

# Coupled Pairs of Chromium(III) Ions in Crystals of CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub>. A Case of Charge Compensation Induced Pair Formation

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**Abstract:** When crystals of CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub> are doped with trivalent chromium there is an extraordinary tendency for the Cr(III) ions to form exchange coupled pairs. The EPR spectra indicate that the majority of the Cr(III) ions enter these crystals as pairs even when the concentration of Cr(III) is as low as 1 part per 1000. The three host materials adopt the linear chain CsNiCl<sub>3</sub> structure. The pairs consist of two Cr(III) ions which are located in magnesium or cadmium ion sites situated on either side of a vacant magnesium or cadmium ion site. The stability of this Cr(III)-vacancy-Cr(III) system appears to result from the charge compensation requirement of the linear chain CsNiCl<sub>3</sub> lattice. The temperature dependence of the EPR spectra suggest that the exchange interactions between the Cr(III) ions in the pairs are antiferromagnetic in the CsMX<sub>3</sub> crystals. The formation of Cr(III)-Cr(III) pairs in the CsMX<sub>3</sub> crystals is dramatically reduced by the presence of small monovalent ions such as sodium and lithium or trivalent ions such as indium. These observations are explained in terms of the localized charge compensation requirement of the host materials. The primary factors governing the distribution of trivalent impurities in the CsMX<sub>3</sub> crystals appear to be electrostatic in nature.

## Introduction

Electron paramagnetic resonance is an extremely powerful tool for probing the electronic structures of paramagnetic systems. In EPR studies involving solids it is common practice to dope the paramagnetic species of interest into a crystal of some diamagnetic host material. Usually the doped crystals are prepared so that the concentration of paramagnetic centers is quite low (less than 1 part in 100). In this way the magnetic interactions between centers are minimized. The use of doped crystals makes it possible to study the EPR spectra of oriented systems which are magnetically "isolated". This technique has been used extensively in the study of paramagnetic metal ions. Over the past 30 years, hundreds of studies of the EPR spectra of different metal ions in various host lattices have appeared in the literature.

During the growth of a doped crystal it is possible that two paramagnetic impurities will enter neighboring sites in the lattice to produce a magnetically interacting dimer or "pair". If the concentration of the paramagnetic species is low, the statistical probability of such an occurrence is quite small. Thus, under normal circumstances the concentration of pairs in a doped crystal is much smaller than that of the isolated paramagnetic centers. A striking exception to this general rule has been observed in our laboratories. When trivalent chromium is doped into crystals of certain halide double salts there is an extraordinary tendency for the Cr(III) ions to cluster in pairs. It is evident from the EPR spectra that the majority of Cr(III) ions enter the lattice as exchange coupled pairs even when the concentration of chromium is less than 1 part in 1000. This phenomenon has been observed in three isostructural host materials, CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub>.

The fact that the Cr(III) ions find each other during the crystallization process indicates that there is actually a "chemistry" to the distribution of trivalent impurities in these particular host lattices. This conclusion is supported by the fact that the introduction of certain other impurities into the doped crystals has a profound influence on the distribution of the Cr(III) ions. This paper presents a spectroscopic characterization of the Cr(III)-Cr(III) pairs in the three host materials and an elucidation of the chemistry of trivalent impurities in the CsMX<sub>3</sub> lattices.

## Experimental Section

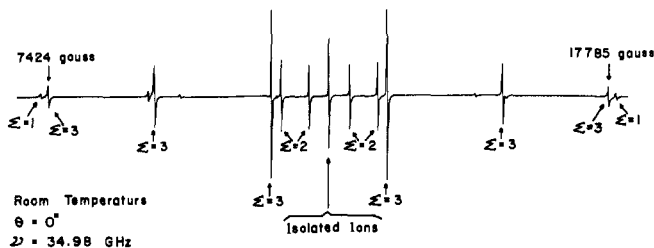
**Preparation of Doped Crystals.** The magnesium salts, CsMgCl<sub>3</sub> and

CsMgBr<sub>3</sub>, were prepared by fusing equimolar mixtures of cesium halide and anhydrous magnesium halide in evacuated Vycor ampules. The CsCdBr<sub>3</sub> was crystallized from aqueous HBr solution. The two magnesium salts are quite hygroscopic while CsCdBr<sub>3</sub> is stable in air. Doped crystals were prepared by adding small amounts of the appropriate metal halide(s) to samples of the CsMX<sub>3</sub> salts. These mixtures were sealed in Vycor ampules under a reduced pressure of either Br<sub>2</sub> or Cl<sub>2</sub> gas. The halogen gas was used primarily to keep the chromium in the trivalent oxidation state. Single crystals were grown from the melt by the Bridgman method. The apparatus and procedure have been previously described.<sup>1</sup> The CsMgCl<sub>3</sub> crystals doped with Cr(III) are red-purple while the Cr(III) containing CsMgBr<sub>3</sub> and CsCdBr<sub>3</sub> crystals are green.

