A Theoretical Study of the Electronic Spectra of Trigonally Distorted Transition Metal Complexes. I. d^1, d^3, d^8, and d^9 Complexes

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Abstract: The Hamiltonian appropriate to trigonally distorted octahedral molecules is restructured in terms of Dq; α, the azimuthal angle; and the ratio $\overline{r^2}/\overline{r^4}$. The transition energies in trigonally distorted d^1, d^3, d^8, and d^9 complexes are calculated in terms of the above variables. The polarized crystal spectra of a number of chromium(III) and nickel(II) complexes (including ruby and emerald) are fitted to the Hamiltonian and the derived parameters discussed in terms of the trigonal distortion. Transition energy and ground state energy space diagrams are constructed and used to rationalize the spectroscopic assignments chosen.

The electronic spectra of trigonally distorted complexes have been a source of intense study for many years. In particular, studies of the spectra of various metal ions dissolved in transparent trigonal lattices, such as alumina, have been used to critically test the crystal-field approach to electronic spectra.[1-14] In this paper we demonstrate that some of the previous studies have not been strictly correct because of the use of an oversimplified Hamiltonian. With the use of a more sophisticated Hamiltonian, crystal-field theory is used to recalculate the energy levels of a number of chromium(III) and nickel(II) complexes in trigonal environments for which polarized single-crystal data are available. The data for ruby (Cr^{3+} in Al_2O_3) are fitted with a much higher degree of accuracy than previously published. In addition, the Hamiltonian is analyzed to provide information concerning the spectra of trigonally distorted complexes involving compression or elongation along the threefold axis. Using the appropriate "ground state energy space diagram,"[15] the effect of distortion upon the ground state can be readily discerned.

Theoretical Development

Using standard techniques,[16] defining α as the angle (azimuthal) between the metal ligand bond vectors and a threefold axis, and using Racah's rationalized harmonics,[15] $C_q{}^k$, the Hamiltonian appropriate to an octahedral complex ML_6, with functions quantized along the threefold axis, is easily shown to be

$$H = (3Ze\overline{r^2}/R^3)(3\cos^2\alpha - 1)C_2{}^0 + (9Ze\overline{r^4}/4R^5)((35/3)\cos^4\alpha - 10\cos^2\alpha + 1)C_4{}^0 + (315/4)^{1/2}(Ze\overline{r^4}/R^5) \times \sin^3\alpha\cos\alpha(C_4{}^3 + C_4{}^{-3}) \quad (1)$$

where the symbols have their usual meaning.[16] For the specific value of α appropriate to an octahedron (0.955 radian), expression 1 collapses to

$$H = -(7Ze\overline{r^4}/3R^5)(C_4{}^0 - (10/7)^{1/2}(C_4{}^3 + C_4{}^{-3})) \quad (2)$$

This equation is appropriate for the evaluation of the wave functions and energies of an octahedral molecule quantized along the threefold axis.[17]

The wave functions and energies of a trigonally distorted octahedron, obtained by elongation or compression along the threefold axis, are often described using expression 2 as a cubic term and adding a perturbing axial term,[8] *viz.*

$$H = a(-C_4{}^0 + (10/7)^{1/2}(C_4{}^3 + C_4{}^{-3})) + bC_2{}^0 + cC_4{}^0 \quad (3)$$

where a contains the radial integral Dq and b and c, describing the axial perturbation, contain the radial integrals Ds and Dt, respectively. While a, b, and c can be functions of α, it is clear that expression 3 can only be equated to expression 1 in the special case of the regular octahedron, or if

$$a = 21Ze\overline{r^4}\sin^3\alpha\cos\alpha/2(2)^{1/2}R^5$$

and

$$c = (Ze\overline{r^4}/R^5)((9/4)(35/3)\cos^4\alpha - 10\cos^2\alpha + 1) + 21\sin^3\alpha\cos\alpha)/2(2)^{1/2}$$

These particular definitions do not appear to be cited in the previous literature. The retention of the $(10/7)^{1/2}$ factor is an error in that from eq 1, it is seen that this factor is an α-dependent term having that particular value for the octahedral solution. If the distortion from octahedral symmetry is very small, the error so introduced will also be small; however, it should be recognized that the $C_4{}^{\pm3}$ harmonics give rise to substantial off-diagonal elements in the energy matrices

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and a Hamiltonian of the type 3 will be quite valueless to describe larger deviations from octahedral symmetry.

Some authors, while using a Hamiltonian of the type 3, have parameterized the data in terms of the trigonal matrix elements v and v' defined by[2, 10]

$$(2/3)v = \langle t_{2g}^{0}|H_{T}|t_{2g}^{0}\rangle \qquad -v/3 = \langle t_{2g}^{\pm}|H_{T}|t_{2g}^{\pm}\rangle$$
$$v' = \langle t_{2g}^{\pm}|H_{T}|e_{g}^{\pm}\rangle \tag{4}$$

where H_T is the trigonal part of the Hamiltonian Such a procedure is quite valid, but one loses thereby some of the information inherent in the Hamiltonian.

In terms of Ds, Dt, and Dq, expression 1 can be rewritten as

$$H = -7DsC_2^0 - 21DtC_4^0 + 21Dq[QC_4^0 + P(C_4^3 + C_4^{-3})] \tag{5}$$

in which

$$Ds = -(3/7)Ze(\overline{r^2}/R^3)(3\cos^2\alpha - 1)$$
$$Dt = -(1/21)Ze(\overline{r^4}/R^5)((3/2)((35/3)\cos^4\alpha - 10\cos^2\alpha + 1) + (14/9))$$
$$Dq = Ze\overline{r^4}/6R^5 \tag{6}$$
$$Q = (3/14)((35/3)\cos^4\alpha - 10\cos^2\alpha + 1) - (4/9)$$
$$P = (45/7)^{1/2}\sin^3\alpha\cos\alpha$$

The definitions of Dq, Ds, and Dt parallel those used by most authors and have the particular advantage of allowing the Hamiltonian to be structured in a manner directly comparable to that for a D_{4h} molecule.[15] It will be noted that for the octahedral solution, with α = 0.955 radian, the angular parts of Ds and Dt go to zero, Q becomes $-2/3$, p becomes $(40/63)^{1/2}$, and expression 5 collapses to expression 2.

