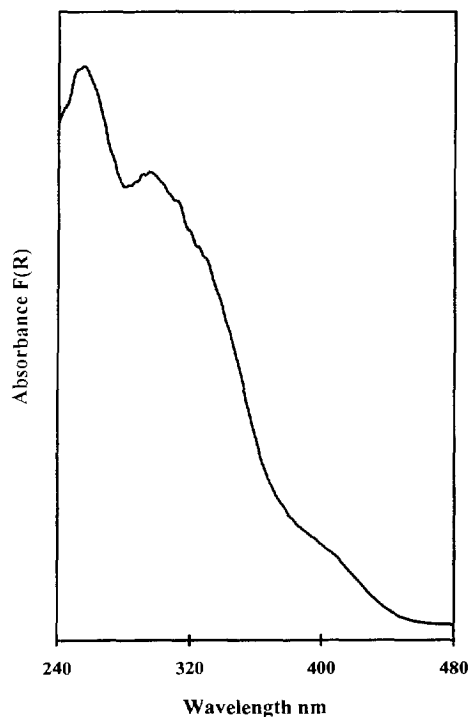


Fig. 1. Diffuse reflectance spectrum of Cs[AuF₆] diluted with NaF.

transitions ¹A_{1g} → ¹T_{1g}, ¹T_{2g}, from which fitting to the Tanabe–Sugano diagram gives $D_q = 3450$ and $B = 350$ cm⁻¹. The assignment of the 41 320 cm⁻¹ band is less clear; a possibility is the two-electron transition to ¹T_{2g} ($t_{2g}^4 e_g^2$). It is unlikely to be a charge transfer band since, for a low spin d⁶ ion in O_h

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symmetry, the lowest energy symmetry allowed transition is predicted as

$$E_{\max} = 30\,000(\chi_{\text{opt}}F - \chi_{\text{opt}}\text{Au}) + 10D_q - D(\text{cm}^{-1})$$

and for this to give a band at ca. $40\,000\text{ cm}^{-1}$, $\chi_{\text{opt}}\text{Au}$ must be ca. 3.6, an unreasonably high value, even allowing for the high oxidation state of the gold [1].

2.2. $\text{Cs}[\text{AuF}_4]$ and AuF_3

Both contain square-planar gold(III) centres. The former has the $\text{K}[\text{BrF}_4]$ structure [10], whilst AuF_3 has an unusual structure in which square-planar AuF_4 units ($\text{Au}-\text{F} = 1.998(2)$ and $1.876(3)\text{ \AA}$) are linked via *cis* bridges into an infinite helical chain [11,12]. There are weak $\text{Au}\dots\text{F}$ interactions perpendicular to the AuF_4 plane at $2.761(3)\text{ \AA}$, but for spectroscopic purposes the local geometry in both may be considered as planar. The energy level ordering and UV-Vis spectra of square-planar d^8 complexes have been intensively studied, and the conclusions have been summarised by Lever [13]. The spectra of powdered $\text{Cs}[\text{AuF}_4]$ and AuF_3 are shown in Fig. 2 and Table 1 lists the energy maxima. The resolution is markedly better in the spectrum of the fluoroanion, but the corresponding energies are very similar. The assignment in Table 1 is based upon the d-orbital ordering $d_{x^2-y^2} (b_{1g}) > d_{xy} (b_{2g}) > d_{xz}, d_{yz} (e_g) > d_{z^2} (a_{1g})$ and for a d^8 ion all are filled except the $d_{x^2-y^2}$ orbital. The lowest energy charge transfer transition $\text{Cl}(\pi) \rightarrow \text{Au}(d_{x^2-y^2})$ in $[\text{AuCl}_4]^-$ is at ca. $31\,000\text{ cm}^{-1}$ [14a,14], and hence the $\text{F}(\pi) \rightarrow \text{Au}(d_{x^2-y^2})$ band is expected on optical electronegativity grounds to be $> 50\,000\text{ cm}^{-1}$ and hence outside the range studied. Therefore the three bands observed are assigned to transitions from the filled gold d orbitals to $\text{Au}(d_{x^2-y^2})$ (Table 1) [13,14,14,15]. The broader bands in the spectrum of AuF_3 may reflect the lower symmetry (C_{2v}).

