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Registry No. $SnCl_2$, 7772-99-8; $Sn^{35}Cl_2$, 58734-92-2; $SnCl_2{}^{13}CO$, 58815-37-5; $Sn^{35}Cl_2{}^{12}CO$, 58815-38-6; $SnCl_2NO$, 58815-39-7; $Sn^{35}Cl_2NO$, 58815-40-0; $SnCl_2N_2$, 58815-41-1; $Sn^{35}Cl_2N_2$, 58815-42-2; PbF_2, 7783-46-2; $PbF_2{}^{12}CO$, 58815-43-3; PbF_2NO, 58815-44-4; PbF_2N_2, 58815-45-5; $Pb^{35}Cl_2$, 36677-74-4; $PbCl_2CO$, 58815-33-1; $Pb^{35}Cl_2{}^{12}CO$, 58815-34-2; $PbBr_2{}^{12}CO$, 58815-35-3; $PbI_2{}^{12}CO$, 58815-36-4.

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Single-Crystal Electronic Spectrum of Tetraphenylarsonium Oxotetrachlorochromate(V), $[(C_6H_5)_4As][CrOCl_4]$, and an ab Initio Calculation of the Bonding and Excited States of Oxotetrachlorochromate(V)

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Polarized single-crystal electronic spectral data have been recorded for $[(C_6H_5)_4As][CrOCl_4]$ at ca. 300 °K and at temperatures approaching that of liquid helium. The features observed are assigned with the aid of ab initio configuration interaction calculations. The experimental and theoretical data are consistent with the two lowest energy absorptions at ca. 13 and 18 kK, respectively, arising from the transitions $d_{xy} \rightarrow d_{xz,yz}$ and Cr–O(π) → Cr–O(σ^*), respectively. It is shown that the band at ca. 18 kK cannot be due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition as is commonly assumed. Several intense absorptions are observed above ca. 20 kK and these are ascribed to particular ligand → chromium charge-transfer transitions.

The electronic structures of the d^1 monooxo chromphores VO^{2+}, CrO^{3+}, and MoO^{3+} have received considerable attention,[1–16] particularly since the pioneering molecular orbital (MO) studies of Gray et al.[17,18] However, ambiguities still persist in the interpretation of the electronic spectra of, and bonding in, the complexes of these cations. As part of a detailed study of the electronic structure of these systems we have completed a single-crystal polarized electronic spectral study of $[(C_6H_5)_4As][CrOCl_4]$ in conjunction with all-electron ab initio MO calculations of the ground and excited states of this anion. This combined approach has provided new and definitive electronic spectral data for a CrO^{3+} complex and an improved basis not only for the assignment of such data but also for a discussion of the nature of the bonding within the $[CrOCl_4]^-$ ion.

Experimental Section

$[(C_6H_5)_4As][CrOCl_4]$ was prepared as described previously[3] and recrystallized from dried CH_2Cl_2. Anal. Calcd for $C_{24}H_{20}AsCl_4CrO$: C, 48.6; H, 3.4; Cl, 24.0; Cr, 8.8. Found: C, 48.5; H, 3.5; Cl, 24.1; Cr, 8.9. X-ray crystallographic studies[19] have shown that this salt crystallizes in the space group $P4/n$ with $Z = 2$, the Cr atoms thus lying on a crystallographic fourfold axis of symmetry (c) and a diagram of the unit cell is shown in Figure 1.

Electronic Spectral Studies. Absorption spectra (10–30 kK) were recorded at ca. 300 °K at temperatures approaching that of liquid helium on a Cary 14 spectrophotometer equipped with Nicol prisms, for suitably thinned single crystals of $[(C_6H_5)_4As][CrOCl_4]$ mounted on glass microscope slides in orientations which permitted the electric vector of the incident beam to be polarized parallel to and perpendicular to the crystallographic c axis. The low-temperature spectra were obtained with the glass slide mounted on the copper block of an Oxford Instruments continuous-flow cryotip. The copper block was cooled to ca. 4 °K and the system allowed to equilibrate for at least 30 min before the spectrum was recorded. Figure 2 and Table

