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Electronic Structures and MCD Spectra of Trigonal CR(III)S_6 Systems*

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MCD, electronic absorption, external heavy atom, and crystal field data are presented for the low energy region (^2E_g, $^2T_{1g}$, $^4T_{2g}$) and high energy region ($^2T_{2g}$, $^4T_{1g}$) of Cr(dtp)$_3$, Cr(dtc)$_3$, and Cr(exan)$_3$. At low energy, MCD intensities of $^2E(^2E_g)$ and $^2E(^2T_{1g})$ are as large or larger than "$^4T_{2g}$", and the MCD technique is advantageous over electronic absorption in this respect. The MCD positions of "^2E_g" and "$^2T_{1g}$" are nearly the same for these molecules (~13 kK and ~13.6 kK) · $^4T_{2g}$ of this region appears trigonally split (~500 cm^{-1}) in the MCD of dtp but to a smaller extent than in the electronic crystal spectrum of Lebedda and Palmer (~600 cm^{-1}). MCD did not resolve such components for exan and dtc. The higher energy region includes $^2T_{2g}$ and $^4T_{1g}$, and the combined MCD and electronic absorption *data* of the three compounds taken together lead us to conclude the ordering $^2A_1(^2T_{2g}) < {}^2E(^2T_{2g}) < {}^4E(^4T_{1g})$. The potentially useful external heavy atom affect on the solution-observed electronic ^2E and ^4E bands of Cr(dtp)$_3$ did not shed additional light on this order of E states. Finally, it is concluded that the order of $^4T_{1g}$ and $^2T_{2g}$ cannot be decided from O_h crystal field *calculations* because of experimental uncertainties about choosing centers of gravity. In addition, "$^4T_{1g}$" and "$^2T_{2g}$" are close together so that ordering $^2E < {}^4E$ does not guarantee $^2T_{2g} < {}^4T_{1g}$. However, it can be concluded that the ratio $C/B \cong 4$ is not correct, whereas the larger $7 < (C/B) < 8$ is consistent with the data of all three molecules because of small B parameters (~0.4). Locating O→O transitions may somewhat decrease C/B and Dq.

In der vorliegenden Arbeit werden folgende Meßergebnisse mitgeteilt; MCD, elektronische Absorption, Einfluß eines äußeren schweren Atoms sowie Kristallfelddaten für den Bereich niedriger Energie (^2E_g, $^2T_{1g}$, $^4T_{2g}$) und den Bereich hoher Energie ($^2T_{2g}$, $^4T_{1g}$) von Cr(dtp)$_3$, Cr(dtc)$_3$ und Cr(exan). Bei niedriger Energie sind die MCD-Intensitäten von $^2E(^2E_g)$ und $^2E(^2T_{1g})$ genau so groß, oder größer als „$^4T_{2g}$“, und die MCD-Technik bietet Vorteile gegenüber der elektronischen Absorptionsmethode. Die MCD-Werte von „^2E_g“ und „$^2T_{1g}$“ sind für die genannten Moleküle etwa gleich (~13 kK und ~13,6 kK). $^4T_{2g}$ dieses Gebietes erscheint trigonal aufgespalten (~500 cm^{-1}) bei MCD von dtp, aber in einem geringeren Maß als im elektronischen Kristallspektrum von Lebedda und Palmer (~600 cm^{-1}) MCD löste solche Komponenten bei exan und dtc nicht auf. Der Bereich höherer Energie enthält $^2T_{2g}$ und $^4T_{1g}$, und aus der Kombination von Daten der MCD-Methode sowie der elektronischen Absorption schlossen wir auf die Anordnung $^2A_{1g}(^2T_{2g}) < {}^2E(^2T_{2g}) < {}^4E(^4T_{1g})$. Der möglicherweise nützliche Effekt eines äußeren schweren Atoms auf die in Lösung beobachteten elektronischen ^2E- und ^4E-Banden von Cr(dtp)$_3$ brachte bezüglich dieser Anordnung der E-Zustände nichts Neues. Weiterhin wird gefolgert, daß die Ordnung von $^4T_{1g}$ und $^2T_{2g}$ nicht aus O_h-Kristallfeldberechnungen entschieden werden kann, da experimentelle Unsicherheiten bezüglich der Wahl von Schwerpunkten bestehen. Außerdem liegen „$^4T_{1g}$“ und „$^2T_{2g}$“ nahe zusammen, sodaß aus der Anordnung $^2E < {}^4E$ nicht notwendig $^2T_{2g} < {}^4T_{1g}$ folgt. Es kann jedoch gefolgert werden, daß das Verhältnis $C/B \cong 4$ nicht korrekt ist, während $7 < (C/B) < 8$ konsistent mit den Daten aller drei Moleküle ist, da die B-parameter klein sind (~0,4). Die Vokalisierung der O→O-Übergänge könnten C/B und Dq etwas erniedrigen.

