

could be greater in In–Mn than In–Co because of the greater nucleophilicity of $-\text{Mn}(\text{CO})_5$ compared to $-\text{Co}(\text{CO})_4$. The trend in N_{p_z} , N_{p_y} , and thus $e^2Qq_{zz}/h(^{115}\text{In})$ would be $\text{Co} > \text{Mn}$.

Registry No. (C_6H_5)₃PAuCo(CO)₄, 15154-50-4; Zn[Co(CO)₄]₂, 16985-99-2; Cd[Co(CO)₄]₂, 16986-00-8; (C_6H_5)₂AsHg[Co(CO)₄]₃, 37336-87-1; In[Co(CO)₄]₃, 38188-07-7; Tl[Co(CO)₄]₃, 41161-30-2; Bi[Co(CO)₄]₃, 62571-22-6; acacGa[Co(CO)₄]₂, 14242-69-4; acac-In[Co(CO)₄]₂, 14242-71-8; BrGa[Co(CO)₄]₂, 62571-21-5; Br-In[Co(CO)₄]₂, 59922-76-8; ClGa[Co(CO)₄]₂, 62601-29-0; Cl-In[Co(CO)₄]₂, 37707-06-5; Cl₃SiCo(CO)₄, 15693-80-8; Cl₃GeCo(CO)₄, 16560-96-6; Cl₃SnCo(CO)₄, 17523-00-1; (C_6H_5)₃SiCo(CO)₄, 14095-19-3; (C_6H_5)₃SnCo(CO)₄, 13964-91-5; (C_6H_5)₃PbCo(CO)₄, 16561-04-9; In[Mn(CO)₅]₃, 36539-52-3; ⁵⁹Co, 7440-48-4; ¹¹⁵In, 14191-71-0.

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Electronic Structure of the Octahedral Hexachloroytterbate Ion

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The absorption spectrum of the ${}^2F_{7/2}(E_u) \rightarrow {}^2F_{5/2}(U_u' + E_u'')$ transitions in single crystals of $\text{Cs}_2\text{NaYbCl}_6$ has been measured at room temperature and 77 K. Extensive vibronic structure was resolved and assigned for both transitions. The intensity of the magnetic dipole induced no-phonon transition to the U_u' term was found to be $\sim 0.25 \mu_B^2$. The fourth-order crystal field parameter, b_4 , was found to be $-21.1 \pm 2.3 \text{ cm}^{-1}$ and the spin-orbit coupling parameter, ζ , to equal $2850 \pm 25 \text{ cm}^{-1}$. The low value of ζ can be explained by assuming an increased interaction with the metal 5p orbitals in the six-coordinate species. Two ligand-to-metal charge-transfer transitions were measured in a single crystal of $\text{Yb}^{3+}:\text{Cs}_2\text{NaYCl}_6$ at ~ 10 K using absorption and MCD. The MCD results allow the first, at 38315 cm^{-1} , to be assigned as the $E_u' \rightarrow {}^2T_{1g}(\pi)$ transition arising from the $t_{1g}(\pi) \rightarrow 4f(t_{1u})$ electron transfer. The second transition is tentatively assigned, based on intensity arguments, as the $E_u' \rightarrow {}^2T_{2g}(\pi)$ transition arising from the $t_{2g}(\pi) \rightarrow 4f(t_{1u})$ electron transfer.

Introduction

Compounds of the type $\text{Cs}_2\text{NaLnCl}_6$ (Ln = trivalent metal ion) have recently been the object of much study. These compounds have the cubic elposolite structure, space group $Fm\bar{3}m$, with the Ln ion at a site of six-coordinate O_h symmetry.¹ As a consequence of this many interesting effects are observed.

Thus far the f–f transitions and vibronic structure have been studied using absorption and magnetic circular dichroism (MCD) spectroscopy for $\text{Cs}_2\text{NaEuCl}_6$,² $\text{Cs}_2\text{NaPrCl}_6$,³ $\text{Cs}_2\text{NaTbCl}_6$,⁴ and $\text{Cs}_2\text{NaTmCl}_6$.⁵ The vibrational structure is similar in all cases studied so far and seems to be due to an interaction of the electrons with a density of vibrational states over the entire Brillouin zone. This contrasts with the results for $\text{Cr}^{3+}:\text{Cs}_2\text{NaYCl}_6$ where the vibrational structure was interpreted assuming interactions only within the CrCl_6^{3-} moiety.⁶ In that case progressions involving both the a_{1g} and, Jahn–Teller active, e_g modes were observed. No progression of any type has been seen in the f–f spectra of the lanthanides.

