Charge Transfer Spectra of Mono-substituted Oxo-ions: Low-temperature Polarised Absorption Spectra and Magnetic Circular Dichroism

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The polarised absorption spectra of CrO_3X^- (X = F or Cl) and OsO_3N^- doped in crystals of $KClO_4$ have been measured at 4 K. The guest ions are oriented in the host lattice by the C_s crystal field at the perchlorate ion sites, so that the observed dichroic ratios lead to assignments of the bands to $^1A_1$ or ^1E states of the C_{3v} oxo-ions. For the CrO_3X^- ions the assignments are confirmed by analysing the room temperature solution m.c.d. spectra. The lowest energy charge transfer configurations of all three ions are formed by donation of an electron from a_2 and e orbitals almost entirely localised on the oxygen atoms, which correlate with t_1 in the parent tetraoxo-ions.

APART from magnetic circular dichroism,[1-4] the technique which has proved most useful for assigning the charge transfer spectra of tetraoxo-ions has been the linear polarisation effects produced by placing the ions at sites of lower than tetrahedral symmetry in host crystal lattices.[5-10] However, such site group splittings are often small, and consequently only observable when the absorption bands are particularly narrow. It occurred to us [11,12] that useful information about the ordering of the ligand based molecular orbitals in oxo-complexes might be derived by looking at the charge transfer spectra of anions in which one of the oxide ligands had been replaced by other groups. In this way the states of the parent tetroxo-species are subjected to a much larger perturbation than merely by placing the tetrahedral ion in a lower symmetry crystalline field.

The substituted oxo-ions most suitable for our purpose are the halogenochromates CrO_3X^- (X = F or Cl) and nitrido-osmate OsO_3N^-, both because the charge transfer spectra of the parent CrO_4^{2-} [12] and OsO_4 [13] are well known, and because the ions themselves are kinetically stable and lend themselves readily to crystal growing. Furthermore, as the ions are mononegative they form substitutional solid solutions with perchlorate salts, so that the absorption spectra can be measured at low temperatures. In the present paper we report polarised spectra at 4 K of CrO_3F^-, CrO_3Cl^-, and OsO_3N^- doped in $KClO_4$, as well as observations on the magnetic circular dichroism (m.c.d.) of the first two ions in solution at room temperature. In doping the ions into $KClO_4$ our primary motivation was to sharpen their absorption bands by lowering the temperature, rather than to observe polarisation effects, because we anticipated that equal numbers of ions would be found in the crystal with threefold axes directed along each of the Cl—O vectors of the ClO_4^- site. However, it turns out that the bands are in fact heavily polarised, *i.e.* that the ions must have some degree of preferred orientation, an effect which can be turned to advantage in making assignments.

EXPERIMENTAL

$KCrO_3F$, $KCrO_3Cl$, and $KOsO_3N$ were prepared by standard literature methods.[14-16] All had satisfactory

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analyses. Crystals of $KClO_4$ doped with all three anions were grown either by slowly evaporating a dimethylformamide solution in a Petri dish or by gel diffusion.[17] The crystals grow as flat plates with the (100) faces developed.

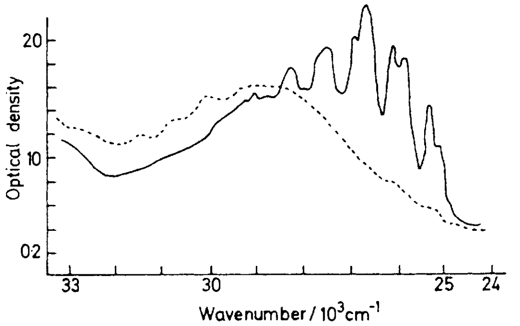

FIGURE 1 The polarised absorption spectrum of CrO_3F^- in $KClO_4$ at 4 K; —— $E//c$; - - - - $E//b$

Polarised spectra could thus be easily measured with the incident electric vector parallel to b and c axes, but only in one case (OsO_3N^-) was it found possible to measure an $E//a$ spectrum. The orientation of the crystal axes was found by measuring the angles between the best developed faces, and comparison with the known morphology.[18]

Absorption spectra were measured using a Cary 14 equipped with an Oxford Instruments CF 100 continuous flow cryostat and a calcite Glan polarising prism. The m.c.d. spectra were measured using an instrument constructed in this laboratory.[19]

Polarised Absorption Spectra.—The polarised absorption spectra of CrO_3F^-, CrO_3Cl^-, and OsO_3N^- in $KClO_4$ crystals at 4 K are shown in Figures 1—3 respectively. Only in Figure 3 do we report the $E//a$, in addition to $E//b$ and $E//c$ spectra. To obtain this result two sets of spectra were recorded with the same crystal, $E//b$ and $E//c$ with the light incident on the (100) face, and $E//a$ and $E//(b,c)$ with light incident on (011). From the ratio of the b_0 and c_0 unit cell dimensions,[18] confirmed by optical measurement of the interfacial angles, one finds that with the incident electric vector parallel to the (011) plane the light excites 0·624 of the $E//c$ spectrum and 0·376 of the $E//b$ spectrum. Hence the four polarised spectra provide an internal check on the axis assignment, when suitably corrected for differences in path length.