Using the tensor techniques described previously,[15] the one-electron (d) matrix elements of this Hamiltonian are

$$\langle\pm2|H|\pm2\rangle = 2Ds - Dt + QDq$$
$$\langle\pm1|H|\pm1\rangle = -Ds + 4Dt - 4QDq$$
$$\langle0|H|0\rangle = -2Ds - 6Dt + 6QDq \tag{7}$$
$$\langle\pm2|H|\mp1\rangle = \pm(35)^{1/2}PDq$$

In D_{3d} symmetry the d orbitals transform as $2e_g + a_{1g}$. Using (7) the "strong-field" matrix elements are found to be

$$\langle e_g(e_g)|H|e_g(e_g)\rangle = (7/3)Dt - (7/3)QDq + (2/3)(70)^{1/2}PDq$$
$$\langle e_g(t_{2g})|H|e_g(t_{2g})\rangle = Ds + (2/3)Dt - (2/3)QDq - (2/3)(70)^{1/2}PDq \tag{8}$$
$$\langle a_{1g}(t_{2g})|H|a_{1g}(t_{2g})\rangle = -2Ds - 6Dt + 6QDq$$
$$\langle e_g(t_{2g})|H|e_g(e_g)\rangle = (2)^{1/2}Ds - (5/3)(2)^{1/2}Dt + (5/3)(2)^{1/2}QDq + (1/3)(35)^{1/2}PDq$$

in which generic representations in octahedral symmetry are given in parentheses.[18] The classical trigonal distortion parameters K,[3] v, v',[2] are how defined

$$-v = 3K = (1/3)(9Ds + 20Dt - 20QDq - 2(70)^{1/2}PDq)$$
$$v' = (1/3)(2)^{1/2}(3Ds - 5Dt + 5QDq + (35/2)^{1/2}PDq) \tag{9}$$

These definitions differ from those previously used by the addition of the QDq and PDq terms.[19] Note that v is equal, approximately, to the splitting of the t_{2g} subshell and is positive when the e_g set lies lower than the a_{1g} orbital.

The F and P term matrix elements and the matrices appropriate for the evaluation of the spin-allowed transition energies of all high-spin d^n configurations are presented in the Appendix.

Experimental Section

All calculations were carried out with an IBM 360/50 computer using programs written in Watfiv. Spectroscopic data were obtained from the literature as referenced in the text.

The variables in expression 5 are α, the azimuthal angle; R, the metal–ligand distance; $\overline{r^2}$ and $\overline{r^4}$, the second- and fourth-power mean d-orbital radii; and Z, the effective nuclear charge. Because of the impossibility of obtaining an *a priori* calculation of any of the radial integrals using a pure ionic crystal-field model, the values of Ds and Dt are scaled against Dq by writing

$$Ds = -(18/7)DqR^2(\overline{r^2}/\overline{r^4})(3\cos^2\alpha - 1)$$
$$Dt = -(2/7)Dq((3/2)((35/3)\cos^4\alpha - 10\cos^2\alpha + 1) + (14/9))$$

which are obtained by rearranging expressions 5 in the text. The data are then expressed in terms of the variables α, Dq, $\overline{r^2}/\overline{r^4}$ (henceforth referred to as G), and, where appropriate, the Racah parameter B. Since G is always associated with R^2, R^2 is given a fixed value of 4. The problem therefore resolves into four unknowns and requires a minimum of four observables for solution.

Results

One Electron Energies. By use of expression 8, the effect of a trigonal distortion upon the d energy levels may be explored. Figure 1 shows how the d-orbital energies are influenced by the compression or elongation of an octahedral complex along a threefold axis. The octahedral solution appears near the center of the diagram with the octahedral value for α. On the left with α = 0, the levels are pertinent to a linear or cylindrical molecule, while on the right with $\alpha = \pi/2$ radians, the symmetry is hexagonal. These diagrams are constructed to be independent of the Racah parameter B. Changing Dq does not greatly influence their overall appearance but will shift the $e_g(e_g)$ level with respect to those derived from the t_{2g} subset. While it is obvious from Figure 1 that a change in G is more critical, values of G and Dq appropriate to first row transition metal complexes (Dq from about 800 to 2000 cm^{-1} and G from about 0.01 to 0.7)[20] yield diagrams which have the common feature of a double inversion of the sequence of the components of the t_{2g} subset at, and close to, the octahedral solution, (Figure 2). The most likely ground states for all d^n configurations in a trigonal

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(18) B. R. Hollebone, A. B. P. Lever, and J. C. Donini, *Mol. Phys.*, **22**, 155 (1971).

(19) Note that for the octahedral value of α, these QDq and PDq terms cancel out.

(20) The range of G quoted is that found experimentally by solving the appropriate matrices for the nickel(II) and chromium(III) complexes described in this paper, and for some vanadium(III) complexes to be published shortly.[21]

(21) A. B. P. Lever and B. R. Hollebone, in preparation.

