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The Electronic Spectrum of the Hexafluorocobaltate(IV) Anion

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A study of the electronic spectrum of the hexafluorocobaltate(IV) anion in Cs_2CoF_6 by diffuse reflection, between 4 and 45 kK, indicates the presence of a low-spin $^2T_{2g}$ $(t_{2g}{}^5)$ ground state. Two very weak bands at 6.4 and 10.3 kK are assigned to transitions to $^4T_{1g}$ and $^4T_{2g}$ states and the complex absorption between 15 and 26 kK is resolved into four bands at 17.3, 18.9, 21.4, and 24.4 kK. These are assigned, respectively, to transitions to $^2A_{2g}$ and $^2T_{1g}$, $^2T_{2g}$, ^2E_g, and $^2T_{1g}$ $(t_{2g}{}^4e_g)$ states, and the intense broad bands at 28.3 and 37.1 kK are assigned to charge-transfer excitations. The bands at 18.9 and 21.4 kK both show vibrational structure which is attributed to a symmetric α_{1g} progression. Least-squares fitting of the d–d bands yields $Dq = 2030$ cm^{-1}, $B = 635$ cm^{-1}, and $\beta = 0.54$, indicating a degree of covalency which is high for a fluoride complex, although not as great as for the $NiF_6{}^{2-}$ ion.

Introduction

Our recent investigation of the hexafluoronickelate(IV) anion[1] showed that very low values of β, the nephelauxetic ratio, may be observed even for fluoride complexes when the metal involved is in a high oxidation state. We now report a similar result from the study of cesium hexafluorocobaltate(IV), Cs_2CoF_6, which was first obtained by Hoppe[2] by the action of fluorine on Cs_2CoCl_4 or $Cs_2Co(SO_4)_2$ at 300°. It was shown[2,3] to have a cubic K_2PtCl_6 type of lattice and a magnetic moment rising from 2.46 BM at 90°K to 2.97 BM at 294°K. A low-spin $(t_{2g}{}^5)$ ground state is therefore likely and we have been able, by courtesy of Professor Hoppe, to obtain samples (sealed under vacuum in our silica cells) whose diffuse reflectance spectra we now record.

Experimental Section

Cesium Hexafluorocobaltate(IV).—This was prepared by Dr. H. Henkel (University of Giessen) and supplied to us by Professor Hoppe.

Diffuse Reflectance Measurements.—These were carried out as before,[1] both at room and liquid nitrogen temperatures, using a Beckman DK 2A spectroreflectometer with a magnesium oxide reference. Intensities are expressed in terms of the Kubelka–Munk function, F_R, and converted to extinction coefficients, ϵ, by the relationship $F_R = \epsilon c/0.434s$ where c = density/molecular weight and s is the scattering coefficient. Oscillator strengths were then derived using the half-height band widths obtained from Gaussian analysis of the curves. The value of s (1.73) obtained by Kortum[4] for $KMnO_4$ was taken as typical for transition metal complexes. Since the particle size of our samples (20 ± 5 μ) was sufficiently small effectively to eliminate any regular reflectance component below about 25 kK, s is essentially constant in that region.

Results

The diffuse reflectance spectrum is recorded in Table 1 and shown in Figures 1 and 2. Two very weak peaks occur at 6.4 and 10.3 kK, and a broad envelope occurs between 15 and 26 kK, containing bands at 17.3, 18.9, 21.4, and 24.4 kK. These are assigned to Laporte-forbidden d–d transitions, and the intense bands at 28.3 and 37.1 kK are assigned to allowed charge-transfer transitions. The band at 32.2 kK is tentatively assigned to a further d–d transition. The 18.9- and 21.3-kK bands show vibrational fine structure which at 77°K is resolved to indicate separate progressions on both bands with a spacing of about 520 ± 50 cm^{-1}.

Table I

The Diffuse Reflectance Spectrum of Cesium Hexafluorocobaltate(IV)

Band position, kK				
Obsd	Calcd[a]	Assignment	ϵ	f
6.4	6.3	$^2T_{2g} \rightarrow {}^4T_{1g}$	0.5	2.3×10^{-6}
10.3	10.9	$^2T_{2g} \rightarrow {}^4T_{2g}$	0.5	4.4×10^{-6}
17.3	17.3	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	32	3.0×10^{-4}
18.9	18.9	$^2T_{2g} \rightarrow {}^2T_{2g}$	34	2.2×10^{-4}
21.4	20.5	$^2T_{2g} \rightarrow {}^2E_g$	106	1.3×10^{-3}
24.4	24.8	$^2T_{2g} \rightarrow {}^2T_{1g}$	198	3.2×10^{-3}
28.3	...	$\pi \rightarrow t_{2g}$	Strong	...
32.2	32.1	$^2T_{2g} \rightarrow {}^2E_g$ (?)	?	...
37.1	...	$\pi \rightarrow t_{2g}$	Strong	...