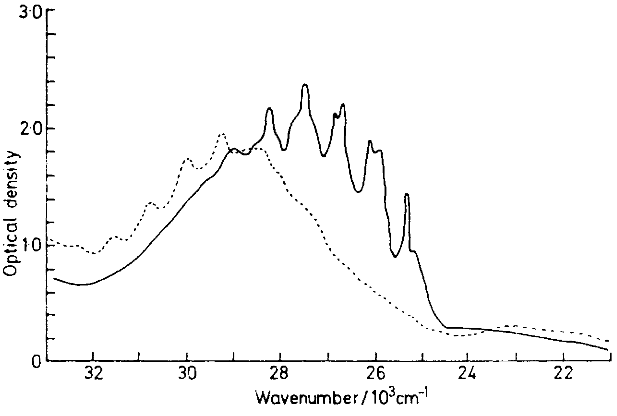

FIGURE 2 The polarised absorption spectrum of CrO_3Cl^- in $KClO_4$ at 4 K; —— $E//c$; - - - - $E//b$

The most remarkable feature of the crystal spectra of all three ions is their high degree of polarisation. If equal numbers of the C_{3v} ions had their threefold axes directed along each of the Cl—O vectors of the perchlorate ion site one would anticipate little or no net polarisation of the resulting spectra. First we investigated whether the dopant had formed an epitaxial layer on the surface of the growing $KClO_4$ crystals, but on crushing, they were found to be homogeneously coloured throughout. We therefore consider the consequences of the guest ions having preferred orientations in the host lattice. (Possible reasons for such orientations are considered later.)

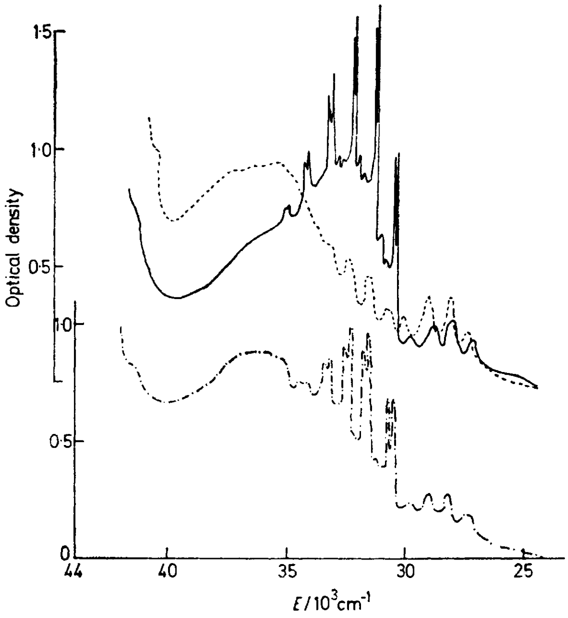

FIGURE 3 The polarised absorption spectrum of OsO_3N^- in $KClO_4$ at 4 K; — · — · — $E//a$; ——$E//b$; - - - - $E//c$

Since the molecular point group of the guest ions is C_{3v}, and their ground states are all $^1A_1$, electric dipole allowed transitions will be completely polarised either parallel ($^1A_1 \longrightarrow {}^1A_1$) or perpendicular ($^1A_1 \longrightarrow {}^1E$) to the molecular threefold axis. Ratios between the intensities of the $E//a$, b, and c spectra were thus calculated for both types of transition on the assumption that the threefold axes of the guest ions were aligned in turn along each of the Cl—O vectors of the perchlorate ion site. Of course, quite aside from the question of the extent of preferred orientation, we have no guarantee that the threefold axes would align themselves precisely parallel to the ClO_4^- ions, nor that the surrounding lattice remains undistorted. On the other hand the Cl–O bond lengths in $KClO_4$ are not grossly different from those of the dopant ions determined either from the crystal structures of the pure compounds or from force field analyses of their vibrational spectra.

Our procedure is to determine the projections of a transition dipole of 1 Å corresponding to either of the allowed

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polarisations of the molecular transitions on to the unit cell axes and then form the dichroic ratios. The results are shown in Table 1, in which the oxygen atom positions are numbered according to ref. 18. In $KClO_4$ the point group of the ClO_4^- is C_s, *i.e.* a mirror plane only. Thus O(1) and O(2) lie within this plane while O(3) and O(4) occupy equivalent positions on either side of it.