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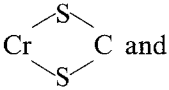
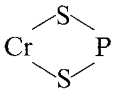
Introduction

The electronic spectroscopic work of Kida and Yoneda [1] and Jorgensen [2] is among the early definitive studies of transition metal sulfur chelates [3]. Jorgensen's papers have been most responsible for initiating more recent studies of this area of chemistry [4–8, 14]. As a coordinating atom within ligands, sulfur has the interesting spectral property of exhibiting a large nephelauxetic effect, i.e., perhaps in the vicinity of iodine, even though it is an element of the third period, whereas its position in the spectrochemical series is not at all in close proximity to the iodide ion but between Cl^- and H_2O [2]. Thus far magnetic circular dichroism (MCD) studies of trigonal chromium(III) chelate compounds have been restricted to CrO_6 and CrN_6 chelate systems such as $Cr(ox)_3^{3-}$ and $Cren_3^{3+}$ [9]. This communication concerns itself with the MCD spectra of the chromium(III) sulfur chelates of diethyldithiophosphate (dtp^-), diethyldithiocarbamate (dtc^-), and ethylxanthate ($exan^-$), i.e., $Cr(dtp)_3$, $Cr(dtc)_3$, and $Cr(exan)_3$[1]. It was of interest to first of all determine effects on the MCD dispersions of coordinated atoms known to have a higher one-electron spin-orbit coupling constant, especially the effect on the intensities of spin forbidden transitions. Furthermore, the intramolecular ring size is now four,  and , rather than five as in the trigonal oxalato and ethylenediamine molecule-ions. This also constitutes the first report of MCD measurements on CrS_6 systems. Finally, the conclusions of this study also relate to the order of excited state assignments for these compounds on the basis of these MCD data, octahedral crystal field calculations, external heavy atom effect observations, and an earlier report [7a] of crystal spectra of one of the compounds, $Cr(dtp)_3$.

Experimental

The compounds were prepared by methods described in the literature [10]. Spectra were obtained in methylenechloride solutions of the complexes. The heavy atom solvents ethylbromide and ethyliodide, impure due to the presence of halogens, were purified by passing each through alumina columns.

The magnetic field for MCD measurements were generated using a Nb/Ti superconducting coil wound by Westinghouse and built into a 300° K – 80° K – 4° K dewar system. Fields of ca. 42 kGauss were employed and were measured to within 1% accuracy using a rotating coil gaussmeter. The latter was calibrated against a more accurate Magnion G-502, and the magnetic field and light directions were made to parallel each other. The circularly dichroic light of the Durrum JASCO model ORD/UV/CD-5 was used, and the xenon source was found not to require shielding in fields used here. However, the end-on photomultiplier tube was removed, shielded, and housed outside the instrument. The instrument is still usable for absorption optical measurements, since the chopper drive cable was lengthened and repositioned by us. The instrument MCD calibration is checked against the spectrum of $K_3[Fe(CN)_6] \cdot 3\,H_2O$ [11]. Wave-

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[1] $dtp^- = [S_2P(OC_2H_5)_2]^-$; $dtc^- = [S_2CN(C_2H_5)_2]^-$; $exan^- = [S_2COC_2H_5]^-$.

length calibrations are made by comparing JASCO and Cary 14 optical absorption spectra of aqueous solutions of the rare earth salts $Nd(NO_3)_3 \cdot 5\,H_2O$ and $UO_2(NO_3)_2 \cdot 6\,H_2O$, and of silicate glasses of holmium oxide and neodymium oxide. The MCD band maxima recorded in Tables 1–3 are such corrected values, but the spectra of Fig. 2 are direct tracings of the JASCO spectra.

Calculations were done on an IBM 360/75 system.