Table I. Electronic Spectral Characteristics of $[(C_6H_5)_4As][CrOCl_4]$

Absorption max,[a] kK			
Single crystal		CH_2Cl_2 soln, room temp	Oscillator strength
Room temp	Liq He temp		
13.4 ($xy > z$)	12.9_6 ($xy >> z$)	13.1[b]	1.8×10^{-4}
	13.4_5 sh ($xy >> z$)		
	13.8_5 ($xy >> z$)		
	14.4_5 ($xy >> z$)		
	15.3_8 ($xy >> z$)		
18.1 ($xy >> z$)	17.8 ($xy >> z$)	18.1	9.3×10^{-4}
	18.2 ($xy >> z$)		
	18.5 ($xy >> z$)		
	18.7 ($xy >> z$)		
21 sh ($xy > z$)	20.3[c] (xy and z)	24.8	7.1×10^{-2}
	22 ($xy >> z$)		
23 sh[d]	23 sh (xy and z)		
25 sh[d]	$24._5$ sh (z, p?)		
		36.8	9.6×10^{-2}

[a] Estimated error ca. ±1 in the last significant figure quoted. [b] Recorded for $[(C_2H_5)_4N][CrOCl_4]$. [c] Possibly comprising two or more components. [d] Only seen in z polarization; xy too intense. Key: sh, shoulder; p, polarized.

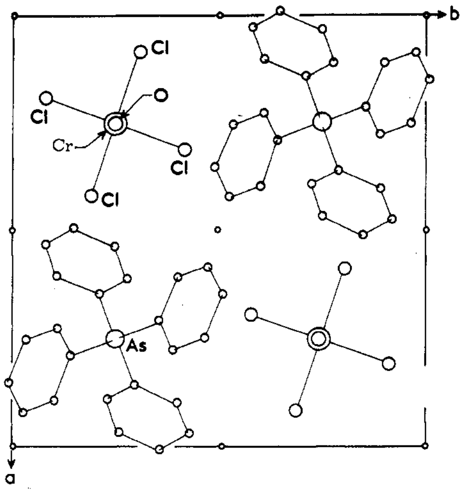

Figure 1. Representation of the unit cell of $[(C_6H_5)_4As][CrOCl_4]$.

I summarize the data so obtained. The absorption spectra of $[(C_6H_5)_4As][CrOCl_4]$ and $[(C_2H_5)_4N][CrOCl_4]$ dissolved in dried CH_2Cl_2 were recorded at room temperature and the relevant data are presented in Figure 3 and Table I.

Computational Method

An all-electron ab initio SCF MO calculation of the ground state of $[CrOCl_4]^-$ was performed by the restricted Hartree–Fock method in a basis of Gaussian type functions (GTF). The oxygen 2s, chlorine 3s, and core orbitals were Slater type orbitals (STO's), with best atom exponents[20] each fitted by three GTF's.[21] The oxygen 2p and chlorine 3p orbitals were double ζ STO's,[22] each fitted by three GTF's. The chromium 3d orbitals were expanded in five GTF's,[23] and this atom's 4s and 4p orbitals were each represented[24] by a single GTF of exponent 0.32. The atomic arrangement was taken to have C_{4v} symmetry,[19] with Cr–O = 1.60 Å, Cr–Cl = 2.25 Å, and Cl–Cr–O = 95.8°, based on structural data obtained from related systems. From the wave function thus calculated for the $^2B_2$ ground state (Table II), excited-state wave functions were calculated by performing configuration interaction (CI) calculations including all of the doublet configurations of the appropriate spatial symmetry constructed by single excitations from the filled and half-filled MO's ($13a_1 - 3b_2$) (Table II) to the half-filled and lowest energy virtual MO's ($3b_2 - 14e$). The calculated transition energies to these various excited states are listed in Table III according to the excited-state symmetry type. The computations were performed using the ATMOL system of programs on the CDC7600 computer of the University of Manchester Regional Computer Center.

Table II. Calculated $^2B_2$ Ground State of $[CrOCl_4]^-$

MO	Energy, au	Atomic character, %							Bond overlap population (per electron)	
		Chromium			Chlorine		Oxygen			
		3d	4s	4p	3s	3p	2s	2p		
13e	+0.1529	80				5		14	Cr(3d)–O(2p)	−0.12
$16a_1$	+0.1509	42		5		10		41	Cr(3d)–O(2p) Cr(3d)–Cl(3p)	−0.12 −0.08
$8b_1$	+0.1323	58			1	40			Cr(3d)–Cl(3p)	−0.26
$3b_2$	+0.2155	95				4			Cr(3d)–Cl(3p)	−0.08
$2a_2$	−0.2542					98				
12e	−0.2714	1		1		96				
$7b_1$	−0.2874					98				
11e	−0.2920					90		9		
$15a_1$	−0.3249				1	95		2		
10e	−0.3408	3		3	2	91			Cr(4p)–Cl(3p)	0.06
$2b_2$	−0.3580	5				94			Cr(3d)–Cl(3p)	0.04
$14a_1$	−0.3769	6			4	74	1	13	Cr(3d)–Cl(3p)	0.16
$6b_1$	−0.3865	38			3	58			Cr(3d)–Cl(3p)	0.16
9e	−0.4579	16				8		76	Cr(3d)–O(2p)	0.08
$13a_1$	−0.4772	50			2	7	5	35	Cr(3d)–O(2p)	0.10