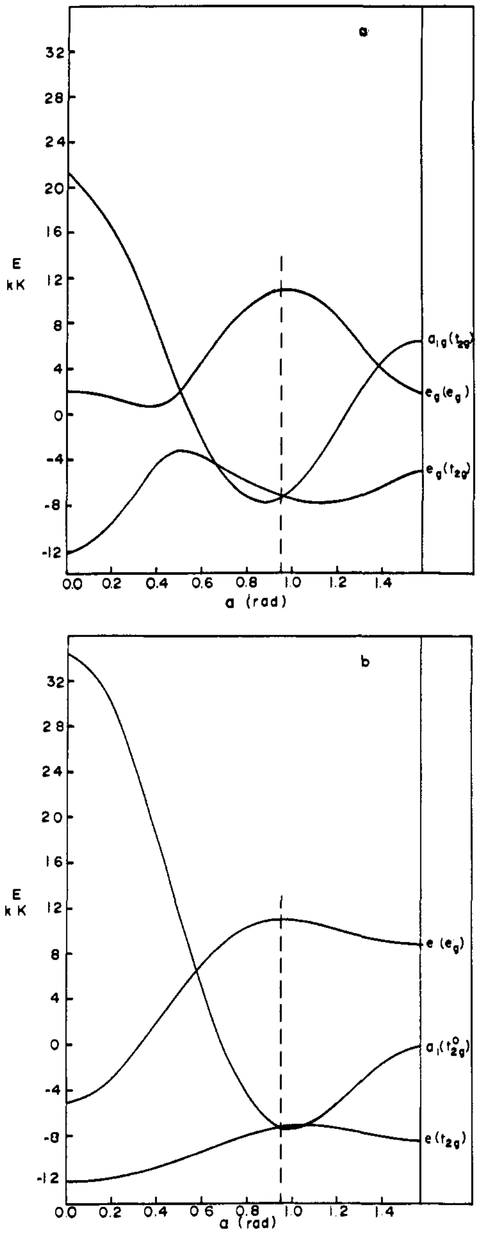

Figure 1. One-electron d-orbital energies as a function of α: (a) Dq = 1830 cm^{-1}, G = 0.016; (b) Dq = 1850 cm^{-1}, G = 0.2.

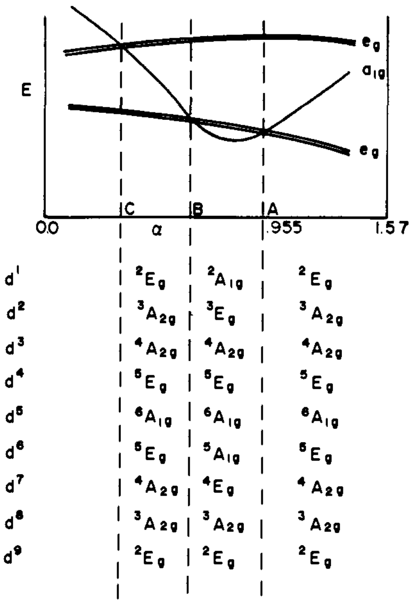

Figure 2. A generalized d-orbital energy diagram as a function of α. The ground terms expected for the d^n configurations are also included as a function of α.

field can be qualitatively determined by consideration of this feature. Since the a_{1g} level always lies above the $e_g(t_{2g})$ level for extreme compression or elongation, Figure 2 is appropriate for all systems. The crossover occurs at A, the octahedral solution, and at B which is arbitrarily placed to the left of A in this figure (elongation) but may appear to the right (compression) (see Figure 1). Outside the A–B region the $e_g(t_{2g})$ level always lies lowest and the ground states appropriate to the various configurations may be readily derived and are indicated. Inside the A–B region a different ground term prevails in d^1, d^2, d^6, and d^7 cases. The A–B region can be very narrow and can disappear, since A and B may be coincident. Thus the ground states peculiar to this interval in the d^1, d^2, d^6, and d^7 complexes exist for only a very narrow range of values of α. Under such circumstances a low-lying excited state, corresponding to the alternate ground term outside this region, must necessarily be present and will influence the magnetic properties of the material. Another ground-state change may occur at C, but this point corresponds to very considerable distortion from octahedral symmetry and will not normally be observed. In the circumstance that A and B are coincident, then elongation or compression of the octahedron always leads to the $e_g(t_{2g})$ level lying lowest. The possibility of this occurrence has not been recognized in the past.

Diagrams of the type shown in Figure 1 may be used to assign the spectra of trigonally distorted d^1 (and d^9) complexes, but little quantitative information may be obtained, since the number of observable transitions is less than the number of variables in the calculation. However, information about the ground states of some trigonally distorted titanium(III) complexes is known. When the Ti^{3+} ion is substituted into the corundum lattice, details of the relative intensities of the polarized crystal spectra suggest the presence of a ^2E ground state.[22] In titanium trisacetylacetonate both visible absorption spectra[23] and electron spin resonance data[24] suggest, on the other hand, that a $^2A_1$ ground state prevails. Similarly, a $^2A_1$ ground term is predicted in[25] $Al(Ti)Cl_3 \cdot 6H_2O$ and[8] $NaMgAl(Ti)(C_2O_4)_3 \cdot 9H_2O$. It is evident from the above discussion that these data cannot be used to infer anything about the nature of the distortion (*i.e.*, compression or elongation) without further information.

It is worth pointing out that the ^2E excited state (and presumably the ^2E ground state) of Ti(III) complexes is frequently split by a tetragonal perturbation induced by the Jahn–Teller effect.[7,22]

d^3 and d^8 Systems. Solution of the F and P matrices in the Appendix yields wave functions and energies appropriate for the discussion of d^3 or d^8 complexes in trigonal environments. Data for d^2 and d^7 can also

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Table I. Calculated Parameter Values[a]

Complex	Dq	Ds	Dt	B	α, radians	α^0	G	v	v'
Cr^{3+}–corundum (ruby) at 80°K	1830	32.5	−74.4	626	0.994	56° 57′	0.016	826	372
Cr^{3+}–beryl (emerald)	1626	651	−50.9	738	0.986	56° 30′	0.454	−1312	1148
Inverse assignment	1623	−722	43.8	783	0.919	52° 49′	0.416	1510	−1253
Cr^{3+}–$AlCl_3 \cdot 6H_2O$ at 300°K	1737	91.7	−45.6	699	0.9815	56° 17′	0.070	305	335
at 20°K	1752	124.7	−43.1	719	0.980	56° 09′	0.100	176	371
Cr^{3+}–GASH[b] at 300°K	1773	757	−43.7	674	0.980	56° 09′	0.600	−1714	1267
at 20°K	1788	487	−70.6	722	0.993	56° 54′	0.252	−584	999
Cr^{3+}–GASeH[c] at 300°K	1764	570	−62.4	710	0.9895	56° 38′	0.329	−929	1082
at 20°K	1761	681	−91.2	754	1.003	57° 28′	0.284	−932	1356
Cr^{3+}–NaMgAlOx[d] at 300°K	1752	297	−15.9	598	0.965	55° 17′	0.604	−681	494
Ni^{2+}–$Zn(bipy)_3SO_4$ at 300°K	1276	200	−27.3	729	0.977	55° 59′	0.250	−249	406
at 80°K	1293	294	−31.8	767	0.980	56° 09′	0.320	−477	560