TABLE 1

Calculated dichroic ratios for MO_3X^- occupying different orientations within the $KClO_4$ lattice

C_3 axis of MO_3X^- parallel to:	Projections of transition moment $//a$	$//b$	$//c$	Dichroic ratios c/b	a/b
(i) $^1A_1 \longrightarrow {}^1A_1$ (*z*-polarised)					
Cl–O(1)	0·45	0	0·55	∞	∞
Cl–O(2)	0·83	0	0·17	∞	∞
Cl–O(3,4)	0·01	0·67	0·33	0·50	0·01
Random	0·32	0·33	0·35	1·04	0·97
(ii) $^1A_1 \longrightarrow {}^1E$ (*xy*-polarised)					
Cl–O(1)	0·27	0·50	0·22	0·45	0·55
Cl–O(2)	0·09	0·50	0·41	0·83	0·17
Cl–O(3,4)	0·49	0·17	0·33	2·01	2·98
Random	0·34	0·33	0·33	0·98	1·01

Experimentally, it is difficult to determine the dichroic ratios of the various bands with any precision because they overlap with one another. Rough estimates are given in Table 2.

TABLE 2

Dichroic ratios observed for MO_3X^- ions in $KClO_4$

	CrO_3F^-	CrO_3Cl^-	OsO_3N^-	
Band	*c/b*	*c/b*	*c/b*	*a/b*
I	0·8	0·7	1·5	0·9
II	2·5	3·5	0·4	0·5
III	0·8	0·7	1·6	1·5
IV	(1·0)	0·7		
V		1·6		

Description of the Spectra.—The spectra of both CrO_3X^- ions commence, from the low frequency end, with a relatively weak broad band (ε *ca.* 170—200 in solution at room temperature), which has no fine structure at 4 K and is more intense in the *E*//*b* than the *E*//*c* spectrum. The spectrum of OsO_3N^- also begins with a weaker band (ε *ca.* 350) but at 4 K it resolves into a well defined vibrational progression of four members with an average frequency of 895 cm^{-1}. Furthermore, the *E*//*c* spectrum is now more intense than *E*//*b*.

Band II, which is the most highly structured in all three spectra, is very much more intense with *E*//*c* than *E*//*b* in the CrO_3X^-, but has the opposite dichroism in OsO_3N^-. In all three compounds, however, the dominant fine structure is a progression of at least six members, with the following average frequencies: 790 cm^{-1} (CrO_3F^-), 780 cm^{-1} (CrO_3Cl^-), and 897 cm^{-1} (OsO_3N^-). Each member of these progressions itself has a further substructure, most complicated of all in OsO_3N^-. In CrO_3F^- and CrO_3Cl^- the substructure consists of a doubling, with an average separation of 238 cm^{-1} in the former and 270 cm^{-1} in the latter. A corresponding doubling, with an average separation of 274 cm^{-1} appears in the OsO_3N^- spectrum but because of the narrower linewidths, two further components are resolved, as well as lattice phonons.

The third band, like the first, has most of its intensity in the *E*//*b* spectrum for CrO_3X^- and in *E*//*c* for OsO_3N^-. Also like the first band, it has only poorly developed fine structure.

At higher frequencies the spectra of the three compounds differ more radically, but because the bands are also more intense we have only fragmentary evidence about their detailed structure and polarisation properties. The fourth band of CrO_3F^- appears with roughly equal intensity in both polarisations while that of CrO_3Cl^- is very much more intense in the *E*//*b* spectrum. The latter also has a long progression with an average frequency 660 cm^{-1}. The fifth band of CrO_3Cl^- on the other hand is mainly polarised parallel to *c*.

TABLE 3

The polarised spectrum of CrO_3F^- in $KClO_4$ at 4 K

E//*b*	*E*//*c*	
22 200	22 200	I
	25 160	II
	25 360	II + ν_3
	25 900	II + ν_1
	26 160	II + ν_1 + ν_3
	26 690	II + $2\nu_1$
	26 950	II + $2\nu_1$ + ν_3
	27 510	II + $3\nu_1$
	27 740	II + $3\nu_1$ + ν_3
	28 290	II + $4\nu_1$
28 750		III
	29 070	II + $5\nu_1$
30 060		III + $2\nu_1$
30 740		III + $3\nu_1$
31 470		III + $4\nu_1$
37 600	38 130	IV