[a] $Dq = 2030$ cm^{-1} and $B = 635$ cm^{-1}.

Discussion

Gaussian analysis of the spectrum between 15 and 26 kK produces four bands with F_R values ranging from 0.4 to 2.4, *i.e.*, comparable in intensity to the spin-allowed bands observed[1] in K_2NiF_6. This therefore indicates that the transitions in this region correspond to spin-allowed excitations and that the ground state is in fact low-spin $^2T_{2g}$ $(t_{2g}{}^5)$, as suggested by the magnetic data, since, for a high-spin $^6A_{1g}$ $(t_{2g}{}^3e_g{}^2)$ ground state, all possible d–d transitions are spin forbidden. Thus, using the Tanabe and Sugano[5] treatment, the bands at 17.3, 18.9, 21.4, and 24.4 kK are assigned to transitions to $^2A_{2g}$ and $^2T_{1g}$, $^2T_{2g}$, ^2E_g, and $^2T_{1g}$ $(t_{2g}{}^4e_g)$ states, respectively, and the very weak absorptions at 6.4 and 10.3 kK are assigned to spin-forbidden transitions to $^4T_{1g}$ and $^4T_{2g}$.

The bands at 18.9 and 21.4 kK both show extensive vibrational fine structure, similar to that of the $^1T_{1g}$ band in $NiF_6{}^{2-}$, but at room temperature the structure is less well-resolved because of the extensive overlapping of the bands involved. At 77°K however distinct progressions are found on both bands, and it is probable

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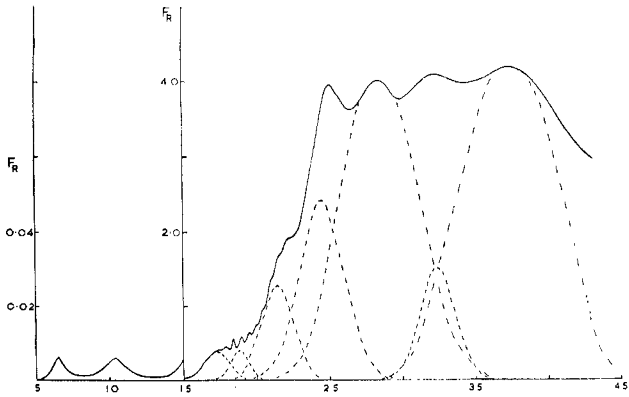

Figure 1.—The diffuse reflectance spectrum of cesium hexafluorocobaltate(IV) in the region 5-45 kK at room temperature: observed spectrum, ———; Gaussian analysis, - - - -.

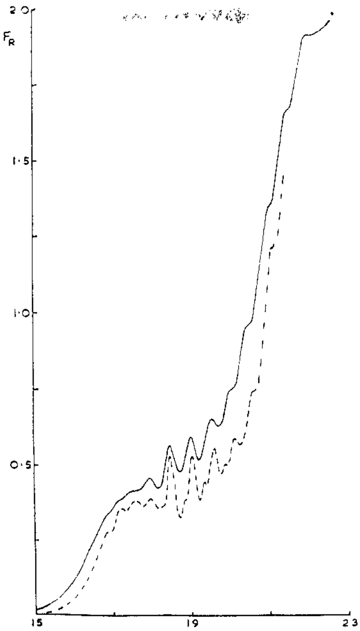

Figure 2.—The diffuse reflectance spectrum of cesium hexafluorocobaltate(IV) in the region 15–23 kK: room temperature, ———; liquid nitrogen temperature, - - - -.

that in CoF_6^{2-} also the structure corresponds to the superposition of a symmetric α_{1g} progression on the vibronically allowed (probably τ_{1u}) transition. The spacings on both bands are about 520 ± 50 cm^{-1} which is consistent with the observation[6] of the Raman α_{1g} mode at 560 cm^{-1}. The reduction of the force constants in the excited states thus indicated is to be expected owing to the increased occupation of the e_g antibonding levels.