[a] Dq, Ds, Dt, B, v, and v' are reported in cm^{-1}, G is dimensionless. [b] GASH = guanidine aluminum sulfate hexahydrate. [c] GASeH = guanidine aluminum selenate hexahydrate. [d] NaMgAlOx = $NaMgAl(C_2O_4)_3 \cdot 8H_2O$.

Table II. Calculated and Observed Transition Energies (wave numbers) from the Ground State (A_{2g})[a]

		E_g ($E1$, T_{2g})	A_{1g} ($A1$, T_{2g})	E_g (E_2, T_{1g})	A_{2g} ($A22$, T_{1g})	E_g ($E3$, $T_{1g}(P)$)	A_{2g} ($A23$, $T_{1g}(P)$)	W[b]	Ref
Ruby	Obsd	18,000	18,450	24,400	25,200	39,000	39,400		2
	Calcd	18,001	18,449	24,394	25,203	39,130	39,535	10	
Cr^{3+}–$AlCl_3$ at 300°	Obsd	17,240	17,420	24,100	24,690				7
	Calcd	17,260	17,421	24,098	24,688	38,193	38,061	25	
at 20°	Obsd	17,540	17,540	24,390	25,500				7
	Calcd	17,441	17,536	24,421	25,000	38,703	38,393	134	
Emerald	Obsd[c]	16,750	15,860	23,000	24,000	37,730?			13
	Calcd	16,450	15,854	23,097	24,017	37,455	34,614	420	
Inverse	Obsd	15,860	16,750	24,000	23,000	37,730?			
	Calcd	15,917	16,752	23,994	22,997	35,697	39,004	68	
Cr^{3+}–GASH at 300°	Obsd	17,860	17,240	24,510	25,000				7
	Calcd	17,991	17,232	24,432	25,003	39,916	36,803	220	
at 20°	Obsd	17,860	17,540	24,690	25,640				7
	Calcd	17,900	17,635	24,678	25,649	39,884	38,086	156	
Cr^{3+}–GASeH at 300°	Obsd	17,860	17,320	24,390	25,160				7
	Calcd	17,744	17,319	24,396	25,278	39,552	37,329	241	
at 20°	Obsd	17,780	17,330	24,450	25,800				7
	Calcd	17,655	17,240	24,456	25,802	39,884	37,229	223	
Cr^{3+}–oxalate	Obsd	17,620	17,316	23,670					8
	Calcd	17,628	17,305	23,673	23,836	38,230	37,048	20[d]	
Ni^{2+}–bipy at 300°	Obsd	12,740	12,660	19,040	19,600				26
	Calcd	12,782	12,663	19,040	19,600	30,247	29,324	45	
at 80°K	Obsd	12,800	12,750	19,410	20,100				26
	Calcd	12,988	12,761	19,391	20,107	31,095	29,680	221	

[a] The spin designations are omitted; they will be quartet for chromium(III) and triplet for nickel(II). In parentheses after the excited state label are cited the label used for this state in Figures 3–5 and the representation of the generic state in octahedral symmetry. [b] W is the absolute sum of the difference between the calculated and observed values of the energies of the first *four* states. [c] In view of the poor agreement between theory and experiment, these bands may be misassigned. [d] Calculated on the basis of the first three bands.

be readily obtained but will be dealt with in a future publication.[21]

The polarized crystal spectra of a number of chromium(III) and nickel(II) complexes have been fitted to these matrices to yield values of Dq, α, B, and G. In general, excellent agreement between the observed and calculated data is achieved. Once the range of G for a particular ion is known, a "ground state energy space diagram"[15] and an energy level diagram may be drawn. D_{3d} symmetry is assumed for these complexes, but the actual symmetry is probably slightly lower.

The spectrum of ruby (Cr(III) substituted in corundum) has been investigated in detail by many authors.[2,3,5,6,14,26] Using the data of McClure,[5] which were obtained at 80°K, values of the four unknowns were derived using an iterative computer program. The first four spin-allowed transitions were iterated to a best fit. The energies of the components of the $^4T_{1g}(P)$ level were then calculated and compared with those observed. It was felt inadvisable to include these components in the iterative program, thereby iterating over six observables, since these high energy components are probably appreciably mixed with charge-transfer transitions, and the simple crystal-field Hamiltonian would be inappropriate. The data are shown in Tables I and II. The agreement between the observed and calculated bands is essentially exact for the first four bands, and the overall agreement is excellent and considerably better than has appeared previously. The most complete previous analysis of the ruby spectrum by McFarlane[2] yielded $Dq = 1810\ cm^{-1}$, $B = 650\ cm^{-1}$, $v = 800\ cm^{-1}$, and $v' = 400\ cm^{-1}$. However, the agreement between the band energies calculated from these quantities and the observed band energies was less exact than that reported here.

The value of α (56° 57′) obtained suggests that the distortion is a compression along the threefold axis (but see below).

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(26) N. S. Hush and R. J. M. Hobbs, *Progr. Inorg. Chem.*, 10, 259 (1968).