Theoretical and Experimental Results

The electronic ground state of $[CrOCl_4]^-$ (Table II) is calculated to be $^2B_2$, with the unpaired electron in the $3b_2$ MO which is essentially the chromium $3d_{xy}$ atomic orbital. This result is in agreement with earlier theoretical predictions for CrO^{3+}, VO^{2+}, and MoO^{3+} complexes.[4,10,17,18] The highest energy doubly occupied MO's ($15a_1 - 2a_2$) are predominantly chlorine 3p in character and are essentially nonbonding in nature. The major contributions to the metal–ligand bonding arise from the lower energy valence MO's ($13a_1 - 10e$). As would be anticipated[10,17,18] the Cr–O bond involves substantial σ-($13a_1$) and π-(9e) components. The bond overlap popu-

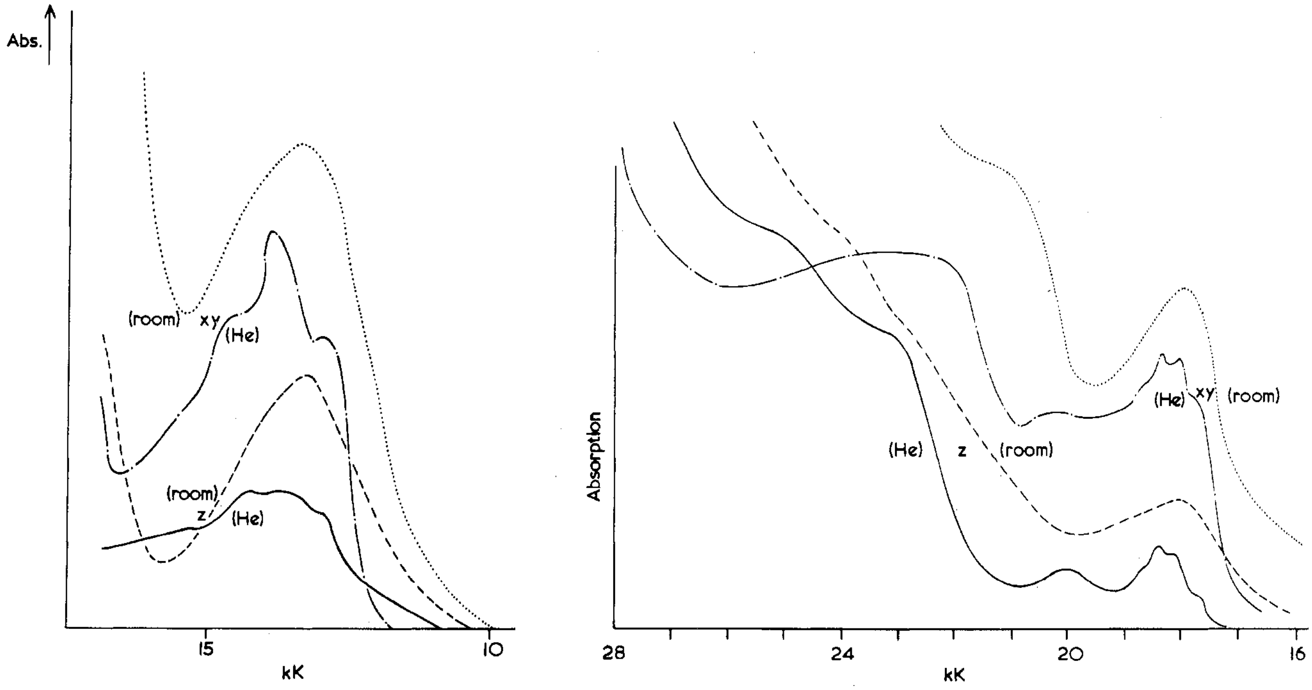

Figure 2. Room-temperature and liquid helium temperature polarized single-crystal spectra of $[(C_6H_5)_4As][CrOCl_4]$.