The crystal field splitting parameter, Dq, the Racah interelectronic repulsion parameter, B, and the nephelauxetic ratio, β, were determined by least-squares fitting of the bands using the full Tanabe and Sugano[5] strong-field matrices. The complexity of the band system rules out any attempt to fit the data to both β_{35} and β_{55}, but we were nevertheless able to obtain a satisfactory correlation using only a single B. Since B [$Co^{4+}(g)$] is not available experimentally, it was estimated, by extrapolation from the Co^{2+} and Co^{3+} values listed by Tanabe and Sugano,[5] as 1175 cm^{-1}. In the calculations the C/B ratio was taken as 4.90 since values of 4.63 and 4.81 were reported[5] for Co^{2+} and Co^{3+}. This yielded $Dq = 2030$ cm^{-1}, $B = 635$ cm^{-1}, and $\beta = 0.54$.

The value of β is very low for a fluoride complex, although such values are more to be expected for quadrivalent metals. The observed value falls between those found[1,7] for Ni^{4+} (0.43) and for Mn^{4+} (0.56) thus reflecting the decreasing stability of the higher valencies toward the end of the first transition series. This feature is also demonstrated in our results[8] for the trivalent metal ions in NiF_6^{3-} and CuF_6^{3-} which also show very low nephelauxetic ratios.

Clearly covalent bonding tendencies will increase with the formal positive charge on the metal even with a ligand such as F^-, and the extent of the expansion of the metal radial function behaves similarly. Jørgensen's[9] procedure for quantitative estimation of the nephelauxetic effect (assuming equal proportions of central-field and symmetry-restricted covalency) predicts about 15% ligand contribution and an effective metal charge of only +2.15 as compared[1] with 20% and +1.6 for NiF_6^{2-}. Thus, even for the d^5 configuration, with fluoride ligands, the quadrivalent metal ion leads to the combination of a high Dq and a small β to produce a strong-field low-spin complex. Our figures for Dq and β give Jørgensen's g and k parameters as 22.6 and 0.58, respectively, compared with 23.0 and 0.55 for Mn^{4+}, 22.2 and 0.71 for Ni^{4+}, 9.3 and 0.24 for Co^{2+}, and 19.0 and 0.35 for Co^{3+}.

Although assumption of a low-spin ground state for the CoF_6^{2-} ion provides a rationalization of the spectrum in accordance with the magnetic data, the actual temperature dependence of the moment does permit more than one explanation. Thus although the low-spin ground state is $^2T_{2g}$ and for T states an orbital contribution to the magnetic moment of about the observed order of magnitude would be expected, our fitting parameters require $Dq/B = 3.20$, and for $C/B = 4.90$ the crossover point of the $^6A_{1g}$ and $^2T_{2g}$ states is quite close at $Dq/B = 3.05$. Therefore, since the position of the crossover point is sensitive to the C/B value, the alternative explanation of a thermal equilibrium between high- and low-spin forms cannot be entirely ruled out. The low-spin ground state is also in agreement with Peacock's[10] suggestion that, since only the cesium salt is known, lattice energy is the critical factor in the stability of the quadrivalent cobalt compound. The $^2T_{2g}$ ground state eliminates the possibility of extra stabilization owing to a half-filled d shell.

Except for the ^2E_g band at 21.4 kK, which is 0.9 kK too high, all of the d–d transitions are fitted to within ±0.6 kK by our parameters. The band at 17.3 kK is rather broader than required by a true Gaussian form, but this is probably due to the superposition of two

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transitions (${}^2T_{2g} \rightarrow {}^2A_{2g}$ and ${}^2T_{2g} \rightarrow {}^2T_{1g}$) which are of almost equal energy.

Above 26 kK lies a broad, intense absorption with maxima at 28.3, 32.1, and 37.1 kK. By analogy with similar low-spin d^5 systems, for example[11] $IrCl_6^{2-}$, the bands at 28.3 and 37.1 kK most probably represent allowed charge-transfer transitions from filled ligand π orbitals to the t_{2g} level ($t_{1u} \rightarrow t_{2g}$ and $t_{2u} \rightarrow t_{2g}$). Although the assignment of the 37.1-kK band as $\pi \rightarrow e_g$ cannot be entirely ruled out, the high *Dq* value renders this rather improbable. Gaussian analysis of the curve in this region is of dubious validity, but the peak at 32.1 kK appears thereby to be quite weak and is therefore more likely to represent a d–d transition than a further charge-transfer band. The peak in fact corresponds almost exactly with the calculated position of a higher ${}^2T_{2g} \rightarrow {}^2E_g$ excitation. It is possible that the peak at 24.4 kK assigned as ${}^2T_{2g} \rightarrow {}^2T_{1g}$ could also be due to a $\pi \rightarrow t_{2g}$ transition, but, here again, the small F_R value makes the d–d assignment more acceptable.