Carlin and Walker[7] have reported the polarized crystal spectra of Cr(III) substituted into $AlCl_3 \cdot 6H_2O$ which also gives rise to a trigonal environment. ($D_{3d}{}^6$, $R\bar{3}c$)[27] for the metal atom. The relevant data are shown in Tables I and II. These data yield $v = 305$ and $v' = 335$ cm^{-1} compared with 360 and 410 cm^{-1}, respectively, cited by the authors. Agreement between the calculated and observed band energies is quite satisfactory. Low-temperature data were also reported and analysis of these leads to an increase in Dq and B but relatively little change in the values of the other parameters. Carlin and Walker[7] have also reported crystal data for chromium(III) substituted in guanidine aluminum sulfate and selenate both at room temperature and at lower temperatures. The data calculated from these results also appear in Tables I and II. As the error factor (W in Table II) indicates, the agreement between the experimental and calculated energies is not quite so satisfactory as with the other complexes above, but the deviation lies within the probable error limits of the experimental data. In these complexes v is negative, yielding a different orbital state sequence than for the chromium complexes described above. The sequence change arises from an order of magnitude increase in G and hence in Ds. Cooling the sample results in little change in Dq, a marked increase in B, and a small increase in the azimuthal angle (slight compression); G, on the other hand, decreases. The comparatively large temperature effect probably arises because of the marked anisotropic thermal properties of these crystals.[28] There is preferential contraction along the c axis which coincides with the threefold axis of the trigonally distorted octahedra; this contraction explains, qualitatively at least, the effect of temperature upon α. Piper and Carlin reported the crystal spectrum of chromium substituted into a sodium magnesium aluminum oxalate lattice.[8] The ${}^4A_{2g} \leftarrow {}^4A_{2g}$ (from ${}^4T_{1g}(F)$) transition, which is strictly forbidden as an electric-dipole transition in D_{3d} symmetry, was not observed; the data in Tables I and II are therefore based on the positions of the three observed bands. The data suggest that of the complexes discussed here, this is the least distorted from cubic symmetry.

The beautiful green color of an emerald also arises from lattice substitution of Cr^{3+} into trigonal sites of an oxide lattice, in this case in beryl, and the polarized spectra of such crystals have been reported.[13] It has not been possible, however, to find a parameter set which gives as satisfactory agreement between theory and experiment as for the other complexes discussed here. The best set yields a W value (Table II) of over 400 cm^{-1}. The excited-state sequence differs from that of ruby and parallels that of Cr^{3+}–GASH. The parameter set leads to values for the energies of the trigonal components of the $T_{1g}(P)$ term in considerable disagreement with the reported experimental positions of these bands.[13] Wood quoted values of 37,730 (A_{2g}) and 41,320 (E_g) cm^{-1}. If this assignment is inverted, then satisfactory agreement between the observed and calculated energies of the E_g component is achieved. In this case it would be necessary to assume that the A_{2g} component is not observed and that the band at 41,320 cm^{-1} must have some alternate assignment.

This point raises the general question of the validity of spectroscopic assignments of trigonal spectra using polarized crystal data. Without very detailed studies, polarized data provide little more than component energies; they do not necessarily provide unequivocal assignments. Thus, in the group D_3 the electric dipole selection rules are

$$A_1, A_2 \overset{\sigma}{\longleftrightarrow} E \quad A_1 \overset{\pi}{\longleftrightarrow} A_2 \quad A_2 \not\longleftrightarrow A_2$$

In the group D_{3d}, however, considering a trigonally distorted ML_6 complex, all the above transitions are vibronically allowed *in either polarization.* In the case of emerald, it is reported[13] that the band intensities are almost independent of temperature, suggesting electronic rather than vibronic transitions; the appearance of the ${}^4A_{2g} \leftarrow {}^4A_{2g}$ transitions may infer a vibronic contribution[13] or a strong C_3 component to the field. It is evident that the assignments cannot be considered unequivocal. Since the 37,730-cm^{-1} band appears strongly in both polarizations, the polarization data provide no definitive information concerning its assignment.

Indeed, if it is assumed that the emerald assignments should all be inverted, the data can be fitted to the Hamiltonian extremely well (Tables I and II) and an elongated distortion is predicted.

We do not feel that the more satisfactory agreement between theory and experiment using the inverted assignment *necessarily* infers that the published assignment is incorrect; however, in view of the ambiguity of the experimental data, further study is warranted.

We have been unable to obtain a satisfactory solution for the crystal data cited by Tomlinson[12] for some trigonally distorted CrS_6 chromophores using his assignments. The agreement between the energies calculated from our model for a "best fit" and the experimental energies is poor. Excellent agreement can be obtained if the assignment is inverted, a good fit ($W <$ 50) being possible. Values of about 0.88 are obtained for α, the B values lie between 425 and 490 cm^{-1}, and the classical v and v' parameters are positive and negative, respectively. However, in view of the fairly large distortion of these complexes from true D_3 symmetry[12,29] and the fact that the chromium–sulfur bond is likely to be sufficiently covalent to invalidate the simple crystal-field model being applied, discussion of this series of complexes is not warranted at this time. The agreement between the calculated and experimental data for an inverted assignment suggests that the assignments should be reconsidered; it would be advantageous to obtain crystal data over an extended temperature range to establish, definitely, whether electronic or vibronic selection rules are operative, and if the latter, to obtain information about the activating vibrations. The matrices appropriate to Cr^{3+} are also suitable for Ni^{2+} in a trigonal environment. There appears to be only one trigonally distorted complex in the literature for which sufficient polarized crystal data are available, namely Ni^{2+} substituted into a zinc trisbipyridyl sulfate lattice.[30] Agreement between the

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(28) Z. I. Ezhkova, G. S. Zhdanov, and M. M. Umanskii, *Kristallografiya*, 3, 231 (1958).