TABLE 4

The polarised spectrum of CrO_3Cl^- in $KClO_4$ at 4 K

E//*b*	*E*//*c*	
23 100	23 400	I
	25 170	II
	25 355	II + ν_3
	25 920	II + ν_1
	26 157	II + ν_1 + ν_3
	26 670	II + $2\nu_1$
	26 970	II + $2\nu_1$ + ν_3
	27 473	II + $3\nu_1$
	27 762	II + $3\nu_1$ + ν_3
	28 265	II + $4\nu_1$
28 480		III
	28 563	II + $4\nu_1$ + ν_3
	29 040	II + $5\nu_1$
29 230		III + ν_1
29 970		III + $2\nu_1$
30 780		III + $3\nu_1$
31 540		III + $4\nu_1$
32 360		III + $5\nu_1$
33 560		IV
34 270		IV + ν_1
34 970		IV + $2\nu_1$
35 530		IV + $3\nu_1$
36 140		IV + $4\nu_1$
36 860		IV + $5\nu_1$
37 520		IV + $6\nu_1$
	40 130	V

In Tables 3—5 we list the frequencies of all the observed peaks and suggest vibrational assignments. In all charge transfer spectra of oxo-ions measured to date, the most intensely excited vibrational sidebands have always been found to be those associated with totally symmetric modes. The MO_3X^- ions each have three a_1 vibrational modes, with ground state frequencies as follows:

	CrO_3F^-	CrO_3Cl^-	OsO_3N^-
ν_1	912	913	1024 cm^{-1}
ν_2	637	438	897
ν_3	338	301	343

Since it is also found normally in charge transfer spectra that the excited state vibrational frequencies are reduced by 10—20% from their ground state values we feel justified in identifying the major progressions attached to the various electronic transitions as ν_1 while the pronounced doublet structure which occurs throughout the progressions of band II in every ion is identified as the coexcitation of a single quantum of ν_3.

TABLE 5

The polarised spectrum of OsO_3N^- in $KClO_4$ at 4 K

$E//a$	$E//b$	$E//c$	
27 280	27 240	27 280	I
28 170	28 130	28 190	I + ν_1
29 060	29 020	29 070	I + $2\nu_1$
29 970	29 920	29 990	I + $3\nu_1$
30 550	30 511	30 520	II
	30 567		II + ν_L
30 790	30 799	30 790	II + ν_3
	30 835		II + ν_3 + ν_L
	31 046		II + ν
	31 191		II + ν
31 410	31 409	31 420	II + ν_1
	31 461		II + ν_1 + ν_L
31 680	31 683	31 690	II + ν_1 + ν_3
	31 735		II + ν_1 + ν_3 + ν_L
	31 948		II + ν_1 + ν
	32 092		II + ν_1 + ν
32 330	32 313	32 340	II + $2\nu_1$
	32 365		II + $2\nu_1$ + ν_L
32 570	32 589	32 580	II + $2\nu_1$ + ν_3
	32 642		II + $2\nu_1$ + ν_3 + ν_L
	32 851		II + $2\nu_1$ + ν
	32 981		II + $2\nu_1$ + ν
	33 216	33 230	II + $3\nu_1$
	33 272		II + $3\nu_1$ + ν_L
	33 478	33 470	II + $3\nu_1$ + ν_3
	33 539		II + $3\nu_1$ + ν_3 + ν_L
	33 749		II + $3\nu_1$ + ν
	33 875		II + $3\nu_1$ + ν
	34 106		II + $4\nu_1$
	34 147		II + $4\nu_1$ + ν_L
	34 376		II + $4\nu_1$ + ν_3
	34 429		II + $4\nu_1$ + ν_3 + ν_L
	34 740		II + $4\nu_1$ + ν
	35 050		II + $5\nu_1$
	35 300		II + $5\nu_1$ + ν_3
		35 580	III
36 300		36 550	III + ν_1
(broad)		37 520	III + $2\nu_1$
		40 720	IV

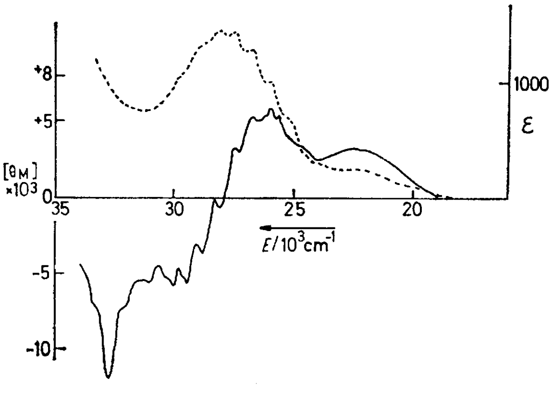

FIGURE 4 Magnetic circular dichroism (——) and absorption (- - - -) of CrO_3F^- in CH_3CN solution at room temperature

Magnetic Circular Dichroism.—The m.c.d. spectra of $KCrO_3F$ and of $KCrO_3Cl$ in CH_3CN solutions are shown, together with the absorption spectra, in Figures 4 and 5. Their main characteristic is a low amplitude in relation to the extinction coefficients of the bands. Under these circumstances we did not think it worthwhile carrying out moments analyses or fits to the curves to extract the m.c.d. parameters. There is also the complication that from the low temperature crystal absorption spectra we know that the envelopes of the bands peaking near 28 700 cm^{-1} contain two transitions, which are not resolved in the solution spectra. We therefore restrict ourselves largely to qualitative comments on the spectra.