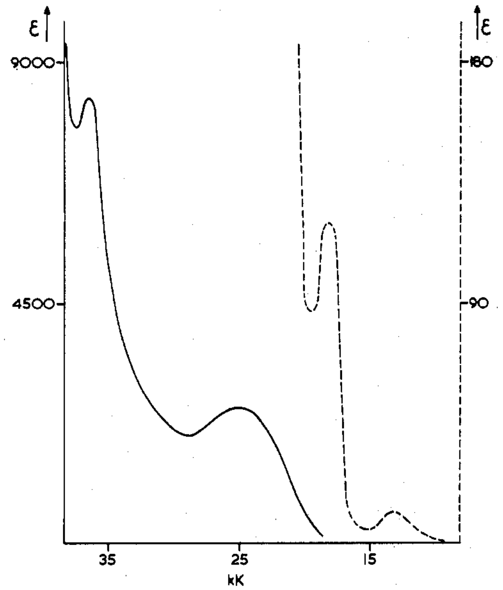

Figure 3. Room-temperature electronic spectrum of $[CrOCl_4]^-$ in CH_2Cl_2.

Table III. Calculated Electronic Transition Energies and Oscillator Strengths for $[CrOCl_4]^-$

Symmetry	Predominant orbital transition	Principal character	Transition energy, kK	Oscillator strength
$^2B_2 \rightarrow {}^2E$	$3b_2 \rightarrow 13e$	$Cr(3d_{xy}) \rightarrow Cr{-}O(\pi^*)$	9.9	5×10^{-4}
	$9e \rightarrow 16a_1$	$Cr{-}O(\pi) \rightarrow Cr{-}O(\sigma^*)$	24.3	3×10^{-3}
	$13a_1 \rightarrow 13e$	$Cr{-}O(\sigma) \rightarrow Cr{-}O(\pi^*)$	25.7	1×10^{-4}
	$9e \rightarrow 16a_1$	$Cr{-}O(\pi) \rightarrow Cr{-}O(\sigma^*)$	30.3	4×10^{-3}
	$13a_1 \rightarrow 13e$	$Cr{-}O(\sigma) \rightarrow Cr{-}O(\pi^*)$	31.6	2×10^{-3}
	$6b_1 \rightarrow 13e$	$(Cr{-}Cl) \rightarrow Cr{-}O(\pi^*)$	33.5	2×10^{-2}
	$12e \rightarrow 8b_1$	$Cl(3p) \rightarrow (Cr{-}Cl)^*$	35.4	4×10^{-3}
	$12e \rightarrow 8b_1$	$Cl(3p) \rightarrow (Cr{-}Cl)^*$	41.1	8×10^{-2}
	$12e \rightarrow 16a_1$	$Cl(3p) \rightarrow Cr{-}O(\sigma^*)$	46.0	1×10^{-1}
	$12e \rightarrow 3b_2$	$Cl(3p) \rightarrow 3d_{xy}$	52.0	2×10^{-1}
$^2B_2 \rightarrow {}^2B_2$	$13a_1 \rightarrow 16a_1$	$Cr{-}O(\sigma) \rightarrow Cr{-}O(\sigma^*)$	27.1	3×10^{-3}
	$9e \rightarrow 13e$	$Cr{-}O(\pi) \rightarrow Cr{-}O(\pi^*)$	32.0	1×10^{-5}
	$6b_1 \rightarrow 8b_1$	$(Cr{-}Cl) \rightarrow (Cr{-}Cl)^*$	35.5	6×10^{-5}
	$9e \rightarrow 13e$	$Cr{-}O(\pi) \rightarrow Cr{-}O(\pi^*)$	39.2	1×10^{-2}
$^2B_2 \rightarrow {}^2B_1$	$3b_2 \rightarrow 8b_1$	$Cr(3d_{xy}) \rightarrow (Cr{-}Cl)^*$	22.4	0
$^2B_2 \rightarrow {}^2A_1$	$3b_2 \rightarrow 16a_1$	$Cr(3d_{xy}) \rightarrow Cr{-}O(\sigma^*)$	33.1	0

lations (Table II) indicate that, as expected, each Cr–Cl bond is weaker than the Cr–O bond and within the C_{4v} point group no real distinction can be made between Cr–Cl σ- and π-bonding interactions. The formal valence-shell atomic configurations are calculated to be Cr $3d^{3.3}$ $4s^{0.5}$ $4p^{0.5}$, O $2s^{2.0}$ $2p^{4.4}$, and Cl $3s^{2.0}$ $3p^{5.8}$ which, when taken together with the electronic distributions within the core orbitals, afford charges of 1.65+ for Cr, 0.40– for O, and 0.56– for Cl in $[CrOCl_4]^-$.