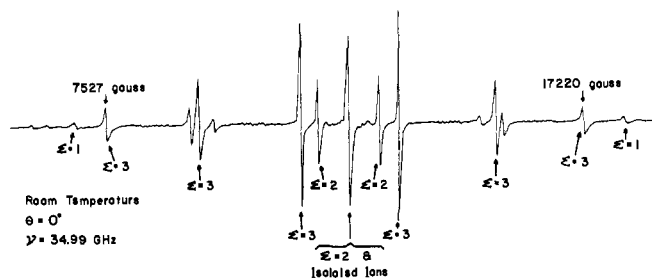
**EPR Measurements.** The fact that the CsMX<sub>3</sub> crystals readily cleave parallel to the crystallographic *c* axis ([110] face) greatly facilitates the preparation and orientation of samples for EPR study. In most cases the crystals were mounted so that the *c* axis was contained in the plane of rotation of the magnetic field. Thus, the spectra could be studied as a function of  $\theta$ , the angle between the magnetic field and the crystallographic *c* axis. Spectra were recorded on a Varian E-3 X-band spectrometer and a Varian E-12 Q-band spectrometer. Both instruments use 100-kHz field modulation. The E-12 is equipped with a Spectromagnetic Industries gaussmeter which allows accurate determination of the peak positions (within 3–5 G) in the spectra. On both instruments, microwave frequencies were read directly from the frequency indicators which had been calibrated previously with polycrystalline DPPH ( $g = 2.0036$ ). Frequencies are expected to be accurate within 0.02 GHz.

## Results and Discussion

**Structure of the Host Materials.** The three salts, CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub>, belong to an extensive series of RMX<sub>3</sub> halides which adopt the hexagonal CsNiCl<sub>3</sub> structure.<sup>2–4</sup> The CsNiCl<sub>3</sub> structure can be described as an array of infinite parallel linear chains composed of [MX<sub>6</sub><sup>4-</sup>] octahedra sharing opposite faces. These chains are negatively charged and have the overall stoichiometry, [MX<sub>3</sub><sup>-</sup>]<sub>n</sub>. The [MX<sub>3</sub><sup>-</sup>]<sub>n</sub> chains have threefold symmetry with the principal axis coincident with the crystallographic *c* axis. The univalent cations occupy positions between chains and serve to neutralize the negative charge. Although the coordination about the divalent metal ion is approximately octahedral, there is a noticeable trigonal distortion. Apparently the electrostatic repulsions between the divalent metal ions cause the [MX<sub>3</sub><sup>-</sup>]<sub>n</sub> chains to "stretch out" from idealized octahedral geometry. The RMX<sub>3</sub> structures which have been reported invariably show the M-X-M bridging angle to be a few degrees larger



**Figure 1.** EPR spectrum of Cr(III) in a crystal of CsMgCl<sub>3</sub>. The spectrum was recorded with an 8-min scan, 10 000-G sweep, 0.03-s time constant, 10-G modulation amplitude, and 12.5 receiver gain.



**Figure 2.** EPR spectrum of Cr(III) in a crystal of CsMgBr<sub>3</sub>. The spectrum was recorded with an 8-m scan, 10 000-G sweep, 0.1-s time constant, 17-G modulation, amplitude, and 63 receiver gain.

**Table I.** Structural Data for CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub>

Compd	Lattice constants, Å		M-X distance, Å	M-X-M angle, deg	Ref
	<i>a</i>	<i>c</i>			
CsMgCl <sub>3</sub>	7.269	6.187	2.496	76.6	2
CsMgBr <sub>3</sub>	7.610	6.502	2.664	75.2	3
CsCdBr <sub>3</sub>	7.658	6.705			4

than that expected for regular octahedra sharing faces (70.5°). Structural data for CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub> are given in Table I.

**EPR Spectra of the Cr(III)-Cr(III) Pairs.** The EPR spectra of a number of divalent transition metal ions doped into CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub> have been reported.<sup>2,4-6</sup> In all cases the spectra arise from a single type of isolated ion in an axially symmetric site. Apparently, the divalent impurities replace the Mg(II) or Cd(II) ions without causing major structural changes in the CsMX<sub>3</sub> lattice. At the doping levels that were used there was no evidence that the divalent impurities tend to cluster in pairs or higher aggregates. The situation changes markedly when trivalent ions are introduced into the CsMX<sub>3</sub> lattices. As was reported in a preliminary communication, the EPR spectrum of CsMgCl<sub>3</sub> crystals doped with trivalent chromium contains resonances from an exchange coupled pair of Cr(III) ions as well as from several types of isolated Cr(III) ions.<sup>7</sup> In most crystals the pair resonances dominate the spectrum which indicates that the majority of the Cr(III) ions enter the lattice as pairs. Similar behavior is observed when crystals of CsMgBr<sub>3</sub> and CsCdBr<sub>3</sub> are doped with Cr(III).