An important general feature is that, like the absorption spectra, the m.c.d. spectra of the two compounds are quite similar in the energies, signs, and amplitudes of the bands.

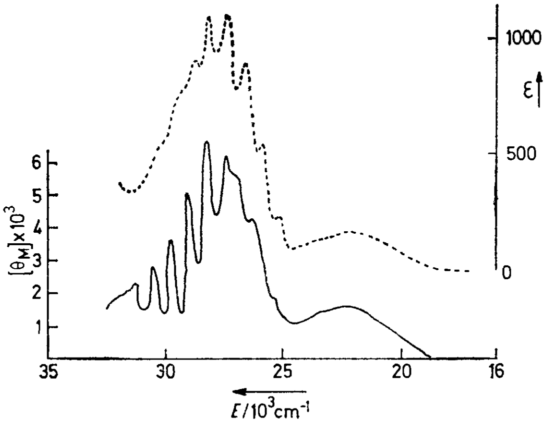

FIGURE 5 Magnetic circular dichroism (——) and absorption (- - - -) of CrO_3Cl^- in CH_3CN solution at room temperature

Since the ground states are singlets we expect only first order Zeeman contributions (*A*-terms) from degenerate excited states, in the present case ^1E. Second-order Zeeman contributions (*B*-terms) may of course contribute to the m.c.d. for all excited states. Recalling that, for a smooth absorption band, *A*-terms have a characteristic sigmoid shape, we note that the line-shapes of the absorption and m.c.d. spectra through band I are very similar, and thus that the m.c.d. at this point is dominated by a *B*-term. Because bands II and III are not resolved we cannot say whether the sigmoid curve in that region results from a single *A*-term from one of these transitions or two *B*-terms, one from each. Anticipating our later discussion, it is worth noticing that bands II and III lie almost at the same energy as the first intense transition of CrO_4^{2-} and that, if the m.c.d. under them is entirely due to an *A*-term, it has the same sign as that of the corresponding CrO_4^{2-} band. Thus for example, if the m.c.d. under bands II and III in CrO_3F^- is dominated by an *A*-term we can set a maximum value to *A* by taking the peak-to-trough separation of its extrema and using equation (1) of ref. 1. If at the same time we use the entire band envelope embracing bands II and III in the absorption spectrum to estimate the dipole strength in this region we shall, of course, be overestimating A/D should the *A*-contribution come from only one of the two bands. However, with all these uncertainties the maximum possible value of A/D under bands II and III is estimated at no greater than $-0{\cdot}1$ B.M.

DISCUSSION

Polarised Absorption Spectra.—First we consider whether the various bands identified by the vibrational and polarisation analyses can be assigned to $^1A_1$ or ^1E molecular excited states, by comparing the measured dichroic ratios of Table 2 with the calculated ones in Table 1. The halogenochromates are discussed separately from OsO_3N^- since the measured dichroic ratios of corresponding bands in their spectra are very similar. Formally, dichroic ratios *c*/*b* less than 1 could be obtained from a $^1A_1 \longrightarrow {}^1E$ transition if the CrO_3X^- ions had their threefold axes aligned parallel to either Cl–O(1) or Cl–O(2), or from $^1A_1 \longrightarrow {}^1A_1$ if their axes were parallel to Cl–O(3,4). Similarly, dichroic ratios *c*/*b* greater than 1 would be compatible with $^1A_1 \longrightarrow {}^1E$ if the molecular axes lay along Cl–O(3,4) or with $^1A_1 \longrightarrow {}^1A_1$ if they were along Cl–O(1) or Cl–O(2). An important pointer is that the *c*/*b* dichroic ratio for band II is greater than would be required for $^1A_1 \longrightarrow {}^1E$ with C_3 along Cl–O(3,4). Indeed, there is practically no trace of the sharply structured *E*//*c* peaks to be seen in this region of the *E*//*b* spectrum. It appears therefore that band II must arise from $^1A_1 \longrightarrow {}^1A_1$, and that the C_3 axes of the halogenochromate ions are consequently ordered either along Cl–O(1) or Cl–O(2). Of these alternatives Cl–O(1) is preferred, partly because some of the *c*/*b* dichroic ratios are smaller than the 0·83 required of $^1A_1 \longrightarrow {}^1E$ if the C_3 axes were along Cl–O(2), and partly because a Cl–O(1) orientation is anticipated by another argument, which we set out below.