The relative energies of the empty d orbitals $d_{x^2-y^2}$ (Cr–Cl σ^*) < d_{z^2} (Cr–O σ^*; Cr–Cl σ^*, π^*) < $d_{xz,yz}$ (Cr–O π^*) differs from that order[17,18] $d_{xz,yz} < d_{x^2-y^2} < d_{z^2}$ generally used [1–16] as the basis for the interpretation of the electronic spectra of CrO^{3+}, VO^{2+}, and MoO^{3+} complexes. However as observed in other nonempirical Hartree–Fock calculations,[24,25] the relative order of the excited-state energies (Table III) does not follow from simple considerations based on the orbital sequence derived from the ground state. In fact the relative magnitudes of the "d–d" transition energies $d_{xy} \rightarrow d_{xz,yz}$, $d_{x^2-y^2}$, d_{z^2} is in accord with that generally accepted for CrO^{3+}, VO^{2+}, and MoO^{3+} complexes. The CI calculations also predict that for $[CrOCl_4]^-$, several reasonably intense "ligand → metal charge-transfer" states will be of comparable energy to the two higher energy and symmetry-forbidden "d–d" transitions. The lowest energy of these charge-transfer transitions ($9e \rightarrow 16a_1$) essentially involves the transfer of an electron from the Cr–O π-bonding orbitals, which are predominantly oxygen 2p in character, to an orbital which is Cr–O, Cr–Cl antibonding and predominantly chromium $3d_{z^2}$ and oxygen 2p in character. Therefore this low-energy charge-transfer transition is effectively confined within the Cr–O moiety.

The next lowest energy charge-transfer transitions, with calculated energies 25.7–32.0 kK, also involve the transfer of an electron from a Cr–O bonding to a Cr–O antibonding orbital, the former being localized essentially on the oxygen and the latter essentially on the chromium.

The remaining charge-transfer transitions included in Table III and having energies between 33 and 52 kK essentially involve the transfer of an electron from an orbital which is predominantly chlorine 3p in character to an empty metal–ligand antibonding orbital, the largest component of which is chromium 3d in character.

There are two states for each charge-transfer orbital transition of the above types corresponding to the two linearly independent doublets arising from three unpaired electrons. Thus in the case of the promotion $9e \rightarrow 16a_1$, one transition energy (the lower) involves an excited state, the major component of which has the unpaired electrons in the $3b_2$ and 9e MO's with opposed spins (singlet coupled), and the other transition energy (the upper) involves an excited state, the major component of which has the unpaired electrons in the 9e and $16a_1$ MO's with opposed spins. The energies for the charge-transfer transitions which involve the promotion of an electron from a ligand orbital into the $3b_2$ MO (e.g., $12e \rightarrow 3b_2$) are calculated to be at significantly higher energies than those which involve promotion into the empty "d orbitals" due to the relatively unfavorable Coulombic repulsions involved in the former transitions.

The electronic spectrum of $[CrOCl_4]^-$ dissolved in CH_2Cl_2 has absorption maxima at 13.1, 18.1, 24.8, and 36.8 kK (Figure 3), the oscillator strengths increasing with the transition energy (Table I). These data are in reasonably good agreement with those details reported for various $[CrOCl_4]^-$ salts by Ziebarth and Selbin.[3] The room-temperature polarized spectra (Figure 2) of $[(C_6H_5)_4As][CrOCl_4]$ clearly indicate that the two lowest energy transitions are *xy* polarized. A shoulder at ca. 21 kK was resolved in *xy*-polarized light and shoulders at ca. 23 and 25 kK were resolved in *z*-polarized light. These observations for the room-temperature single-crystal spectra are also manifest at liquid helium temperatures. Also in the case of the latter, fine structure is distinctly resolved for the lowest energy band (Figure 2), clearly indicated for that at ca. 18 kK, and an additional absorption maximum is identified at ca. 20.3 kK (Figure 2).