When two Cr(III) ions interact to form a magnetically coupled pair, the spins ( $S = 3/2$ ) on each ion combine as vectors to produce a manifold of four spin states each characterized by a total spin quantum number,  $\Sigma$  ( $\Sigma = 0, 1, 2, \text{ and } 3$ ). The degeneracy of this four-state manifold is lifted by the exchange interactions. The spectra of CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub> crystals doped with Cr(III) contain resonances which can be assigned to the  $\Sigma = 1, 2, \text{ and } 3$  states of a coupled pair. (The  $\Sigma = 0$  state is nonmagnetic.) Figures 1 and 2 show the spectra of Cr(III) in crystals of CsMgCl<sub>3</sub> and CsMgBr<sub>3</sub>. The spectrum of Cr(III) in CsCdBr<sub>3</sub> is very similar to that of Cr(III) in CsMgBr<sub>3</sub>.

If the exchange energies are large compared to the other magnetic interactions in a coupled pair, a separate spin Hamiltonian may be written for each spin state.<sup>8,9</sup> The Hamiltonian for a given  $\Sigma$  state contains the terms appropriate for a paramagnetic system with a total spin of  $\Sigma$ . In all three host lattices the pair resonances exhibit axial symmetry about the crystallographic *c* axis. The resonances from the  $\Sigma = 1$  state are satisfactorily described by the axial Hamiltonian

$$H = g_{\parallel}\beta H_z \hat{\Sigma}_z + g_{\perp}\beta(H_x \hat{\Sigma}_x + H_y \hat{\Sigma}_y) + D_{\Sigma}[\hat{\Sigma}_z^2 - (1/3)\Sigma(\Sigma + 1)]$$

The  $\hat{\Sigma}$  operators represent the electron spin operators for the coupled pair of Cr(III) ions. The first two terms describe the electron Zeeman interaction while the third term describes the zero-field splitting. The resonances from the  $\Sigma = 2$  and  $\Sigma = 3$  states are described by similar Hamiltonians except that additional higher order terms are needed to completely explain the zero-field splittings. The  $\Sigma = 2$  resonance requires a fourth-order term while the  $\Sigma = 3$  resonance requires both fourth- and sixth-order terms. The necessary fourth-order zero-field term takes the form

$$(F_{\Sigma}/180)[35\hat{\Sigma}_z^4 + 30\Sigma(\Sigma + 1)\hat{\Sigma}_z^2 + 25\hat{\Sigma}_z^2 - 6\Sigma(\Sigma + 1) + \Sigma^2(\Sigma + 1)^2]$$

Similarly, the sixth-order term can be expressed as follows.

$$(G_{\Sigma}/1260)[231\hat{\Sigma}_z^6 - 316\Sigma(\Sigma + 1)\hat{\Sigma}_z^4 + 735\hat{\Sigma}_z^4 + 105\Sigma^2(\Sigma + 1)^2\hat{\Sigma}_z^2 - 525\Sigma(\Sigma + 1)\hat{\Sigma}_z^2 + 294\hat{\Sigma}_z^2 - S\Sigma^3(\Sigma + 1)^3 + 40\Sigma^2(\Sigma + 1)^2 - 60\Sigma(\Sigma + 1)]$$

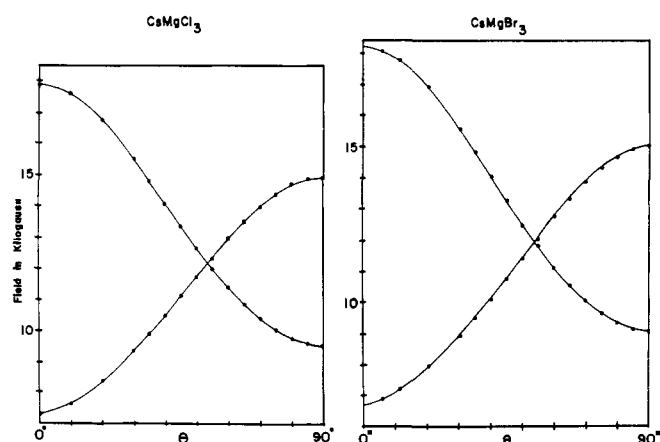
These higher order terms contribute only to the diagonal elements of the Hamiltonian matrices. (A complete discussion of higher order zero-field terms is available in a number of EPR texts such as that of Abragam and Bleaney.<sup>10</sup>)