The crystals of $KClO_4$ used for the spectral measurements are very dilute, containing only of the order of 0·1% CrO_3X^-. Thus the fact that the guest ions show preferred orientations cannot be due to co-operative interactions between them, but must result from the nature of the sites which they occupy in the host. If one imagines taking out a perchlorate ion from the $KClO_4$ lattice, the remaining part of the lattice will exert a net electric field on the resulting hole, because the point symmetry of a ClO_4^- ion in $KClO_4$ is only C_s. This electric field may then serve to orient the dipolar MO_3X^- guest ion. To estimate the direction of the orienting field in the lattice we simply calculate the orientation of the dipole of a single ClO_4^- ion due to its distortion by the C_s site, taking the Cl–O bond lengths and angles from the crystal structure of $KClO_4$, and determining the charge baricentre of the four oxygens in relation to the position of the chlorine atom. We find that with respect to the crystallographic axes the dipole lies along the direction a_0 0·24, b_0 0, c_0 0·03, *i.e.* constrained to the *ac*-plane by the requirement for the C_s mirror plane, and with its negative end towards O(2). Of course, we have no experimental information about the sense of the dipoles in the MO_3X^- ions, but an ionic calculation using the bond lengths and angles for CrO_3Cl^- suggests that the negative end may lie towards the chlorine atom. The important conclusion, however, is that the dipolar field will orient the threefold axes of the C_{3v} guest ions in $KClO_4$ parallel to the *ac*-plane.

Based on all these arguments we thus conclude that the bands in the halogenochromates are to be assigned as follows: I, $^1A_1 \longrightarrow {}^1E$; II, $^1A_1 \longrightarrow {}^1A_1$; III, $^1A_1 \longrightarrow {}^1E$. In the chlorochromate spectrum, the higher energy region of which is better defined than in CrO_3F^-, we also suggest that band IV is $^1A_1 \longrightarrow {}^1E$ and V $^1A_1 \longrightarrow {}^1A_1$.

Table 2 shows that the *c*/*b* dichroic ratios for the bands of OsO_3N^- in $KClO_4$ are almost the inverse of those of the halogenochromates, which may mean either that the assignments are: I, $^1A_1 \longrightarrow {}^1A_1$; II, $^1A_1 \longrightarrow {}^1E$; III, $^1A_1 \longrightarrow {}^1A_1$ or that the OsO_3N^- ions have different, or incomplete, orientations in the host lattice. Despite the elaborate vibronic structure observed on several of the bands we do not therefore feel able to advance any definite assignment of the nitrido-osmate spectrum.

The most striking feature of the two halogenochromate spectra is their extreme similarity, with regard to the energies, relative intensities, and polarisations of the first three band systems. This is clear evidence that the donor orbitals from which the lowest excited configurations are constructed are almost entirely localised on the oxygen atoms. Noting also that the baricentre of bands II and III is close to the energy of the first intense band in the spectrum of CrO_4^{2-} a plausible orbital assignment is at once established.

In CrO_4^{2-}, as in MnO_4^-, the lowest excited configuration is $t_1^5e^1$, which gives rise to two singlet terms, $^1T_1$ and $^1T_2$, of which the former is electric-dipole forbidden and the latter allowed from the $^1A_1$ ground state. Lowering the molecular symmetry from T_d to C_{3v} causes $^1T_1$ to split into $^1A_2 + {}^1E$ and $^1T_2$ into $^1A_1 + {}^1E$. In C_{3v}, transitions are electric-dipole allowed from $^1A_1$ to either $^1A_1$ or ^1E, but forbidden to $^1A_2$. Thus a trigonal perturbation introduces a degree of allowedness into the $^1A_1 \longrightarrow {}^1T_1$ transition, as we have already demonstrated quantitatively in the case of MnO_4^- substituted into the trigonal host $Ba(ClO_4)_2,3H_2O$.[2] In the latter example, the trigonal distortion is quite small, much more so than substituting a halide ion for one of the oxides. A more appropriate, though in the end equivalent, description of the CrO_3X^- situation might be to envisage the $t_1(T_d)$ orbital, which is non-bonding to the central metal, being split into $a_2 + e(C_{3v})$, so that two excited configurations, $a_2^1e(\mathrm{m})^1$ and $e(\mathrm{l})^3e(\mathrm{m})^1$ result. (Here e(l) is the e-orbital of mainly ligand character while e(m) is that formed from the Cr 3*d* shell.) From the former configuration we derive ^1E and from the latter $^1A_1 + {}^1A_2 + {}^1E$. Thus band I in the CrO_3X^- spectra, which is a transition to ^1E, can be thought of either as the component of $^1T_1(t_1^5e)$ in T_d symmetry, rendered allowed by the trigonal distortion, or, in the limit that the halide and oxide orbitals are almost totally disengaged from one another, as the lone singlet term from $a_2^1e(\mathrm{m})^1$. Of the three linear combinations of oxygen $2p\pi$ orbitals derived from $t_1(T_d)$, it is noteworthy that the one correlating with a_2 (C_{3v}) in MO_3X^- has three oxygen–oxygen modes while the two e (C_{3v}) combinations have only two. Consequently a_2 is expected to be more weakly bound than e(l).