Discussion

The results of the CI calculations (Table III) provide a useful basis for the interpretation of the electronic spectral data (Table I). The lowest energy transition is calculated to involve the promotion $3b_2 \rightarrow 13e$. This may be considered to be the d–d transition $d_{xy} \rightarrow d_{xz,yz}$, the $3b_2$ and 13e MO's being respectively 95 and 80% chromium 3d in character and the latter involving a significant Cr–O π-antibonding interaction. The electronic spectral data are consistent with this interpretation. Thus the band is *xy* polarized and the detailed fine structure is consistent with the assignment. The spatial degeneracy of the ^2E excited state arises within an MO which is predominantly chromium 3d in character and therefore[26] it is anticipated that the orbital degeneracy would be relieved by spin–orbit coupling effects at this metal center. This would result in a splitting of the ^2E excited state into two orbital singlets >400 cm^{-1} apart (taking the ζ value[27] for chromium(V) as 380 cm^{-1} and making some allowance for second-order spin–orbit coupling interactions), and the two electronic origins are suggested to occur at 12.9_5 and 13.5_1 kK. The additional features observed at 13.8_5, 14.4_5, and 15.3_8 kK can be interpreted reasonably well assuming vibronic coupling with the electronic transitions as $E_1 + \nu$, and $E_2 + 2\nu$ respectively, where ν has a value of ca. 920 cm^{-1}. The obvious assignment of ν is that of the Cr–O stretching mode in the first excited state; in the electronic ground state this mode has a frequency of 950 cm^{-1}. Thus the A_1 symmetry of this mode is correct for coupling with the allowed electronic transitions. Furthermore, these transitions are essentially localized within the CrO moiety, and the first excited state, . . .$(13e)^1$, is expected to have a weaker Cr–O bonding interaction than that in the . . .$(3b_2)^1$ ground state.

The absorption at ca. 18 kK is assigned to the transition 9e → $16a_1$, for several reasons. The *xy* polarization of this absorption indicates that it is a $^2B_2 \rightarrow {}^2E$ transition. An inspection of the data presented in Table II shows that not only is 9e → $16a_1$ the second lowest energy $^2B_2 \rightarrow {}^2E$ transition but also the ratio of the calculated oscillator strength for $3b_2$ → 13e and 9e → $16a_1$ transitions, 1:6, is in good accord with the experimental value, 1:5. The next $^2B_2 \rightarrow {}^2E$ transition, $13a_1$ → 13e, is a less likely candidate for the second band since, with respect to the first transition, the calculated oscillator strength ratio is 5:1. The origin of the fine structure (average separation ca. 300 cm^{-1}) of the 9e → $16a_1$ transition calls for some comment. The promotion of an electron from the 9e to the $16a_1$ MO produces a spatial degeneracy within the 9e oribitals which are (Table II) localized predominantly on the oxygen atom. The low value of the spin–orbit coupling constant for oxygen makes it rather unlikely that the excited-state orbital degeneracy of the 9e → $16a_1$ transition will be removed effectively by spin–orbit coupling effects. Therefore, it is anticipated[26] that this orbital degeneracy will be removed by coupling with a suitable vibrational mode. Symmetry requirements dictate[26] that this mode should have either B_1 or B_2 symmetry. Within the $[CrOCl_4]^-$ ion, there are three such possible vibrational modes, a B_1 Cr–Cl stretching and B_1 and B_2 Cr–Cl bending modes. The nature of the fine structure is consistent with the orbital degeneracy of the excited state being lifted by vibronic coupling with the B_1 Cr–Cl stretching vibration. The ν(Cr–Cl) stretching modes occur at ca. 400 cm^{-1} in $[(C_6H_5)_4As][CrOCl_4]$, and since the promotion 9e → $16a_1$ decreases the Cr–Cl bond overlap population (Table II), the observed magnitude of the vibronic coupling of ca. 300 cm^{-1} is thus consistent with the above arguments.