The luminescence of $\text{Cs}_2\text{NaNdCl}_6$ and $\text{Nd}^{3+}:\text{Cs}_2\text{NaYCl}_6$ have been studied and show the longest lifetimes yet reported for Nd^{3+} .⁷ The luminescence of $\text{Cs}_2\text{NaTbCl}_6$ originating on the 5D_4 term showed vibrational structure on ΔJ even transitions and only magnetic dipole origins for the ΔJ odd transitions.⁴ Long-range energy transfer from Tb^{3+} to Eu^{3+} has also been observed in this crystal system.⁸

The low-temperature EPR spectra of a number of ions doped into $\text{Cs}_2\text{NaYCl}_6$ have been reported. Ce^{3+} , Dy^{3+} , and Yb^{3+} show isotropic g values⁹ but orientation-dependent line widths.¹⁰ The orientation dependence of the Γ_8 (quartet) ground term of Er^{3+} has been studied and the $\pm^1/2 \rightarrow \pm^3/2$ transition observed in addition to the usually studied $-^1/2 \rightarrow +^1/2$ transition.¹¹ The resonance of Gd^{3+} has been recorded as a function of host lattice (Ln = La, Pr, Tb, Yb, Y) and temperature.¹¹ A crystalline phase transition has been found to occur between room temperature and 77 K in those compounds with Ln = La–Eu and found not to occur down to 4.2 K for Ln = Tb–Yb and Y.¹² Finally no indications of

magnetic ordering were seen for any of the pure compounds down to 4.2 K.¹³

Additional optical studies have involved some of the $f \rightarrow d$ transitions in $\text{Ce}^{3+}:\text{Cs}_2\text{NaYCl}_6$ ^{14a} and some ligand-to-metal charge-transfer transitions in $\text{AuCl}_4^-:\text{Cs}_2\text{NaYCl}_6$.^{14b} In the former case the vibronic structure was explained almost entirely in terms of progressions in $\nu_1(a_{1g})$ of the CeCl_6^{3-} moiety with low-frequency lattice modes superimposed. The latter crystal showed vibrations primarily associated with the AuCl_4^- species, again with low-frequency lattice modes superimposed.

As part of this continuing study the absorption spectrum of $\text{Cs}_2\text{NaYbCl}_6$ has been studied in the $f-f$ transition range ($\sim 10\,000\text{ cm}^{-1}$) and the absorption and MCD spectra of $\text{Yb}^{3+}:\text{Cs}_2\text{NaYCl}_6$ have been studied in the charge-transfer region ($36\,000\text{--}50\,000\text{ cm}^{-1}$). Each of these regions provides its own interest. In the former region interest is supplied by observing and assigning the vibrational structure. This is the first odd-electron system in this series to be studied in detail (vibrations were reported for the Nd^{3+} luminescence but not assigned⁷) and it is desirable to find out if the odd-electron system affects the vibronic structure. In addition both the crystal field parameters (b_4 and b_6) and the spin-orbit coupling parameter (ζ) have been determined.

Most previous work dealing with Yb^{3+} has concerned sites of lower symmetry. Some papers have appeared dealing with Yb^{3+} (and the other $4f^{13}$ ion Tm^{2+}) in sites of eight-coordinate octahedral (cubic) symmetry. This coordination changes the sign of the fourth-order crystal field parameter (but not the sixth-order parameter) relative to six-coordination¹⁵ and so reverses the order of the crystal field terms. Both optical¹⁵ and magnetic resonance measurements on $\text{Yb}^{3+}:\text{CaF}_2$ have been reported as well as optical and magnetic susceptibility results on $\text{Yb}^{3+}:\text{SrCl}_2$.¹⁸ Tm^{2+} has also been studied by a variety of techniques in these two hosts.¹⁷ In addition to the $f-f$ transitions¹⁹ a number of $f-d$ transitions²⁰ have been observed for this ion. This contrasts with Yb^{3+} where in the six-coordinate chloride host some ligand-to-metal charge-transfer transitions are lower in energy than the $f-d$ transitions.²¹

No charge-transfer transitions have been reported for cubic Yb^{3+} but one such transition has been seen in a solution of YbCl_6^{3-} in acetonitrile.²¹ In general the charge-transfer spectra of lanthanides have been much less studied than those of the 4d and 5d transition metals. The major interest here is that with the lanthanides the Laporte-allowed charge-transfer bands will originate on gerade ligand orbitals as opposed to transitions with d-electron metals where they originate on ungerade orbitals.²² In fact, while assignments have been proposed for certain ligand-to-metal charge-transfer transitions in octahedral lanthanide hexachloro and hexabromo complexes,²¹ there has been, until this study, no direct experimental evidence supporting these assignments.