Bands II and III in CrO_3X^- are now straightforwardly assigned as the allowed $^1A_1$ and ^1E from $e(\mathrm{l})^3e(\mathrm{m})^1$ or, if the trigonal splitting were smaller than the electron repulsion splitting of $^1T_1$ and $^1T_2$ in the parent $\mathrm{CrO_4}^{2-}$, as having their parentage in the allowed $^1T_2$ $(t_1{}^5e)$ of the latter. This general conclusion is supported and quantified by a closer analysis of the m.c.d. spectra of the two ions, set out in the following section.

Magnetic Circular Dichroism Spectra.—The qualitative result of the m.c.d. measurements is that the first order Zeeman splittings of those bands assigned as $^1A_1 \longrightarrow {}^1E$ from the linear polarisations are small: A/D is negligible for band I and certainly less than $-0{\cdot}1$ B.M. for band III. Let us therefore calculate A/D for various possible $^1A_1 \longrightarrow {}^1E$ transitions in these C_{3v} molecules.

With the usual definitions,[1] we find

$$A/D = \langle E + 1|L_z|E + 1\rangle \qquad (1)$$

where $E + 1 = (1/\sqrt{2})(E_x + iE_y)$. Orbital excitations giving rise to ^1E excited states are $a_2 \longrightarrow e(\mathrm{m})$, $e(\mathrm{l}) \longrightarrow e(\mathrm{m})$, $a_1 \longrightarrow e(\mathrm{m})$, $e(\mathrm{l}) \longrightarrow a_1$, so we evaluate $\langle E + 1|L_z|E + 1\rangle$ for each of these excited configurations.

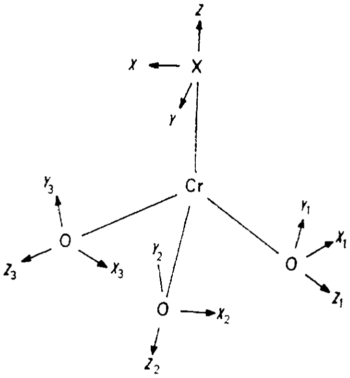

FIGURE 6 Axes of $\mathrm{MO_3X^-}$

Note that C_{3v} is a subgroup of O_h and that the coupling coefficients of the octahedral group may therefore be used. The resulting expressions are as follows:

$$\begin{aligned} a_2 &\longrightarrow e(\mathrm{m})\colon\ i[\langle e_x(\mathrm{m})|l_z|e_y(\mathrm{m})\rangle] \\ e(\mathrm{l}) &\longrightarrow e(\mathrm{m})\colon\ -i[\langle e_x(\mathrm{m})|l_z|e_y(\mathrm{m})\rangle + \\ &\qquad\qquad \langle e_x(\mathrm{l})|l_z|e_y(\mathrm{l})\rangle] \qquad (2) \\ a_1 &\longrightarrow e(\mathrm{m})\colon\ i\langle e_x(\mathrm{m})|l_z|e_y(\mathrm{m})\rangle \\ e(\mathrm{l}) &\longrightarrow a_1\colon\ i\langle e_x(\mathrm{l})|l_z|e_y(\mathrm{l})\rangle \end{aligned}$$

Of these matrix elements, only that involving $e(\mathrm{l})$ differs from zero, so one can state at once that only the $^1A_1 \longrightarrow {}^1E[e(\mathrm{l}) \longrightarrow e(\mathrm{m})]$ excitation will have any A-term component in its m.c.d. Thus the absence of an A-term under band I, assigned as a $^1A_1 \longrightarrow {}^1E$ transition from its dichroic ratio, is consistent with its assignment to the $a_2 \longrightarrow e(\mathrm{m})$ orbital excitation.