It is not possible to be as unequivocal about the assignments of the higher energy transitions observed for $[CrOCl_4]^-$. However, one reasonable basis for the interpretation of these data appears to be to assume (vide infra) that the CI calculations overestimate the energy of each charge-transfer transition by ca. 25%, this quantity being derived from the experimental (18.1 kK) and theoretical (24.3 kK) values for the 9e → $16a_1$ transition. Thus for *xy* polarization at liquid helium temperatures, the $13a_1$ → 13e transition (at ca. 19 kK) is concealed beneath the higher energy wing of the 9e → $16a_1$ transition discussed above, the group of transitions 9e → $16a_1$, $13a_1$ → 13e, $6b_1$ → 13e, and 12e → $8b_1$ are contained within the broad absorption between ca. 22 and 24 kK, and the absorption finally rises rapidly due to the very intense energy charge-transfer transitions at ca. 30 kK. Similarly, for *z* polarization at liquid helium temperature the $13a_1$ → $16a_1$ transition is suggested to occur at ca. 20 kK, the shoulders resolved at ca. 22 and 24 kK may be due to the 9e → 13e and $6b_1$ → $8b_1$ transitions, respectively, and the 9e → 13e and other higher energy charge-transfer transitions result in the rapidly rising absorption at >29 kK. These assignments of the higher energy spectral data afford good agreeement between the experimental and theoretical data in respect of both the relative energies and relative intensities of the various transitions.

We now comment on the accuracy of the CI calculations described here. Such calculations, when only single excitations and a rather limited atomic basis are used, usually overestimate the energy of charge-transfer transitions due to their inability to describe completely the large amount of electron reorganization which accompanies such a transition.[28] Individual self-consistent field (SCF) calculations on the various excited states tend to have greater variational freedom and with an adequate atomic basis usually underestimate the transition energy because of correlation energy differences between the ground and excited states.[29] However, the well-known problems associated with using the SCF method for the calculation of a number of excited states of the same symmetry such as are required here led us to use the CI method. It is of interest to note that we have found that both the SCF and CI methods gave very similar transition energies for d–d transitions where less electron reorganization occurs.[30] We consider the value of the present CI calculations to be in discussing the relative ordering and energy separation of the charge-transfer states, rather than in the accurate prediction of the values of their transition energies. We have previously described SCF calculations of the excited states of $[CrOF_5]^{2-}$ and suggested that the lowest energy charge-transfer transition is associated with electron promotion from the Cr–O π-bonding e MO's to the half-filled b_2 MO.[4] In the absence of SCF calculations on the charge-transfer configurations involving three unpaired electrons, which are here found to be of lower energy, we cannot unequivocably characterize the lowest charge-transfer transition in CrO^{3+} complexes, but we are able to state that the associated electronic rearrangement is almost certainly localized within the CrO group. The computational results for the lowest energy transition (d–d) appear to indicate that the CI calculations significantly *underestimate* the "d–d" transition energies. Therefore, the calculated values of 22.4 and 33.1 kK (Table III) are anticipated to be low estimates of the "$d_{xy} \rightarrow d_{x^2-y^2}$" and "$d_{xy} \rightarrow d_{z^2}$" transition energies, respectively.

Despite the comments concerning the absolute accuracy of the ab initio calculations described here, our theoretical results have provided a very valuable insight into the nature of the various electronic transitions within the $[CrOCl_4]^-$ ion.

This study represents the first reported polarized single crystal spectral investigation of a CrO^{3+} complex. The results obtained show that the first two bands in the spectrum of $[CrOCl_4]^-$ may be assigned to the "$d_{xy} \rightarrow d_{xz,yz}$" and "Cr–O($\pi$) → Cr–O($\sigma^*$)" transitions, respectively. This latter assignment is at variance with the general assumption[18] that the second band in the electronic spectrum of CrO^{3+} complexes is due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. It is possible to argue that this second absorption *is* due to the symmetry-forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ transition "allowed" by vibronic coupling with an E vibrational mode and/or spin–orbit coupling between the $^2B_1$ and an adjacent ^2E excited state. In certain respects this former interpretation has apparent parallels with the accepted assignment[31] for the 26-kK absorption of $[PtCl_4]^{2-}$. Thus an electronically forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ transition is allowed by an $\nu(M-Cl_4)$ E stretching vibration and the corresponding vibrational fine structure becomes evident on cooling to low temperatures. However, on balance we favor the alternative assignment that the 18-kK transition represents the $^2B_2 \rightarrow {}^2E$ promotion Cr–O(π) → Cr–O(σ^*) for the following reasons: (i) the intensity of this absorption is significantly greater than that for the symmetry-allowed $d_{xy} \rightarrow d_{xz,yz}$ transition; (ii) this intensity is only slightly reduced on cooling from room temperature to temperatures approaching that of liquid helium;