Results and Discussion

Octahedral (O_h) and trigonal (D_3) $d-d$ state diagrams for a d^3 metal ion are shown in Fig. 1. The ordering of several excited states was decided on the basis of MCD, external heavy atom effect, and crystal field data to be discussed here, and in part it is based on polarized crystal data [7] of the two optically intense regions of one of the complexes, $Cr(dtp)_3$. The solution MCD and electronic absorption spectra in the $d-d$ region of the representative sulfur chelate $Cr(dtp)_3$ are shown in Fig. 2, and higher energy $d-d$ bands in the ${}^4T_{1g}$, ${}^2T_{2g}$ region are shown in Fig. 3. The MCD spectra of the $Cr(S_2)_3$ will be considered next in two parts, viz., the low energy portion containing components *a*, *b*, *c*, and *d*, and the higher energy portion containing extrema *e*, *f*, and *g* (Figs. 2 and 3 and Tables 1–3).

The lower energy region of the MCD spectra will arise from transitions to the four D_3 states ${}^2E({}^2E_g)$, ${}^2E({}^2T_{1g})$, ${}^4E({}^4T_{2g})$ and ${}^4A_1({}^4T_{2g})$ (Fig. 1) according to spatial MCD and formal electric dipole selection rules. Since the spin doublets arise from "t_{2g}^3" intraconfigurational transitions, they are expected to be narrow and of very low dipole strengths. Consequently, ${}^2E({}^2E_g)$ and ${}^2E({}^2T_{1g})$ are only barely discernible in electronic absorption spectra of $Cr(dtp)_3$ [7, 8], $Cr(dtc)_3$ and $Cr(exan)_3$ even at low temperature [8]. Also, this problem arises in large part because these ${}^2\Gamma$ are located under the relatively very intense ${}^4T_{2g}$ band. Quite on the contrary, the two doublets are very clearly seen in the MCD spectra

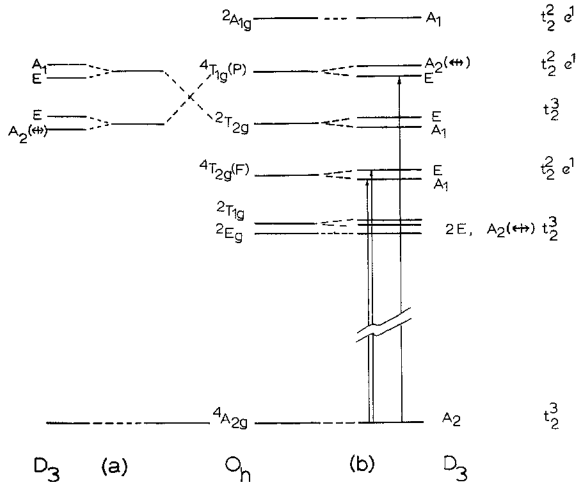

Fig. 1. Several O_h and D_3 states of Cr(III) $d-d$ transitions (see text)

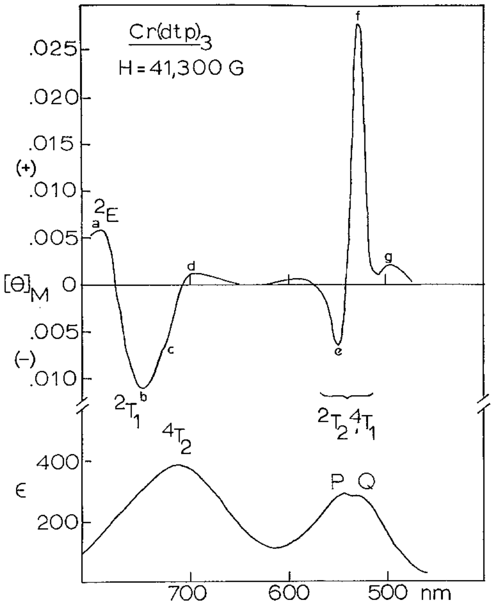

Fig. 2. MCD and electronic absorption spectra of Cr(dtp)$_3$ in CH_2Cl_2 solution. $[\Theta]_M$ = molar ellipticity/Gauss = deg-cm^2 – dmole^{-1} – Gauss^{-1}, or deg-dl-dm^{-1} – mole^{-1} – Gauss^{-1}