Experimental Section

All spectra in the charge-transfer region were recorded at the University of Virginia. Crystals of $\text{Yb}^{3+}:\text{Cs}_2\text{NaYCl}_6$ with $\sim 0.2\%$ (by weight) Yb^{3+} , as determined by spark source mass spectroscopy, were used. Absorption spectra were recorded at room temperature, 77 K, and $\sim 10\text{ K}$ on a Cary 14RI. MCD spectra were measured at $\sim 10\text{ K}$ using a JASCO J10-B spectropolarimeter. The spectral resolution is not machine limited. As the lines are extremely broad, any wavelength misalignment between the two instruments is not significant. The magnetic field was supplied by an Oxford Instruments superconducting magnet and cryostat system capable of a field of 55 kG at a current of 40 A. The MCD was recorded at a current of $\sim 1\text{ A}$ and this introduces a significant uncertainty ($\pm 50\%$) in the magnitude of the field. Uncertainty in the temperature at $\sim 10\text{ K}$ ($\pm 50\%$) is another major source of error. Both of these errors will affect only the MCD C term²³ and not the absorption intensity. This will lead to an error in the ratio C/D . D is the dipole strength. There is also a large uncertainty ($\pm 50\%$) in the Yb^{3+} concentration; however

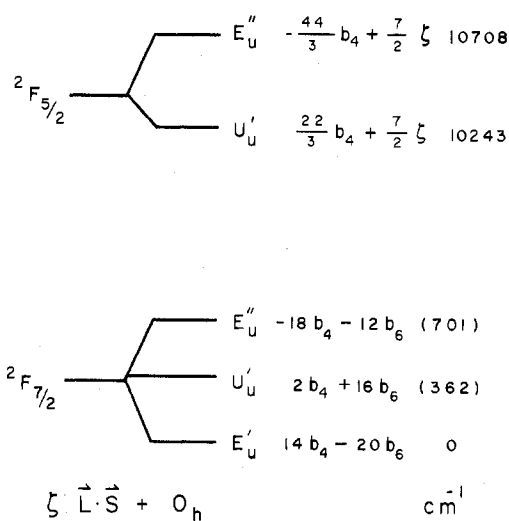


Figure 1. Energy level diagram, not to scale, for the $4f^{13}$ electron configuration.

Table I. Correlation of Various Crystal Field Parameter Sets for Octahedral $4f^{13}$

This work ^a	b	c	d	e	Exptl value, cm^{-1}
b_4	$60B_4$	λ	$3/7b_4'$	$15/2B_0^4$	-21.1 ± 2.3
b_6	$1260B_4$	6μ	b_6'	$315/4B_0^6$	2 ± 2
					$\zeta = 2850 \pm 25$

$$b_4(s/2)\beta(s/2)^f = b_4(7/2)\beta(7/2)$$

$$b_4 = b_4(s/2) = 3/11 b_4(7/2)$$

^a Also, ref 26a. ^b Reference 15. ^c Reference 19. ^d Reference 17. ^e B. J. Wybourne, "Spectroscopic Properties of Rare Earths", Interscience, New York, N.Y., 1965; corrected by A. J. Kassman, *J. Chem. Phys.*, 53, 4118 (1970). ^f Values for $J = 5/2$ and $J = 7/2$.

C/D is unaffected by this. Peak energies and energy differences in this region should be good to $\pm 50\text{ cm}^{-1}$.

Spectra were also recorded in the $f-f$ transition region using these dilute crystals. Spectral resolution varied between 5 and 10 cm^{-1} for these measurements. In all cases only one prominent absorption (vide infra) was observed with a width at half-height equal to the spectral resolution. There were indications of one or two additional bands but the maximum absorbance, 0.07 OD, was too weak for convenient study. Absorption spectra were also recorded at room temperature and 77 K in this region using a crystal of $\text{Cs}_2\text{NaYbCl}_6$ and a Cary 14. Spectral resolution for these measurements was $\sim 30\text{ \AA}$ and caused severe broadening of some lines. The error in integrated intensity, exclusive of broadening, should be $\pm 50\%$. Peak energies are good to $\pm 5\text{ cm}^{-1}$, except for very broad lines or shoulders where the error could be as large as $\pm 10\text{ cm}^{-1}$.