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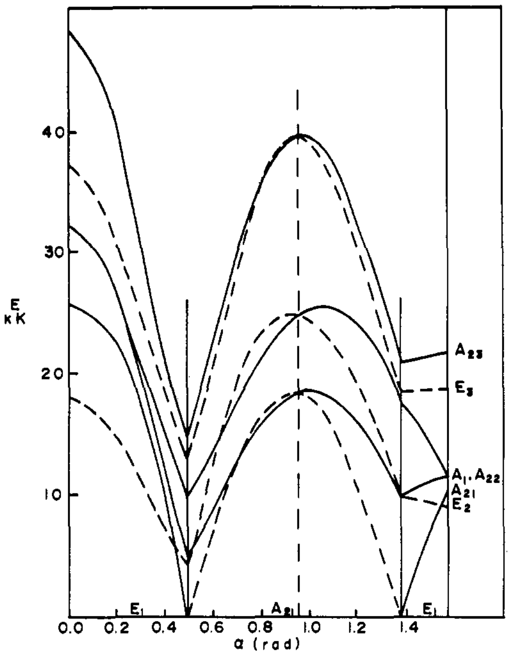

Figure 3. Transition energy diagram (d^3) as a function of α; parameters pertinent to ruby ($Dq = 1830\ cm^{-1}$, $B = 625\ cm^{-1}$, $G = 0.02$).

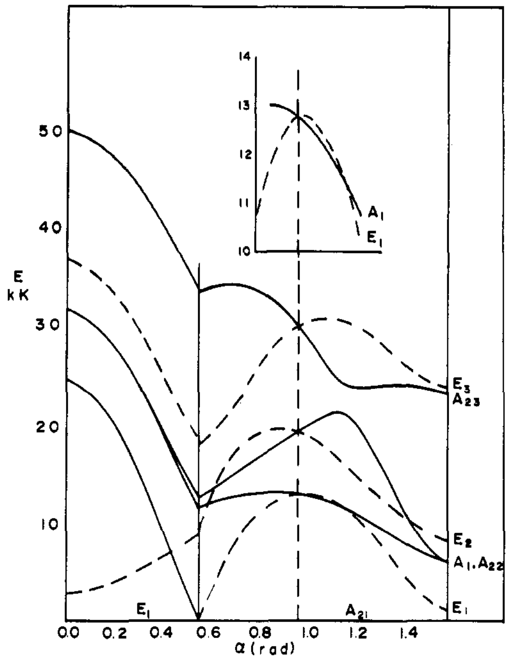

Figure 5. Transition energy diagram as a function of α; parameters pertinent to Ni^{2+}-$Zn(bipy)_3SO_4$ ($Dq = 1276\ cm^{-1}$, $B = 729\ cm^{-1}$, $G = 0.25$).

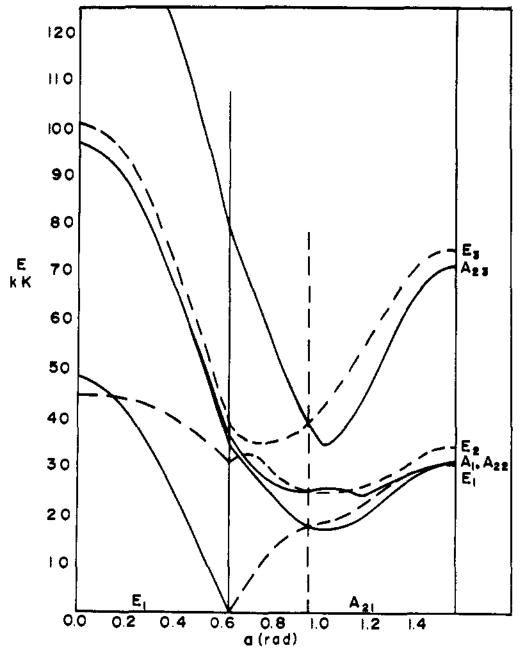

Figure 4. Transition energy diagram (d^3) as a function of α; parameters pertinent to Cr^{3+}-GASH ($Dq = 1773\ cm^{-1}$, $B = 674\ cm^{-1}$, $G = 0.6$).

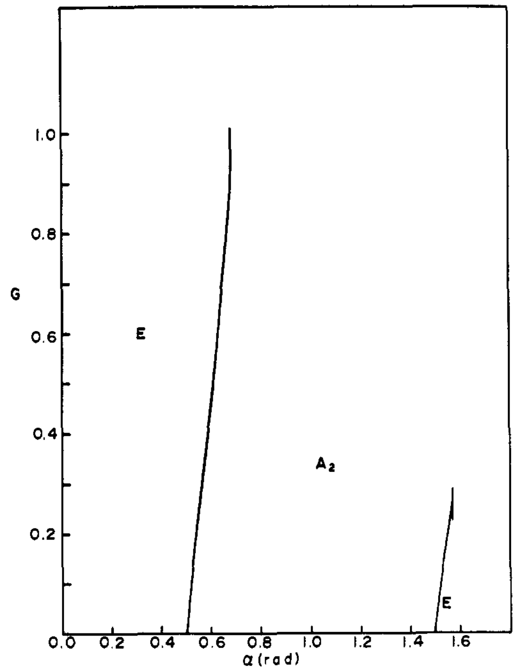

Figure 6. A plot of G vs. α illustrating the E_g-A_{2g} ground state changeover. The position and slope of the left-hand boundary line in this diagram are almost independent of Dq and B (within the ranges encountered in this paper). The upper limit of the right-hand boundary line is somewhat sensitive to Dq and B.

calculated and observed transition energies is quite satisfactory (Tables I and II) using the room-temperature spectrum. The low-temperature spectrum yields a less satisfactory but still acceptable fit. The Dq, B, and α parameters all increase on cooling in agreement with the behavior of the chromium(III) complexes.