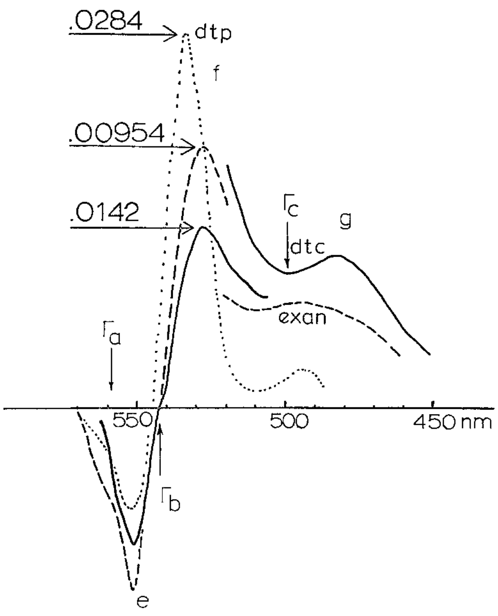

Fig. 3. MCD spectra of Cr(dtp)$_3$, Cr(dtc)$_3$ and Cr(exan)$_3$ (in CH_2Cl_2) between 600 nm and 450 nm (Molar ellipticity values per Gauss of several band maxima appear above arrows)

Table 1. Band extrema of $Cr(dtp)_3$[a]

Bands	O_h	D_3	MCD[b]	Electronic			Crystal field predictions				
				Present work[c]	Jorgensen[d]	Lebedda[f] and Palmer		I[e]	II[f]	III[g]	IV[h]
g	$^4T_{1g}$; $^2T_{2g}$	$(^4A_2)$, ^4E; ^2E, $^2A_1$	20.38				$^2A_{1g}$	21.0	25.8	25.83	24.84
f			19.05	19.2	18.8 (“$^4T_{1g}$”)	19.25 ($^2T_{2g}$)	$^2T_{2g}$	12.83	19.25	19.62	19.39
e			18.45	18.69	18.6 19.1 (“$^2T_{2g}$”)	18.75 ($^4T_{1g}$)	$^4T_{1g}$	18.77	18.7	18.72	19.67
			(∼17)			17					
d	$^4T_{2g}$	^4E	14.43	14.3	14.3 (“$^4T_{2g}$”)	14.5	$^4T_{2g}$	14.3	14.5	14.25	13.8
c		$^4A_1$	13.95			13.86					
b	$^2T_{1g}$	^2E	13.59		13.6	13.6	$^2T_{1g}$	8.58	13.1	13.44	13.57
a	^2E_g	^2E	13.04		13.1	13.1	^2E_g	8.23	12.8	13.14	13.04
							$Dq =$	1.43	1.45	1.425	1.38
							$B =$	0.42	0.389	0.42	0.60
							$C =$	1.68	3.26	3.30	2.88
							$C/B =$	4.0	8.38	7.86	4.8

[a] Positions and crystal field parameters in units of kK.

[b] Recorded on JASCO but positions corrected as described in experimental section.

[c] Cary 14.

[d] Ref. [4].

[e] Present calculation using Jorgensen's parameter [4].

[f] Ref. [7b].

[g–h] This work (see text).

Table 2. Band extrema of $Cr(dtc)_3$[a]

Bands	O_h	D_3	MCD[b]	Electronic		Crystal field predictions					
				Present work[c]	Jorgensen[d]		I[e]	II[f]	III[g]	IV[h]	V[i]
g			21.01			$^2A_{1g}$	22.38	27.20	27.40	27.60	26.80
f	$^4T_{1g}$;	$(^4A_2)$, ^4E;	19.21	20.2	20.4 ("$^4T_{1g}$")	$^2T_{2g}$	13.22	20.03	20.06	20.09	18.87
e	$^2T_{2g}$	^2E, $^2A_1$	18.45	(18.55)		$^4T_{1g}$	20.11	19.73	19.94	20.14	20.25
			18.18	(18.2)							
c, d	$^4T_{2g}$	^4E, $^4A_1$	15.50	15.6	15.5 ("$^4T_{2g}$")	$^4T_{2g}$	15.50	15.40	15.60	15.80	15.90
b	$^2T_{1g}$	^2E	13.61			$^2T_{1g}$	8.80	13.59	13.60	13.60	12.70
a	^2E_g	^2E	12.93			^2E_g	8.44	13.33	13.33	13.34	12.43
						$Dq =$	1.55	1.54	1.56	1.58	1.59
						$B =$	0.430	0.400	0.400	0.400	0.40
						$C =$	1.720	3.400	3.400	3.400	3.10
						$C/B =$	4.00	8.500	8.500	8.500	7.75

[a–e] See footnotes of Table 1. [f–i] This work (see text).