Results and Discussions

$f-f$ Transitions. The $4f^{13}$ electron configuration of Yb^{3+} gives rise to two spin-orbit split terms, the ${}^2F_{5/2}$ being about $10\,000\text{ cm}^{-1}$ higher in energy than the ${}^2F_{7/2}$. Each of these terms is then further split by the O_h crystal field. An energy level diagram is shown in Figure 1. Also shown are the energies of the levels, to first order, in terms of the crystal field parameters and the spin-orbit coupling parameter. At least four different parameter sets have been used to describe the O_h crystal field for the $4f^{13}$ electron configuration. These parameters are correlated in Table I. The correlation between b_4 for the $J = 5/2$ and b_4 for the $J = 7/2$ terms is also shown.²⁴ With an E_u' ground state only transitions to U_u' levels are magnetic dipole allowed.²⁵

Figure 2 shows the absorption spectrum in the $10\,000\text{-cm}^{-1}$ region at room temperature and 77 K. Peak energies and assignments are given in Table II. The most intense peak,

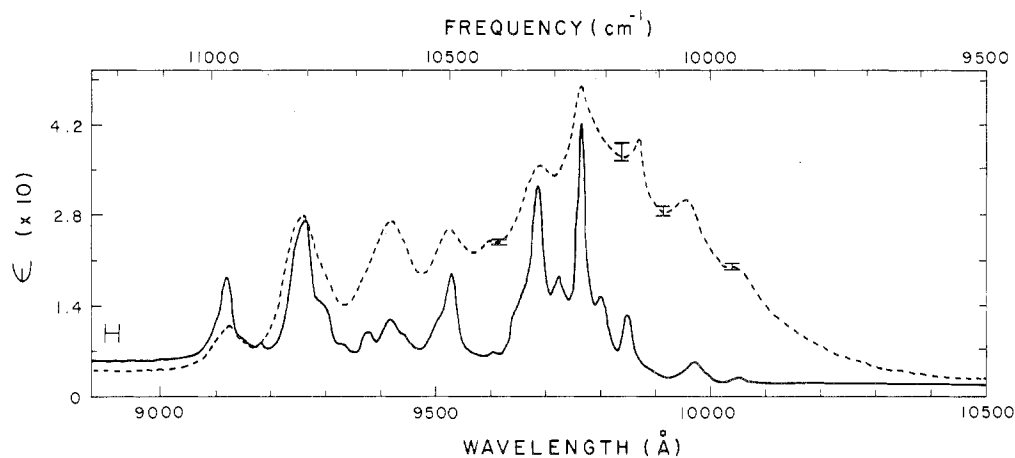


Figure 2. Room-temperature (---) and 77-K (—) f-f absorption spectrum of $\text{Cs}_2\text{NaYbCl}_6$. The slit width and noise levels are shown. When no noise level is explicitly shown, it is equal to the line thickness.

Table II. Peak Energies and Assignments for the 77-K Absorption Spectrum of $\text{Cs}_2\text{NaYbCl}_6$

Energy, cm^{-1}	$\Delta E, \text{cm}^{-1}$	Assignment ^b
9 955	-288	?
10 029	-214	?
10 121	-122	I - $S_7(t_{1u})$ hot
10 155	-88	I - $S_8(t_{1u}) - S_{10}(t_{2u})$ hot ^c
10 206	-37	I - $S_3(t_{1g}) - S_5(t_{2g}) - S_9(t_{1u})$ hot ^c
10 243	0	$E_u''(^2F_{7/2}) \rightarrow U_u'(^2F_{5/2}) = 0-0 = \text{I}$
10 288	45	I + $S_3(t_{1g}) + S_5(t_{2g}) + S_9(t_{1u})$ ^c
10 329	86	I + $S_8(t_{1u}) + S_{10}(t_{2u})$ ^c
10 360	117	I + $S_7(t_{1u})$
10 417	164	I + $S_4(t_{2g})$
10 500	257	I + $S_6(t_{1u})$ ^e
10 526	283	I + $S_8(t_{1u})$ ^e
10 590	-118	II - $S_7(t_{1u})$ hot
10 623	-85	II - $S_8(t_{1u}) - S_{10}(t_{2u})$ hot ^c
10 666	-42	II - $S_3(t_{1g}) - S_5(t_{2g}) - S_9(t_{1u})$ hot ^c
(10 708) ^d	0	$E_u''(^2F_{7/2}) \rightarrow E_u'(^2F_{5/2}) = \text{II}$
10 714	6	II + ν (acoustic)
10 760	52	II + $S_3(t_{1g}) + S_5(t_{2g}) + S_9(t_{1u})$ ^c
10 795	87	II + $S_8(t_{1u}) + S_{10}(t_{2u})$ ^c
10 817	109	II + $S_7(t_{1u})$
10 887	179	II + $S_4(t_{2g})$
10 932	224	?
10 965	257	II + $S_6(t_{1u})$ ^e
10 990	282	II + $S_8(t_{1u})$ ^e