We have derived as before[1] approximate values for the extinction coefficients and oscillator strengths of the d–d bands, and the values thus obtained are given in Table I. The intensities of the ${}^2A_{2g}$ and ${}^2T_{1g}$, ${}^2T_{2g}$, and ${}^2T_{1g}$ bands are all reasonable for Laporte-forbidden transitions, and the ${}^4T_{1g}$ and ${}^4T_{2g}$ bands are as weak as expected for spin-forbidden excitations. The actual intensities of the spin-forbidden bands are rather less in CoF_6^{2-} than in NiF_6^{2-}, possibly owing to the greater energy gap between the interacting states in the cobalt compound.

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Phosphorus–Phosphorus Spin–Spin Coupling in Metal Carbonyl Complexes of Phosphorus Trifluoride

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Fluorine nmr parameters are reported for $M(CO)_5PF_3$, *cis*-$M(CO)_4(PF_3)_2$, and *trans*-$M(CO)_4(PF_3)_2$ (where M = Cr, Mo, and W) and for $Fe(CO)_4PF_3$, $Fe(CO)_3(PF_3)_2$, and $Ni(CO)_2(PF_3)_2$. Values of ${}^2J_{PP}$ for the disubstituted complexes are discussed in terms of the relatively large degree of s character expected in the phosphorus–metal bond compared to that in analogous complexes of other trivalent phosphorus ligands.

Introduction

In another paper[2] we report ${}^{31}P$–${}^{31}P$ coupling constants for over 30 complexes containing two phosphorus ligands. Because ligands such as $P(N(CH_3)_2)_3$, $P(CH_3)_3$, $P(OCH_3)_3$, and $P(OCH_2)_3CCH_3$ used in that study contained from 6 to 18 protons, the ${}^1H$ nmr spectra of the complexes could be classed as $X_nAA'X'_n$ systems where n is the number of protons and X and A represent hydrogen and phosphorus, respectively. In all these systems except $P(CH_3)_3$ the coupling constants $J_{XX'}$ and $J_{AX'}$ could be assumed to be zero owing to the three-bond separation of the A and X nuclei in the ligands and the magnitude of ${}^2J_{PP}$ was calculated from the ${}^1H$ nmr spectra using a computer program to simulate the observed envelope of the unresolved lines.

Recent interest[3] in the unusual ligand properties of PF_3 in metal carbonyls made it attractive to determine the ${}^{183}W$–${}^{31}P$ coupling constant in $W(CO)_5PF_3$ reported elsewhere[4] and the ${}^{31}P$–${}^{31}P$ spin–spin interaction constants herein reported, inasmuch as the magnitude of such couplings is undoubtedly related to the nature of the bonding between the coupling nuclei. The ${}^{19}F$ nmr spectra of the PF_3 complexes are still representative of the $X_nAA'X'_n$ system where $n = 3$ but the separation of the X (fluorine) nuclei from the A (phosphorus) nucleus by only one bond allows significant coupling of fluorines on one PF_3 ligand with those on the other ($J_{XX'}$) as well as with the phosphorus on the second ligand ($J_{AX'} = J_{XA'}$).

Experimental Section

The compounds were prepared and separated by simple variations on procedures used to prepare these compounds earlier.[5-7] The iron compounds were prepared by the high-pressure thermal reaction between $Fe(CO)_5$ and PF_3 and separated by glpc on a 7 m × 1/4 in. 40% DC-702 silicone column on Chromosorb P. The group VI compounds[6] were prepared by the irradiation of $M(CO)_6$ and PF_3 in about 1:2 molar ratios in a sealed Pyrex vessel which was heated to about 80–100°. Irradiation with an AH-6 1000-W lamp for 2–3 hr served to convert 1–2 g of $M(CO)_6$ into a mixture of liquid intermediates. Through the use of this technique, the distribution of species could be controlled in overall composition to approximately $M(CO)_{4.5}(PF_3)_{1.5}$. The complexes were separated on the 7-m silicone column. Alternately, shorter columns were used to obtain compositional cuts of mono-

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