Table 3. Band extrema of $Cr(exan)_3$[a]

Bands	O_h	D_3	MCD[b]	Electronic		Crystal field predictions					
				Present work[c]	Jorgensen[d]		I[e]	II[f]	III[g]	IV[h]	V[i]
g			20.6–21.0			$^2A_{1g}$	22.24	26.51	27.40	27.84	26.80
f	$^4T_{1g}$;	$(^4A_2)$, ^4E;	19.25	20.3	20.26 ("$^4T_{1g}$")	$^2T_{2g}$	12.16	18.48	19.69	20.13	18.87
e	$^2T_{2g}$	^2E, $^2A_1$	18.45	(18.65)		$^4T_{1g}$	20.26	20.69	20.25	19.86	20.25
			(18.03)	(18.3)							
c, d	$^4T_{2g}$		15.82	16.1	16.0 ("$^4T_{2g}$")	$^4T_{2g}$	16.0	16.0	15.9	15.9	15.90
b	$^2T_{1g}$		13.83			$^2T_{1g}$	8.0	12.45	13.3	13.57	12.70
a	^2E_g		12.95			^2E_g	7.7	12.14	13.04	13.36	12.49
						$Dq =$	1.6	1.6	1.59	1.59	1.59
						$B =$	0.390	0.436	0.40	0.36	0.40
						$C =$	1.56	2.921	3.30	3.50	3.10
						$C/B =$	4.00	6.70	8.25	9.7	7.75

[a–e] See footnotes of Table 1. [f] This work, using Witzke's [5] parameters. [g–i] This work (see text).

of all three compounds[2] as they are of relatively large intensity, e.g., bands *a* and *b* of Fig. 2 are $^2E(^2E_g)$ and $^2E(^2T_{1g})$ of $Cr(dtp)_3$. The separation of their band maxima is about 550 cm^{-1}. The locations of these band maxima and those reported by others [4, 7b] are shown in Table 1 and are in good agreement.

The two trigonal components of $^4T_{2g}$ are also apparent in the $Cr(dtp)_3$ MCD spectrum as bands *c* and *d* of Fig. 2, and the higher energy component of $^4T_{2g}$ is known to have E symmetry [7] (Fig. 1). While the MCD band locations do not infer that $^4E(^4T_{2g})$ has a dominating A-term, a small A contribution compared to the intensity contribution from $(B+C/kT)$ cannot be ruled out. The trigonal splitting of $^4T_{2g}$ (MCD bands at 13.95 kK and 14.43 kK) derived from these data is ca. 500 cm^{-1} compared to 600 cm^{-1} obtained from the polarized absorption data [7]. The solution electronic absorption spectrum does not show this trigonal splitting [2, 4]. The ability to locate these *spin-forbidden* transitions is the major advantage of the MCD spectrum over all previously reported electronic absorption results [2, 7a, 8]. This and other reported results for $^4T_{2g}$ of $Cr(dtp)_3$ are also given in Table 1, i.e., Jorgensen [2, 4] observed only one component ("$^4T_{2g}$"), but Lebedda and Palmer [7] observed components at 13.86 kK and 14.50 kK.

The comparison of band positions in the low energy portion of MCD spectra for $Cr(dtp)_3$, $Cr(dtc)_3$, and $Cr(exan)_3$ are summarized in Tables 1–3. One important feature to be noted is that the positions of MCD band maxima *a* and *b* remain almost constant for the three compounds. This behavior is indeed expected of $^2E(^2E_g)$ and $^2E(^2T_{1g})$ to good approximation [12]. On the other hand the MCD position of "$^4T_{2g}$" showed significant dependence on the ligand, viz., transition energies to $^4T_{2g}$ increased in the order $Cr(exan)_3 > Cr(dtc)_3 > Cr(dtp)_3$, and the MCD based order follows the previously found [4] spectrochemical series, $\ldots Cl^- < dtp^- < F^- < dtc^- < exan^- < H_2O \ldots$. The locations of ^2E_g and $^2T_{1g}$ were not reported for $Cr(dtc)_3$ and $Cr(exan)_3$ by Jorgensen [4]. On the other hand, he reports "$^4T_{2g}$" as a single component for dtc and exan. These electronic band positions agree well with our own, and $^4T_{2g}$ also appears unsplit in the MCD of these two compounds. However, the intraconfigurational spin doublets are nicely located again and are given in Tables 2 and 3. Crystal field predictions (*vide infra*) agree with the above order $^2E_g < {}^2T_{1g} < {}^4T_{2g}$.