It remains to consider the form of the $e(\mathrm{l})$ molecular orbital. Using the axis orientations shown in Figure 6, the molecular orbitals transforming as $e_x(\mathrm{l})$ are $(1/\sqrt{6})(2\pi x_1 - \pi x_2 - \pi x_3)$, $(1/\sqrt{6})(2\pi y_1 - \pi y_2 - \pi y_3)$, $(1/\sqrt{6})(2\sigma_1 - \sigma_2 - \sigma_3)$ and p_x(halogen). If, following the similarity between the transition energies of $\mathrm{CrO_3F^-}$ and $\mathrm{CrO_3Cl^-}$, we assume that $e(\mathrm{l})$ is confined to oxygen $p\pi$ orbitals,

$$\begin{aligned} \langle e_x(\mathrm{l})|l_z|e_y(\mathrm{l})\rangle = {} & \\ (1/\sqrt{12})[a^2\langle 2\pi x_1 - \pi x_2 - \pi x_3|l_z|\pi x_1 - \pi x_2\rangle &+ \\ b^2\langle 2\pi y_1 - \pi y_2 - \pi y_3|l_z|\pi y_3 - \pi y_2\rangle &+ \\ ab\langle 2\pi x_1 - \pi x_2 - \pi x_3|l_z|\pi y_3 - \pi y_2\rangle &+ \\ ab\langle 2\pi y_1 - \pi y_2 - \pi y_3|l_z|\pi x_3 - \pi x_2\rangle] & \qquad (3) \end{aligned}$$

where a,b are the coefficients in the linear combination of πx and πy sets, and the local oxygen atom co-ordinates have been transformed to the molecular threefold axis. Now because they give rise, on expansion, to pairs of one-centre matrix elements such as

$$\langle \pi x_2|l_z|\pi x_2\rangle - \langle \pi x_3|l_z|\pi x_3\rangle \qquad (4)$$

each of the terms in equation (3) is zero, in other words the only contribution to A/D from $e(\mathrm{l})$ comes from the halogen p-orbitals. Thus the value of A/D gives an upper limit to the halogen contribution to the orbital concerned.

Writing

$$e(\mathrm{l}) = c_{\mathrm{O}x}e_{\mathrm{O}x} + c_{\mathrm{Hal}}e_{\mathrm{Hal}} \qquad (5)$$

it is straightforward to show that for the two possible $^1A_1 \longrightarrow {}^1E$ excitations involving $e(\mathrm{l})$ we have:

$$\begin{aligned} e(\mathrm{l}) &\longrightarrow a_1\colon\ A/D = c_{\mathrm{Hal}}{}^2 \\ e(\mathrm{l}) &\longrightarrow e(\mathrm{m})\colon\ A/D = -c_{\mathrm{Hal}}{}^2 \end{aligned}$$

The A-term contribution to band III is in fact negative, which is consistent with its assignment as $^1A_1 \longrightarrow {}^1E$ $(e(\mathrm{l}) \longrightarrow e(\mathrm{m}))$. Given our estimate of an upper limit of $-0{\cdot}1$ to A/D in $\mathrm{CrO_3X^-}$, the maximum possible value of c_{Hal} in the highest $e\pi$ ligand orbital is about $0{\cdot}3$. In view of the rather drastic assumptions used in estimating the magnitude of A/D, however, it is likely that the true value of c_{Hal} is a lot less than this.

CONCLUSIONS

The combination of linear polarisation measurements with m.c.d. in this work leads us to a set of conclusions about the assignment of the $\mathrm{CrO_3X^-}$ charge transfer spectra, and their relationship to the spectrum of $\mathrm{CrO_4}^{2-}$, which can be summarised as follows:

(1) In the low temperature polarised absorption spectra the energies, relative intensities, and dichroic ratios of the first three band systems are only marginally altered on replacing chloride by fluoride. Thus the lowest charge transfer configurations involve donor orbitals localised almost completely on the oxygen atoms.

(2) The energies of band I, and of bands II and III together, are very similar to those of $^1A_1 \longrightarrow {}^1T_1(t_1{}^5e^1)$ and $^1A_1 \longrightarrow {}^1T_2(t_1{}^5e^1)$ in $\mathrm{CrO_4}^{2-}$. Thus we believe that these two terms of $t_1{}^5e$ provide the parentage of the first three excited states of $\mathrm{CrO_3X^-}$.

(3) From the linear polarisation experiments band II is $^1A_1 \longrightarrow {}^1A_1$ and band III is $^1A_1 \longrightarrow {}^1E$, stemming from $^1A_1 \longrightarrow {}^1T_2$ of the parent $\mathrm{CrO_4}^{2-}$. (This is further confirmed by the sign of the m.c.d. A-term in this region.)

(4) The magnitude of A/D places an upper limit of about 10% on the halogen $p\pi$ admixture into the frontier e-orbital.

(5) Despite the superficial resemblance between the CrO_3X^- and OsO_3N^- spectra, the dichroic ratios in the $KClO_4$ crystals indicate that the excited states of the latter are not being assigned by any straightforward analogy to the former. It is probably significant that although it is bands II and III in CrO_3X^- which lie closest in energy to the first intense band of the parent CrO_4^{2-}, in the case of OsO_3N^- it is band I which has this relationship to the OsO_4 spectrum. M.c.d. measurements on the u.v. transitions of OsO_3N^- will be needed before this relationship can be explored in any greater detail.

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