^a Energy from appropriate origin. ^b The notation is that used in ref 2. Assignments are given using the notation of the Γ point even though the observed vibrations represent a density of states over the Brillouin zone. ^c Higher resolution spectra in other systems have shown multiple vibrations are present at these energies. See ref 3. ^d Not observed. For arguments leading to this energy assignment see the text. ^e Longitudinal and transverse modes split at the Γ point.

at 10243 cm^{-1} , is assigned as the magnetic dipole induced origin $E_u'(^2F_{7/2}) \rightarrow U_u'(^2F_{5/2})$. The width at half-height for this band is equal to the spectral resolution and is severely broadened (vide infra). With this peak assigned, a comparison of the vibrational structure for this transition with that observed for other lanthanides in this crystal system leads to the assignments given in Table II. Some energy assignments in the present case are confirmed by the presence of hot bands.

The transition $E_u'(^2F_{7/2}) \rightarrow E_u''(^2F_{5/2})$ will not show any origin. To locate this term it was assumed that the energy of the best resolved, highest frequency vibration (257 cm^{-1}) was the same in both terms. This procedure leads to the vibrational assignments and location of the "origin" for the $E_u''(^2F_{5/2})$ term also given in Table II.

Crystal field parameters derived from magnetic susceptibility data have been reported previously for $\text{Cs}_2\text{NaYbCl}_6$.²⁶

Those measurements did not directly measure the energy differences between crystal field terms. By use of the energies of the ($^2F_{5/2}$) U_u' and E_u'' levels and the first-order equations in Figure 1, $b_4 = -21.1 \pm 2.3 \text{ cm}^{-1}$. Within experimental error this is equal to the better of the two values given previously.^{26b} However as b_4 was determined directly in the present case and has a smaller uncertainty, it is felt to be a better value. (Note that inclusion of higher order terms^{17,18} changes b_4 , and the other parameters, by much less than the experimental uncertainty and so these terms are not included.)

The parameter b_6 cannot be determined with the present data. The previously found value^{26b} of $2 \pm 2 \text{ cm}^{-1}$ was used along with b_4 to determine ζ , the spin-orbit coupling constant. A value of $2850 \pm 25 \text{ cm}^{-1}$ was found for this parameter. The energies of the ($^2F_{7/2}$) U_u' and E_u'' levels given in Figure 1 were calculated using the above values of b_4 and b_6 .

The value of ζ_{Yb} in $\text{Cs}_2\text{NaYbCl}_6$ is at the low end of the range for this parameter as compared to other crystals. It has been suggested that the variation in ζ from the free ion value is due primarily to interaction with the 5p configuration.²⁷ In the present case the unfilled f orbital transforms as $t_{1u}(O_h)$ as do the p orbitals. The combination of the same symmetry and proximity in space could account for the enhancement of this effect. ζ_{Yb} in YbCl_6^{3-} is between 45 and 95 cm^{-1} less than the value in the cubic coordination of SrCl_2 . In this latter case the unfilled metal orbital has a_{2u} symmetry and coupling with the 5p orbitals may not be as efficient.

The dipole strength, D , of the $E_u'(^2F_{7/2}) \rightarrow U_u'(^2F_{5/2})$ magnetic dipole origin was determined from data on both pure $\text{Cs}_2\text{NaYbCl}_6$ and dilute $\text{Yb}^{3+}:\text{Cs}_2\text{NaYbCl}_6$. By use of the peak intensities and widths at half-height a value of ~ 0.25 ($\pm 50\%$) μ_B^2 is found in both crystals. In the dilute crystal the width at half-height for this line was $\sim 5 \text{ cm}^{-1}$ and the ϵ_{max} was 3.3. These latter two values are more accurate than those shown in Figure 2 (data for pure $\text{Cs}_2\text{NaYbCl}_6$) where low instrumental resolution has broadened this line and greatly reduced its peak intensity. The vibronic intensity for both transitions was 3.0×10^{-4} ($\pm 10\%$) D^2 at room temperature and 7.9×10^{-5} ($\pm 10\%$) D^2 at 77 K.