We now turn to the higher energy region of each MCD spectrum which includes $^2E(^2T_{2g})$, $^2A_1(^2T_{2g})$ and $^4E(^4T_{1g})$, and perhaps $^2A_1(^2A_{1g})$ (Fig. 1), using D_3 spatial selection rules again. This region is not as simple to analyze due to the close proximity of $^4T_{1g}$ and $^2T_{2g}$ in the region 18 kK – 20 kK, i.e., several pieces of data support the assignment $^2T_{2g} < {}^4T_{1g}$, whereas other data seem to indicate $^2T_{2g} > {}^4T_{1g}$. $Cr(dtp)_3$ data will be considered by itself and with those of exan and dtc in an attempt to resolve the ambiguity.

First, bands *P* and *Q* of $Cr(dtp)_3$ are known to be *E* states [7]. However, it has not as yet been unambiguously ascertained [7b] whether band *P* (or *Q*) is $^2E(^2T_2)$ or $^4E(^4T_1)$. For example, regardless of whether *octahedral* crystal field calculations (Tables 1–3) predict $^2T_{2g} > {}^4T_{1g}$ or $^2T_{2g} < {}^4T_{1g}$, either D_3 order $^2E < {}^4E$ or $^2E > {}^4E$ is possible (Fig. 4), especially in the light of $Cr(dtp)_3$ data

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[2] It was recognized by McCaffery *et al.* [9] that $^4A_2 \rightarrow {}^2\Gamma$ positions are advantageously located for $Cr(III)L_6$ (L = N, O) chromophores by means of MCD.

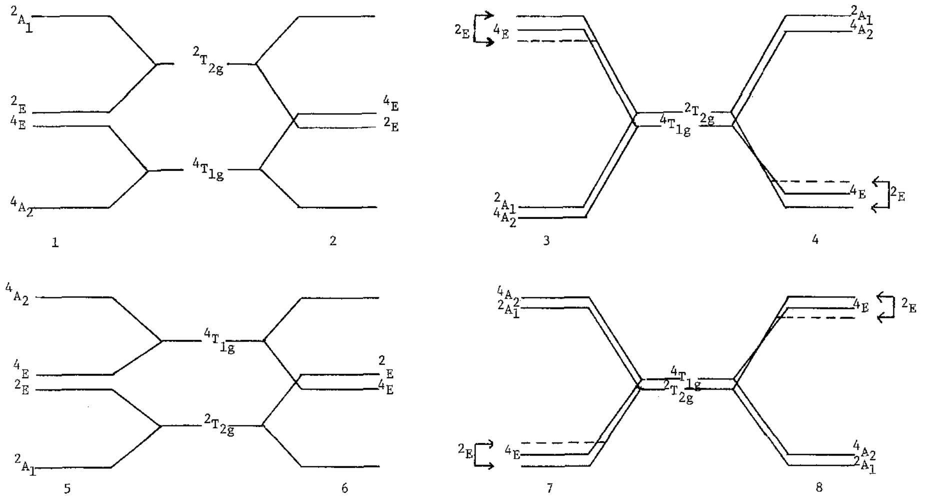

Fig. 4. Possible orders of D_3 components for $^4T_{1g} > {}^2T_{2g}$ and $^4T_{1g} < {}^2T_{2g}$

above, because the bands are close to each other. The following information supports $^2E < {}^4E$. First, we note that a transition to $^2E(^2T_{2g})$ is t_2^3 intraconfigurational and will essentially be independent of ligand field strength within the strong field approximation of the energy matrix constructed with strong field functions [12]. However $^4E(T_1)$ will be dependent. We discuss dtc first.