Energy Level Diagrams. Traditional Tanabe–Sugano diagrams depict the energy levels of cubic complexes by plotting E/B against Dq/B. With the four variables extant for trigonal complexes, a family of such curves would be needed. For example, E/B could be plotted against Dt/B keeping Ds and Dq constant. Families of such curves with different values of Dq and Ds would be necessary to portray the energy levels of a range of different complexes. Of greater utility in this case is a plot of α against E for given values of Dq, G, and B. Such diagrams are shown in Figures 3–5 using values of Dq, B, and G pertinent to ruby, Cr^{3+}–GASH, and to the $Ni(bipy)_3{}^{2+}$ ion, respectively. The diagrams may be used in a general way to appreciate the effect of

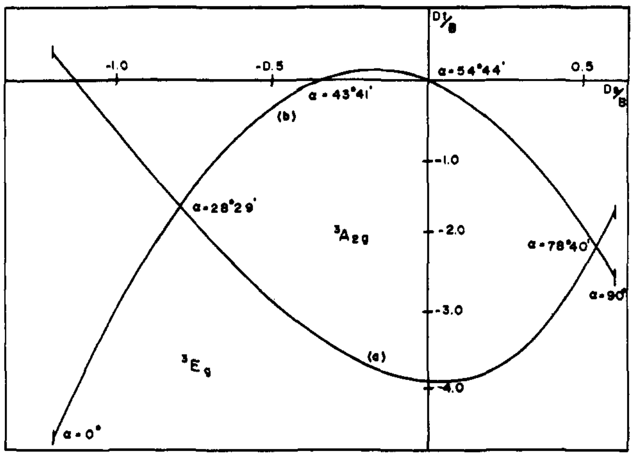

Figure 7. Ground state energy space diagram depicting the regions of existence of the E_g and A_{2g} ground terms (their boundary line is parabola a) as a function of Ds/B and Dt/B. The diagram is suitable for ruby (Dq = 1830 cm^{-1}, B = 626 cm^{-1}, G = 0.016). The parabola b defines the line of existence of ruby in this space.

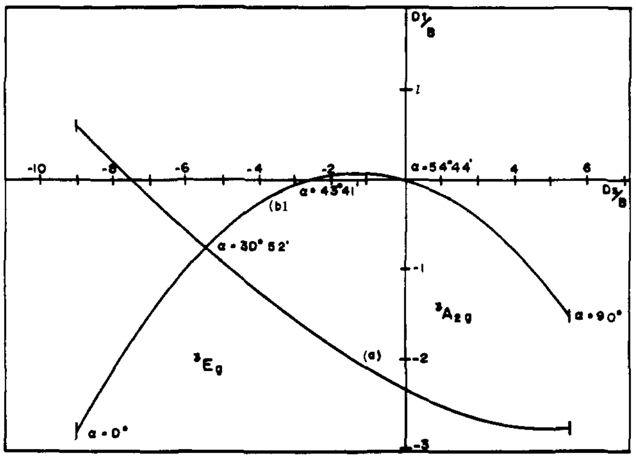

Figure 8. See Figure 7. This ground state energy space diagram is suitable for Ni^{2+}–$Zn(bipy)_3SO_4$ with Dq = 1276 cm^{-1}, B = 729 cm^{-1}, and G = 0.25.

the angular distortion upon the excited state energies. Small changes in Dq, B, or G have little effect upon these diagrams, but large changes, particularly in B and/or G, will change the relative order of the components of the various triplet states.

The extreme left-hand side of the diagram describes the energy level sequence in linear molecules, while on the right-hand side, the levels are pertinent to hexagonal molecules. With sufficient elongation *or* compression, trigonally distorted chromium(III) complexes could exist with ^4E_g ground terms. The position, with respect to α, of the ^4E_g to $^4A_{2g}$ crossover on the left-hand side of the diagram (compressed) is essentially independent of Dq, G, or B (Figure 6). The changeover on the right, however, disappears for larger values of G (Figure 6) and is not observable in Figures 4 and 5. It will be of interest to see whether trigonal chromium(III) complexes with ^4E_g ground terms can be designed.

An alternate way to appreciate the behavior of these trigonal complexes is through "ground state energy space" diagrams.[15] Consider the family of curves alluded to above, obtained in a three-dimensional space with axes E/B, Ds/B, and Dt/B, holding Dq/B constant. The ground state for all Ds/B and Dt/B lies at $E/B = 0$. The plane defined by $E/B = 0$ will contain the ground state and will intersect with a particular excited-state surface only if, for particular values of Ds/B and Dt/B, this excited state becomes the ground state. Ground state space diagrams appropriate for chromium(III) (ruby) and nickel(II) are shown in Figures 7 and 8, respectively. These diagrams clearly show the values of Ds/B and Dt/B needed to generate A_{2g} or E_g ground terms, a parabola (a) defining the boundaries between the regions of existence of these ground states. However, not all values of Ds/B and Dt/B are permitted to exist. With fixed values of Dq, B, and G, parabola b defines a "line of existence" on which all real complexes must lie according to their value of α. This line corresponds to the "cone of existence" possible for tetragonal complexes[15] but is a line *only* since there is only one chemical kind of ligand in D_{3d}. For chromium(III) (or nickel(II)) complexes in general, with slightly differing values of Dq, G, and B, there will exist a closely spaced family of such lines. Thus it is evident that trigonally distorted chromium(III) or nickel(II) complexes cannot exist with large positive values of Dt/B and that the allowed values of Ds/B and Dt/B lie in a narrow range.

Note that Figure 3 is a parabolic vertical cross section of the family of transition energy diagrams with the line of existence in Figure 7 as its base. A similar relationship prevails between Figures 5 and 8. A more conventional transition energy type diagram would be obtained as a noncurved vertical cross section based on a fixed value of Ds/B or Dt/B of the distortion energy space. These would intersect the line of existence at a single value of the variable, requiring one such diagram for each real complex; examples appropriate for tetragonal complexes have been published.[15]

Significance of G and α. It is well known that the crystal-field radial integrals if calculated *a priori* give poor agreement between calculated and observed values because of the inadequacy of the simple crystal-field model.[31] Nevertheless, comparison of the relative values of Dq in various cubic complexes often provides useful chemical information.[32] While values for the radial integrals Ds and Dt have often been calculated, apart from using the sign of Dt as an indication of tetragonal compression or elongation and to calculate in-plane and axial crystal field strengths,[31,33] these data have not generally been converted into useful chemical information.