(iii) there are detailed similarities[4,32] in the electronic structures of CrO^{3+}, VO^{2+}, and MoO^{3+} complexes and we observed that the first two electronic transitions of these complexes appear to be essentially independent of the in-plane ligands; $d_{xy} \rightarrow d_{x^2-y^2}$ represents $10Dq$ for these ligands and thus should show a considerable dependence on their nature; and (iv) the theoretical results described above support this assignment. The explanation that the 18-kK transition represents $d_{xy} \rightarrow d_{x^2-y^2}$ allowed by spin–orbit coupling also seems to be unlikely. Thus, taking the form of the wave functions from Table II and the energies from Table III it is readily seen that the lowest energy ^2E excited states do not mix sufficiently with the $^2B_1$ state under spin–orbit coupling to produce an intensity as great as that observed. If the assignment of the 18-kK absorption favored here is correct, the unambiguous location of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in the electronic spectra of CrO^{3+} complexes may well be extremely difficult. In the particular case of $[CrOCl_4]^-$, this transition is probably obscured by the low-energy charge-transfer transitions. The energies of this and the other $^2B_1$ state arising from the $6b_1 \rightarrow 3b_2$ orbital transition are necessary[12] for the interpretation of $g_{\parallel}$ in the ESR spectra of these complexes. This latter $^2B_1$ state is probably at a reasonably high energy (in the case of $[CrOCl_4]^-$ the results of the CI calculations and considerations[33] of the ESR spectrum of $[CrOCl_4]^-$ suggest that the $6b_1 \rightarrow 3b_2$ transition should occur >35 kK) and is therefore difficult to locate. Since interpretations of the ESR spectra of CrO^{3+} complexes[1,2,8,9,13] usually assume that the "$d_{xy} \rightarrow d_{x^2-y^2}$" $^2B_1$ state follows from Gray et al.[17,18] and then suggest a "reasonable" value for the other $^2B_1$ state, it follows[33] that these interpretations may be erroneous.

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Registry No. $[(C_6H_5)_4As][CrOCl_4]$, 57298-28-9.

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Absorption Spectra of the Tetrachloropalladate(II) Ion Doped in Cesium Hexachlorozirconate(IV) Type Single Crystals at 2 K[1]

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The optical absorption spectra of the tetrachloropalladate(II) ion doped as an impurity in Cs_2ZrCl_6, Cs_2HfCl_6, and Rb_2HfCl_6 has been measured at 2 K. Six bands have been observed in the region of 15000–40000 cm^{-1}. The five bands lowest in energy are assigned to d–d electronic transitions by means of a crystal field model with spin–orbit coupling. The detailed vibrational structure for each of these transitions is assigned to ungerade vibrational states. The highest observed energy band between 32710 and 37100 cm^{-1} is assigned as the charge-transfer transition $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_5(^1E_u)$. Franck–Condon analysis of this spectrum has shown that the Pd–Cl equilibrium distance in the $\Gamma_5(^1E_u)$ state is 0.35 Å greater than in the $\Gamma_1(^1A_{1g})$ ground state. A comparison has been made of the effect of changing the cation from Cs^+ to Rb^+ for various d electronic states vs. a charge-transfer state.

I. Introduction

Optical studies of the $PdCl_4^{2-}$ complex have, until now, consisted of solution and single-crystal studies. Francke and Moncuit[2] have studied single crystals of K_2PdCl_4 at 300 and 12 K and have assigned transitions observed at 21000, 22500, and 33000 cm^{-1} to the singlet–singlet d–d transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1E_g$, and $^1A_{1g} \rightarrow {}^1B_{1g}$, respectively, based on a crystal field analysis ($d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$) with no spin–orbit interaction. Day, Orchard, Thomson, and Williams[3] have studied single K_2PdCl_4 crystals at room temperature and concluded that an absorption observed at 20000 cm^{-1} is the d–d transition $^1A_{1g} \rightarrow {}^1A_{2g}$. Also, McCaffery, Schatz, and Stephens[4] have studied the MCD solution spectra of $PdCl_4^{2-}$ at room temperature and concluded that a band seen at 21100 cm^{-1} is $^1A_{1g} \rightarrow {}^1E_g$.

We have doped the tetrachloropalladate(II) ion into the host lattices Cs_2ZrCl_6, Cs_2HfCl_6, and Rb_2HfCl_6 and measured the optical spectra of the mixed crystals at 2 K. In working with mixed crystals we have the opportunity to study the $PdCl_4^{2-}$ ion in the limit of no Pd–Pd metal–metal interactions and to