In Fig. 3 we indicate by arrows (Γ_a, Γ_b, Γ_c) the positions of electronic absorption band maxima of Cr(dtc)$_3$, which can be observed at 80° K in glassy media as well as in the 4° K unpolarized crystal spectrum. Since Γ_a and Γ_b have extremely small dipole strengths with $\varepsilon \leqq 1$ they correspond to $^2A_1$ and ^2E of $^2T_2$. Thus, dispersion e–f is an apparent A-term. However, since we estimate that A/D is an order of magnitude too large for e–f to be a true A-term, it must be assigned to the sum of two $(B + C/kT)$ bands having opposite signs (probably Kramer's $2\bar{A}$ and $\bar{E}_a$ of ^2E). Γ_c is the location of $^4E(T_1)$, and its MCD activity is region g of Figs. 2 and 3.

We conclude that the state ordering in the high energy region of Cr(dtc)$_3$ is $^2A_1 < {}^2E < {}^4E$, and probably $^2T_2 < {}^4T_1$, which is the order of Fig. 1(b). Our reasons, then, for this order are as follows. First, the content of the above paragraph based on intensities. Second, the two $^2T_2$ components (Γ_a, Γ_b) are unshifted in exan and dtc, as expected of t_2^3 spin doublets. Also, Γ_b of dtp is also unshifted, whereas Γ_a is only slightly so. Third, MCD band g corresponding to ^4E in these compounds shifts qualitatively in the direction expected on the basis of the spectrochemical series [4] of the ligands. Fourth, prominent MCD extrema e, f, and g are extremely similar in the three compounds. (By the way, the lower energy 18.2–18.3 kK components of exan and dtc appear as red MCD shoulders on the more intense band e.) These data taken together lead us to conclude $^2T_{2g} < {}^4T_{1g}$ for each of the three molecules is probably the correct order. Certainly one knows $^2A_1, {}^2E < {}^4E$, or $^2T_{2g} < {}^4E$; whereas the location of $^4A_2(T_1)$ is unknown.

The alternative order of these two bands (Γ_b and Γ_c) is $^4E(^4T_{1g}) < {}^2E(^2T_{2g})$. However, the trigonal splitting of $^2T_{2g}$ (energy of Γ_c minus energies of red shoulders on band *e*) would take on unprecedented, exceedingly high values, i.e., $> 2000\ \mathrm{cm}^{-1}$. Furthermore, this would be inconsistent with observed electronic absorption intensities.

The external heavy-atom solvent effect [13] of ethylbromide and ethyliodide on the electronic absorption intensity and structure of the $^4T_{1g}$, $^2T_{2g}$ region of Cr(dtp)$_3$ was measured, since the two bands of the compound are clearly resolved in solution. It was considered possible that the experiment might give additional support to our assignment $^2E(^2T_{2g}) < {}^4E(^4T_{1g})$. The measurements are summarized in Table 4. It can be seen that, while the intensity of this $^4T_{1g}$, $^2T_{2g}$ region increases in the order $C_2H_5I > C_2H_5Br$, both bands increase by about an equal amount. Furthermore, the $^4T_{2g}$ region was effected in the same way. This experiment is not considered to be definitive for our purposes, therefore.

Table 4. External heavy atom effect on molar extinction coefficients of Cr(dtp)$_3$

	$^4T_{2g}$	$(^2T_{2g}, {}^4T_{1g})$			
Solvant	$\varepsilon_{703\mathrm{nm}}$	$\varepsilon_{535\mathrm{nm}}$	$\varepsilon_{525\mathrm{nm}}$	$\varepsilon_{535}/\varepsilon_{703}$	$\varepsilon_{535}/\varepsilon_{525}$
Cyclohexane	355	248	248	0.697	1.000
Methylenechloride	373	268	265	0.718	1.011
Ethylbromide	361	256	255	0.709	1.004
Ethyliodide	393	276.5	275	0.703	1.0055

We initially considered the Γ_c (MCD band *g*) as "$^2A_{1g}$"$(t_{2g}^2 e_g^1)$, but any choice of crystal field parameters from a reasonable range rules out this possibility (Tables 1–3). Thus using Griffith's strong field two-electron matrix elements [12], and allowing all states of t_{2g}^3 and $t_{2g}^2 e$ of the same spin-space identity to interact, the calculation appears to successfully account for the approximate locations of ^2E_g, $^2T_{1g}$, $^4T_{2g}$, $^2T_{2g}$, and $^4T_{1g}$ of these configurations to within a few hundred wavenumbers (Tables 1–3). Therefore, it is reasonable to expect that it will predict the location of $^2A_{1g}(t_{2g}^2 e_g^1)$ equally well. Since the prediction for $^4A_{2g} \rightarrow {}^2A_{1g}$ is 25 kK to 26 kK, we discount the possibility that our 20.4 kK MCD band *g* is $^2A_{1g}$.