2.3. $\text{K}[\text{AgF}_4]$ and AgF_3

Again, both contain square-planar AgF_4 centres, the $\text{K}[\text{AgF}_4]$ having the $\text{K}[\text{BrF}_4]$ structure [10,12]. The structure of AgF_3 is similar to that of AuF_3 with the silver coordinated to two bridging fluorine atoms at $1.990(3)\text{ \AA}$ and two terminal ones at $1.863(4)\text{ \AA}$, but with relatively shorter

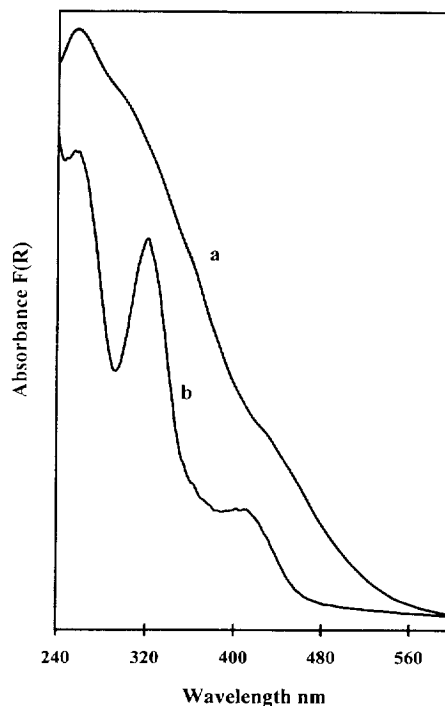


Fig. 2. Diffuse reflectance spectra of (a) AuF_3 and (b) $\text{Cs}[\text{AuF}_4]$ diluted with NaF .

contacts perpendicular to the plane at $2.540(4)\text{ \AA}$ (cf. $2.761(3)\text{ \AA}$ in AuF_3). The spectra are shown in Fig. 3 and E_{\max} values given in Table 1. The spectra of AgF_3 and $\text{K}[\text{AgF}_4]$ are similar in profile, but the E_{\max} values show greater variation than between the spectra of the gold analogues. The origin of these differences is uncertain, both the lower actual symmetry in the AgF_3 and the more significant axial interaction in AgF_3 (compared with AuF_3) may be involved. Unfortunately no single crystal X-ray structure of $\text{K}[\text{AgF}_4]$ is available which would permit a detailed comparison of the silver environments. The similar energies in the gold and silver compounds, confirm that the transitions are not charge transfer in origin, since the very strongly oxidising Ag(III) would exhibit a large bathochromic shift in the charge transfer energies. Only one example of a genuine octahedral $[\text{AgF}_6]^{3-}$ species is known, the elpasolite $\text{Cs}_2\text{K}[\text{AgF}_6]$ [16], whose UV-Vis spectrum was reported and assigned by Allen and Warren [7]. The spectrum which

Table 1
Diffuse reflectance spectra of Au(III) and Ag(III) compounds^a

$\text{Cs}[\text{AuF}_4]$		AuF_3		$\text{K}[\text{AgF}_4]$		AgF_3		Assignment
E_{\max}		E_{\max}		E_{\max}		E_{\max}		
(cm^{-1})	(nm)	(cm^{-1})	(nm)	(cm^{-1})	(nm)	(cm^{-1})	(nm)	
24 400	410	23 250	430	23 800	420(sh)	22 830	438	$b_{2g} \rightarrow b_{1g}$
31 150	321	32 800	306	27 800	360	30 300	330	$e_g \rightarrow b_{1g}$
38 910	257	38 760	258	35 090	285	38 450	260	$a_{1g} \rightarrow b_{1g}$

^a Samples diluted with NaF .