In a physical sense α clearly has more tangible significance than G. While there may not be a direct correspondence between the value of α obtained from analysis of the electronic spectrum, an electronic α, and the crystallographic value, it is probable that the relative changes in the electronic α do reflect a measure of the elongation or compression along the threefold axis. All the complexes shown in the tables appear to be compressed, no definite examples of elongation having been found. As discussed, emerald or the CrS_6 trigonal chromophores discussed by Tomlinson[12] may be examples of such elongated systems. Unfortunately,

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all the systems discussed here involve impurity ions in host lattices; there is no reason to suppose that the azimuthal angle to a host ion will necessarily equal that subtended at the impurity ion, since substitution may involve distortion of the lattice.

The significance of the ratio G is less obvious;[15,34,35] because of the fixed value of R^2 used in these calculations, G is not exactly equal to $\overline{r^2}/\overline{r^4}$ but is related thereto. Indeed, from eq 12 of ref 15, it is evident that $R^2G = 4G = \gamma_2/\gamma_4$. The values of G in Table II vary over an order of magnitude with no obvious correlation with any of the other parameters. Hopefully, when more data have been collected and analyzed and the study has been extended over a wider range of ions, the behavior of G will become more predictable and meaningful. It is clear from Table I that the inversion of the splitting of the (one-electron) t_{2g} subshell in passing from the first two complexes to the later complexes, as indicated by the change in sign of v, arises because of the marked change in G (and therefore in Ds). If $\overline{r^4}$ derives primarily from the cubic field and remains roughly constant, then G is a measure of the second-order axial contribution to the total crystal field.

Certain simplifying assumptions have been made in this approach, but they should not alter the general chemical conclusions that can be derived from a study of this nature. Additional terms to the Hamiltonian arising from the fact that a given complex may not have strict D_{3d} symmetry will usually be small, and consideration of the relative values of the various parameters should be valid. Gross distortions such as markedly unequal metal–ligand bond lengths or angles[29] or twisting distortions about the C_3 axis (which have been discussed recently)[36,37] may, however, render this model invalid. The model has also assumed electronic rather than vibronic transition energies and, where such occur, this will introduce a small error into the absolute values of the parameters calculated.

Acknowledgment. We are indebted to the National Research Council (Ottawa) for financial support.

Appendix

Using the definitions in the text, the F and P term matrix elements are (relative to the free ion F term as zero)

F term diagonal elements $\langle L, M_L|H|L, M_L\rangle$

$$\langle 3, \pm3|H|3, \pm3\rangle = -Ds - 3Dt + 3QDq$$

$$\langle 3, \pm2|H|3, \pm2\rangle = +7Dt - 7QDq$$

$$\langle 3, \pm1|H|3, \pm1\rangle = +(3/5)Ds - Dt + QDq$$

$$\langle 3, \pm0|H|3, \pm0\rangle = +(4/5)Ds - 6Dt + 6QDq$$

off-diagonal elements

$$\langle 3, \pm3|H|3, 0\rangle = 3(7)^{1/2}PDq$$

$$\langle 3, \pm2|H|3, \pm1\rangle = -(14)^{1/2}PDq$$

P term diagonals

$$\langle 1, \pm1|H|1, \pm1\rangle = 15B + (7/5)Ds$$

$$\langle 1, 0|H|1, 0\rangle = 15B - (14/15)Ds$$

The off-diagonal is zero. The group theoretical trigonal matrix elements derived from the above are

$$A_{1g} = -Ds - 3Dt + 3QDq$$

A_{2g} Matrix

$$A(1, 1) = -(14/3)Dt + (14/3)QDq - (4/3)(70)^{1/2}PDq$$

$$A(1, 2) = -2(5)^{-1/2}Ds + (2/3)(5)^{1/2}Dt - (2/3)(5)^{1/2}QDq - (1/3)(14)^{1/2}PDq$$

$$A(1, 3) = 4(5)^{-1/2}Ds - (4/3)(5)^{1/2}Dt + (4/3)(5)^{1/2}QDq + (2/3)(14)^{1/2}PDq$$

$$A(2, 1) = A(1, 2)$$

$$A(2, 2) = -(1/5)Ds - (13/3)Dt + (13/3)QDq + (4/3)(70)^{1/2}PDq$$

$$A(2, 3) = -(8/5)Ds + (8/3)Dt - (8/3)QDq + (1/3)(70)^{1/2}PDq$$

$$A(3, 1) = A(1, 3)$$

$$A(3, 2) = A(2, 3)$$

$$A(3, 3) = 15B - (14/5)Ds$$

E_g Matrix

$$E(1, 1) = (1/2)Ds + (1/3)Dt - (1/3)QDq - (1/3)(70)^{1/2}PDq$$

$$E(1, 2) = -(1/2)(5)^{-1/2}Ds + (4/3)(5)^{1/2}Dt - (4/3)(5)^{1/2}QDq - (2/3)(14)^{1/2}PDq$$

$$E(1, 3) = -4(5)^{-1/2}Ds - (5)^{1/2}Dt + (5)^{1/2}QDq + (7/2)^{1/2}PDq$$

$$E(2, 1) = E(1, 2)$$

$$E(2, 2) = (1/10)Ds + (17/3)Dt - (17/3)QDq + (1/3)(70)^{1/2}PDq$$

$$E(2, 3) = (4/5)Ds + Dt - QDq + (35/2)^{1/2}PDq$$

$$E(3, 1) = E(1, 3)$$

$$E(3, 2) = E(2, 3)$$

$$E(3, 3) = 15B + (7/5)Ds$$

The above energy matrices are suitable for d^3 and d^8 ions in trigonal environments. They may be converted for use with d^2 and d^7 ions by multiplying the coefficients of Dq, Ds, and Dt by -1.

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