The following additional comments need be made regarding the usefullness of the crystal field calculations. The results for Cr(dtp)$_3$ are shown in Table 1. The previously published parameters [4] used in our calculation I (Table 1) are ruled out because of ~ 5 kK deviations between calculated and observed positions of the two low energy doublets. However, the set of parameters from Lebedda and Palmer are in close agreement with ours (calculations II and III). Yet, since the center of gravity of $^4T_{1g}$ is not known and $10\,Dq$ may be chosen between ~ 14.5 kK and ~ 13.9 kK, the order of *octahedral* parents $^4T_{1g}$ and $^2T_{2g}$ can be reversed (compare predictions IV with II and III, Table 1) and a reasonable fit maintained. Computationally $^2T_{2g} > {}^4T_{1g}$ is favored only *if* $^2T_2 \sim 19.2$ kK, but either $^4T_{1g} > {}^2T_{2g}$ or $^4T_{1g} < {}^2T_{2g}$ can permit $^4E < {}^2E$ or

$^4E > {}^2E$ (Fig. 4). But, work in progress now indicates $^2T_2 \sim 18$ kK and $^4E(T_1) \sim 19.2$ kK.

It was also necessary to exercise caution when the crystal field calculations were carried out for the dtc and exan compounds. Considering Cr(dtc)$_3$ first (Table 2), we rule out the parameters [4] of our calculation I, e.g., $C/B = 4.0$, because the predicted energies of ^2E_g and $^2T_{1g}$ are about 4.5 kK too low. The search for our parameters was constrained by our observation of approximate band locations of "^2E_g", "$^2T_{1g}$", and the two intense electronic absorption band maxima of "$^4T_{2g}$" and "$^4T_{1g}$" at, respectively ~ 13 kK, ~ 13.6 kK, ~ 15.6 kK, and ~ 20 kK. However, again it is difficult to decide upon centers of gravity for $^2T_{1g}$, $^4T_{2g}$, and $^4T_{1g}$. For this reason only approximate parameters $Dq \cong 1.6$, $B \cong 0.4$, $C \cong 3$–3.3 can be given. The low energy region can be fitted nicely (^2E_g, $^2T_{1g}$, $^4T_{2g}$), but the order of $^4T_{1g}$ and $^2T_{2g}$ cannot unambiguously be decided, since several similar sets of parameters produce cross-overs of these two states (calculations II–V, Table 2). However, we definitely rule out the 21 kK MCD band as $^2A_{1g}$. Furthermore, $^4T_{1g}$ and $^2T_{2g}$ are predicted to be very close to each other, so that their D_3 components are expected to interact severely upon spin-orbit coupling.

The crystal field predictions and experimental situation for Cr(exan)$_3$ resemble those of Cr(dtc)$_3$, and are summarized in Table 3. Again, the parameters [4] of calculation I do not predict the bands of the low energy region. Second, while Witzke's [5] Racah parameters (calculation II: $B = 0.436$ kK, $C = 2.921$ kK), derived when the low energy spin doublets were not observed yet, are much better than Jorgensen's [4] (calculation I: $B = 0.39$ kK, $C = 1.56$ kK), the first two calculated spin doublets ^2E_g and $^2T_{1g}$ are still underestimated. Improved parameters are $Dq = 1.59$ kK, $B \cong 0.40$ kK and $C \cong 3.1$ kK. While this particular set of parameters predicts $^4T_{1g} > {}^2T_{2g}$ (calculation V), a quite similar set (calculation IV) has $^4T_{1g} < {}^2T_{2g}$ but the high energy region is not fitted well.

We are in the process of broadly extending this MCD work in order to determine effects of ring size[3]; of inductive effects of R of the ligand; of replacing S with Se; and of variations of temperature on MCD intensities and mechanisms. We defer trigonal crystal field and molecular orbital interpretations until these and our polarized crystal spectral data are completed.

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[3] This will be necessary because both ring size and types of coordinating atoms were changed simultaneously in going from Crox$_3^{3-}$ of Ref. [9] to Cr(III)S_6 of this study.

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