Table 2
Diffuse reflectance spectra of Cs[AuF₆] and Cs₂Cu_{1.5}F₆^a

Cs[AuF ₆]			Cs ₂ Cu _{1.5} F ₆		
E_{\max}		Assignment	E_{\max}		Assignment ^b
(cm ⁻¹)	(nm)		(cm ⁻¹)	(nm)	
25 650	392	¹ A _{1g} → ³ T _{1g}	7250	1380	
33 780	296	¹ A _{1g} → ¹ T _{1g}	9170	1090	³ A _{2g} → ¹ E _g
39 060	256	¹ A _{1g} → ¹ T _{2g}	13 775	726	³ A _{2g} → ³ T _{2g}
41 320	242	¹ A _{1g} → ¹ T _{2g} (⁴ E _g ²)?	20 500	488	³ A _{2g} → ³ T _{1g}
			27 275(sh)	361	F(π) → Cu(eg)
			30 680	326	F(π) → Cu(eg)
			39 680	252	F(π) → Cu(eg)

^a Samples diluted with NaF.

^b Assignments based upon those for [CuF₆]³⁻ in Ref. [7].

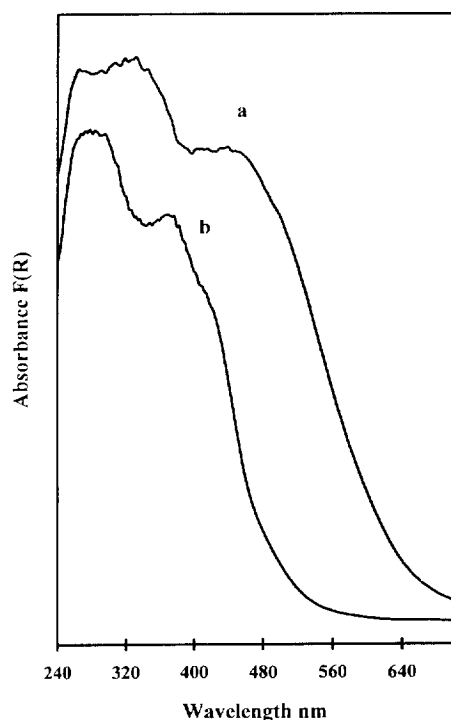


Fig. 3. Diffuse reflectance spectra of (a) AgF₃ and (b) K[AgF₄] diluted with NaF.

shows weak features at 6300, 12 900, 18 400 and 23 400 cm⁻¹ and more intense charge transfer bands at 27 500 and 37 500 cm⁻¹, is very different from those of the essentially planar AgF₃ and K[AgF₄] confirming that a square planar geometry is the correct model for interpreting the spectra of the last two compounds. The orange Cs[CuF₄] with the K[BrF₄] structure has been prepared by Fleischer and Hoppe [17], by fluorination of Cs[CuCl₃] under the extreme conditions of 350 atm/400°C. Under the lower pressure obtainable with our equipment (ca. 100 atm/200°C) we obtained only inhomogeneous black materials from this reaction. Similarly whilst the copper(IV) compound, orange Cs₂[CuF₆] is obtainable [18] from the fluorination of CsCl + Cs[CuCl₃] at 350 atm/400°C, under the lower pressures, the product was

a brown material identified by its X-ray powder pattern [19] as the mixed-valence Cs₂Cu_{1.5}F₆. The UV–Vis spectrum of this brown material (Table 2) is very similar to that [7] of Cs₂K[CuF₆] confirming the presence of Cu(III); presumably the Cu(II) absorptions are weak and obscured by those of the Cu(III).

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 < 5 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–Vis spectra checked for consistency.

The compounds were prepared by literature methods or minor modifications thereof: AgF₃ from K[AgF₄] and BF₃ in AHF [12], AuF₃ by fluorination of Au₂Cl₆·nH₂O at 200°C/2 atm followed by grinding in a mortar and refluorination 200°C/1atm [20], K[AgF₄] by fluorination of KCl + AgF 300°C/3 atm [10], Cs[AuF₄] by combination of AuF₃ and CsF in BrF₃ followed by heating to 200°C in vacuum [21]. Cs[AuF₆] was made by fluorination of Cs[AuF₄] at 350°C/3 atm [9]. Cs₂Cu_{1.5}F₆ was made by fluorination of CsCl + CsCuCl₃ in an alumina crucible at 10 atm/200°C [19], which yielded a red–brown powder containing a few black particles which were separated manually.

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