The ratio of the integrated intensity at room temperature to that at 77 K is 3.8 ($\pm 20\%$). With this value the "hyperbolic cotangent law"²⁸ leads to a value of 57 cm^{-1} for the energy of the activating vibration. This does not correspond to the energy of any known vibration. If, on the other hand, 15% of the room-temperature intensity is assumed to be due to transitions from the slightly populated $U_u'(^2F_{7/2})$ level, then a value of 85 cm^{-1} is found for the energy of the activating vibration. This is the energy of the most intense vibration in both transitions and as such is a reasonable choice.

Table III. Charge-Transfer Spectrum in YbCl_6^{3-}

Transition	Energy, ^a cm ⁻¹	C, ^b μ _B × D ²	D, ^b D ²	C/D	
				Exptl ^b	Calcd ^c
$E_u''(^2F_{7/2}) \rightarrow ^2T_{1g}(\pi)$	38 315	0.12	0.17	0.67	0.67
$E_u''(^2F_{7/2}) \rightarrow ^2T_{2g}(\pi)$ or $^2E_g(\sigma)$	47 410	-0.07	0.19	-0.37	-0.67

^a Energy of peak absorption. ^b C/D determined using peak height and equations given in ref 29. C and D determined as explained in the text. ^c Calculated ignoring spin-orbit coupling in the excited state as explained in the text. ^d Most likely assignment; see text.

A comparison of the integrated intensity in $\text{Cs}_2\text{NaYbCl}_6$ with that found in $\text{Cs}_2\text{NaEuCl}_6$ and $\text{Cs}_2\text{NaPrCl}_6$ shows some interesting effects. As expected, the magnetic dipole transition in YbCl_6^{3-} is much stronger than those in PrCl_6^{3-} (between 6 and 250 times stronger, depending on the particular origin³) and in EuCl_6^{3-} (10 times²). However the vibronic intensity in YbCl_6^{3-} is also greater than in PrCl_6^{3-} (between 4 and 16 times) and in EuCl_6^{3-} (about 30 times at room temperature and 10 times at low temperature). This may indicate a better electron lattice coupling in the ytterbium salt than in the others, and this point requires further investigation.

Charge-Transfer Transitions. The excited electron configurations due to ligand-to-metal charge-transfer transitions will be particularly simple for YbCl_6^{3-} . The 4f level will be filled and the configurations will consist of a hole in the ligand orbital from which the electron originated. Laporte-allowed transitions will consist of electron jumps from gerade orbitals. The order of these orbitals has been suggested²¹ as $t_{1g}(\pi) > t_{2g}(\pi) > e_g(\sigma) > a_{1g}(\sigma)$, where the t_{1g} orbital is closest in energy to the metal f orbitals. Thus the possible transitions are, in order of increasing energy, $E_u''(^2F_{7/2}) \rightarrow ^2T_{1g}$, $^2T_{2g}$, 2E_g , and $^2A_{1g}$. Any spin-orbit splitting will depend on ζ for the chloride.²² This splitting is much smaller than the observed line width and so is not considered below.

The absorption and MCD spectra at ~ 10 K are shown in Figure 3. All pertinent information is collected in Table III. The integrated intensities of the two bands have been measured at room temperature, 77 K, and ~ 10 K. The peak ϵ increases as the temperature decreases but the line width narrows also. To within experimental error ($\pm 20\%$) the intensity is constant.

The lower energy transition is assigned as $E_u''(^2F_{7/2}) \rightarrow ^2T_{1g}(\pi)$. This transition is predicted to be lowest in energy²¹ and the MCD is consistent with this assignment (Table III). The peak in absorption falls slightly to the low-energy side of the peak in MCD. This is indicative of an unresolved negative A term, whose sign is also consistent with the assignment. This is the only band reported for YbCl_6^{3-} in solution.²¹ Agreement is adequate considering the different conditions of measurement.

The assignment of the second band is not as straightforward. It has been suggested that it could be a transition to either a $^2T_{2g}(\pi)$ or a $^2E_g(\sigma)$ term.²¹ Within experimental error C/D is consistent with either of these assignments. From the charge-transfer spectra of second- and third-row transition metal hexahalides the intensity of a transition originating on a σ ligand orbital is found to be a factor of 10 more intense than one originating on a π orbital.²² On the basis of the same type of ligand-metal overlap arguments a similar effect is expected in the present case. The higher energy transition in this complex is not significantly more intense than the first transition. On this basis it is assigned as $E_u''(^2F_{7/2}) \rightarrow ^2T_{2g}(\pi)$. Additional work with other lanthanide hexachlorides and hexabromides is planned which it is hoped will remove any uncertainty in this assignment.

The value of D was found by assuming that at room temperature the lower energy transition has the same ϵ value

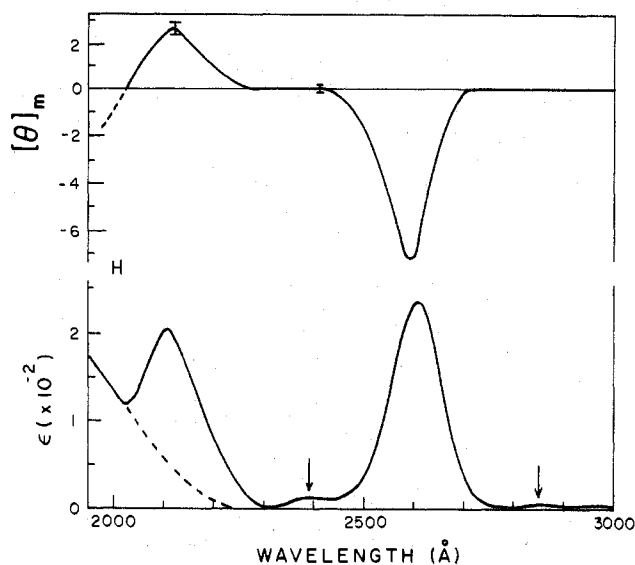


Figure 3. Absorption and MCD spectra of $\text{Yb}^{3+}:\text{Cs}_2\text{NaYCl}_6$ taken in the charge-transfer region at ~ 10 K. The slit width and noise levels are shown. $[\theta]_m$ is in units of $(\text{deg dL})(\text{dm mol})^{-1} \text{G}^{-1}$. In absorption the dotted line is the host absorption as determined with an "undoped" crystal of $\text{Cs}_2\text{NaYCl}_6$. The arrows show absorptions that are also present in the "undoped" sample. In MCD the dotted line was measured with almost no light reaching the phototube and so may be a machine artifact.

(160) as found for YbCl_6^{3-} in acetonitrile solution.²¹ This enabled the ϵ value, and hence D , to be determined at any temperature. C/D was determined using peak deflections and an equation given previously,²⁹ C was then determined from the ratio of these two values.

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Low-Temperature Luminescence and Absorption Spectra of the d^6 Hexafluoroplatinate(IV) Ion Doped in a Cs_2GeF_6 -Type Host Lattice

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The optical luminescence and absorption spectra of the $5d^6$ hexafluoroplatinate(IV) ion doped in the cubic hosts Cs_2GeF_6 , Cs_2SiF_6 , and Rb_2SiF_6 , as well as in Cs_2PtF_6 , have been measured at 20 and 2 K. Seven absorption bands with associated vibrational structures occur between 20 000 and 36 000 cm^{-1} . Electronic assignments for all of these bands have been made by means of a crystal field model with spin-orbit coupling and the relative intensities of the d-d transitions predicted with various models. The vibrational structure in the absorption bands has been assigned in terms of the PtF_6^{2-} ungerade vibrational motions. Also, luminescence has been observed for the hexafluoroplatinate ion in the host materials and in the pure material, and the vibrational structure of the luminescence band has been analyzed to give information about the change in platinum-fluorine internuclear equilibrium distance from the ground state to the excited emitting state. Finally, several conclusions are stated about d-d $t_{2g}^n \rightarrow t_{2g}^{n-1}e_g$ transitions in $5d$ MF_6^{2-} complexes.

I. Introduction

This paper reports the first high-resolution optical study of a $\text{MF}_6^{2-} 5d^n$ transition metal ion system at liquid helium temperature. We have doped the $5d^6$ hexafluoroplatinate(IV) ion in an antifluorite cubic lattice of the type Cs_2GeF_6 to the extent of about 2 mol % and measured the luminescence and absorption spectra of the complex ion between 12 000 and 50 000 cm^{-1} . The only previously reported optical studies of the hexafluoroplatinate(IV) ion have been in solution at room temperature¹ and in a CaF_2 matrix² at room temperature. For the 3d transition metal series low-temperature optical studies have been reported, for example, for (d^6) NiF_6^{2-} ,³ (d^3) CrF_6^{3-} ,⁴ and (d^3) MnF_6^{2-} .⁵

In the study of the PtF_6^{2-} ion as an impurity ion in a single Cs_2MF_6 ($M = \text{Si}, \text{Ge}$) crystal at liquid helium temperature any interactions between PtF_6^{2-} ions possibly present in the pure system have been eliminated, the PtF_6^{2-} ion is at a site of cubic symmetry, and the system is in an initial state with no excited vibrational modes. It is hoped that this will result in experimental spectra with a maximum amount of detailed information. In the analysis of the experimental data there are four objectives. First, we want to count the number of different observed electronic transitions occurring in the energy range of interest and make electronic assignments with a crystal field model. Second, we want to contrast the vibrational mode energies and geometry of the PtF_6^{2-} ion in excited electronic states with the ground state. Third, when the host lattice is changed from Cs_2GeF_6 to Cs_2SiF_6 or Rb_2SiF_6 , we want to measure the changes in the electronic and vibrational energies to understand the role of the host lattice in an electronic d-d transition. Finally, it is of interest to investigate couplings between vibrational and electronic motions of the Herzberg-Teller type to predict accurate relative intensities for d-d transitions in a $5d$ transition metal MF_6^{2-} type system.

Crystallographic studies by Sharpe⁶ have shown that Cs_2PtF_6 has the hexagonal K_2GeF_6 structure at room temperature. Also, x-ray measurements of Cs_2GeF_6 and Cs_2SiF_6 have shown that both substances have the cubic structure at

room temperature with M-F distances of 1.80 and 1.69 Å, respectively. Brown and co-workers⁷ have found that when 5% of K_2GeF_6 is doped into the K_2SiF_6 cubic host, the infrared spectrum of the mixed-crystal system shows sharp unsplit infrared peaks for the GeF_6^{2-} species characteristic of cubic site symmetry. Thus, when Cs_2PtF_6 is doped to the extent of 1-5 mol % in the cubic hosts Cs_2SiF_6 and Cs_2GeF_6 , the observed optical spectrum should be for an octahedral PtF_6^{2-} species with cubic site symmetry. The optical studies of Helmholtz and Russo⁵ on Cs_2MnF_6 in Cs_2GeF_6 have shown that Cs_2GeF_6 does not absorb up to 2500 Å. Our studies for Cs_2GeF_6 and Cs_2SiF_6 are in agreement with their work.

II. Experimental Section

Cs_2PtF_6 was prepared by fluorinating Cs_2PtCl_6 with BrF_3 as the fluorinating agent, according to a procedure given in ref 8. A Teflon reaction vessel was used for the preparation to minimize any contamination from the SiF_6^{2-} ion. The product was recrystallized from hot water.

The Cs_2GeF_6 used in this study was obtained from Alfa Inorganics and used without further purification. The Cs_2SiF_6 was prepared by mixing a solution of 30% H_2SiF_6 with a concentrated solution of CsF containing the proper stoichiometric amount of the salt. The precipitated Cs_2SiF_6 was washed and then dried in a stream of nitrogen gas.

Mixed crystals of Cs_2PtF_6 with Cs_2SiF_6 , Cs_2GeF_6 , or Rb_2SiF_6 were grown from a solution which initially contained about 0.1 g of Cs_2PtF_6 and about 0.2 g of host material dissolved in a minimum amount of 49% hydrofluoric acid at 60 °C. The solution was filtered and placed in a Teflon beaker at 60 °C and cooled slowly. Mixed crystals were harvested in 4-7 days. The crystals were 1-2 mm across a face and were yellow.

A selected number of the mixed crystals were analyzed by atomic absorption spectroscopy to determine the mole percent of platinum complex in the mixed crystals by techniques previously reported.⁹ The crystals were found to contain 1-2 mol % of Cs_2PtF_6 . Also, the Cs_2PtF_6 - Cs_2GeF_6 mixed crystals were analyzed for contamination of SiF_6^{2-} by infrared spectroscopy using a KBr mull and found to not contain any measurable amount of SiF_6^{2-} .

Infrared measurements between 250 and 4000 cm^{-1} were carried out at room temperature with a Perkin-Elmer Model 457 spectrophotometer. Raman studies at room temperature were done with a Cary Model 81 spectrometer. The optical measurements at liquid

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