The spin Hamiltonian parameters for the  $\Sigma = 1, 2, \text{ and } 3$  resonances of the Cr(III)-Cr(III) pairs were derived from spectra recorded with the magnetic field either parallel or perpendicular to the crystallographic *c* axis. The data for the three host lattices are given in Table II. If this spin Hamiltonian treatment is valid, it should be possible to describe the spectrum observed at any crystal orientation. The angular dependence of any resonance may be calculated by solving the appropriate Hamiltonian as a function of the angle  $\theta$  (where  $\theta$  is the angle between the crystallographic *c* axis and the magnetic field). The exact solutions to the  $\Sigma = 1, 2, \text{ and } 3$  Hamiltonians may be readily obtained by computer diagonalization of the Hamiltonian matrices. Figures 3 and 4 show the excellent agreement between the observed and calculated angular dependences of  $\Sigma = 1$  and  $\Sigma = 3$  resonances in CsMgCl<sub>3</sub> and CsMgBr<sub>3</sub>. Similar results are obtained for the pairs in CsCdBr<sub>3</sub>. The angular dependences of the  $\Sigma = 2$  resonances are rather unusual because of the large magnitude of the fourth-order zero-field term ( $F_2$ ). Unfortunately, there are small but noticeable discrepancies between some of the observed and calculated resonance fields at  $\theta$  angles greater than 30° (see Figure 5). These discrepancies are significantly greater in the spectra recorded at 35 GHz than in those observed at 9.5 GHz. The only explanation we can offer is that the exchange energies may not be large enough to completely justify the use of independent spin Hamiltonians for the  $\Sigma = 1, 2, \text{ and } 3$  states. Such a treatment will break down as the magnitudes of the Zeeman interactions begin to approach those of the exchange energies. Thus, one would expect the disagreement to be greater at 35 GHz than at 9.5 GHz. In spite

**Table II.** Spin Hamiltonian Parameters<sup>a</sup> for the Cr(III)–Cr(III) Pairs

Temp, K	Host lattice	$\Sigma$	$g_{\parallel}$	$g_{\perp}$	$D_{\Sigma}, \text{cm}^{-1}$	$F_{\Sigma}, \text{cm}^{-1}$	$G_{\Sigma}, \text{cm}^{-1}$
296	CsMgCl <sub>3</sub>	1	1.984 (4)	1.998 (4)	+0.492 (4)		
		2	1.983 (3)	1.983 (10)	−0.0218 (3)	+0.0913 (8)	
		3	1.983 (3)	1.981 (3)	−0.0974 (5)	+0.0020 (3)	+0.0002 (1)
	CsMgBr <sub>3</sub>	1	2.011 (5)	2.023 (5)	+0.542 (4)		
		2	2.013 (5)	2.009 (10)	−0.0089 (5)	+0.0781 (8)	
		3	2.013 (5)	2.008 (5)	−0.0939 (5)	+0.0018 (5)	+0.0003 (1)
CsCdBr <sub>3</sub>	1	2.01 (1)	2.024 (5)	+0.596 (5)			
	2	2.011 (5)	2.01 (1)	−0.0124 (5)	+0.112 (1)		
	3	2.012 (5)	2.006 (5)	−0.104 (1)	+0.0022 (5)	+0.0002 (1)	
77	CsMgCl <sub>3</sub>	1	1.985 (4)	1.993 (4)	+0.492 (4)		
		2	1.985 (3)	1.985 (10)	−0.0206 (3)	+0.0764 (9)	
		3	1.986 (3)	1.982 (3)	−0.0976 (5)	+0.0017 (3)	+0.0002 (1)
	CsCdBr <sub>3</sub>	1	2.01 (1)	2.017 (5)	+0.664 (6)		
		2	2.011 (5)	2.01 (1)	−0.0150 (5)	+0.0963 (8)	
		3	2.011 (5)	2.007 (5)	−0.114 (1)	+0.0023 (5)	+0.0002 (1)

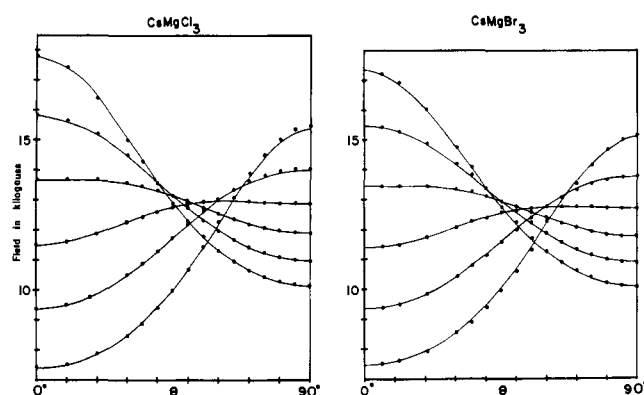
<sup>a</sup> The signs of the zero-field parameters are based on the analysis presented in Table III. The numbers in parentheses represent the estimated maximum error in the last place of the reported parameter.



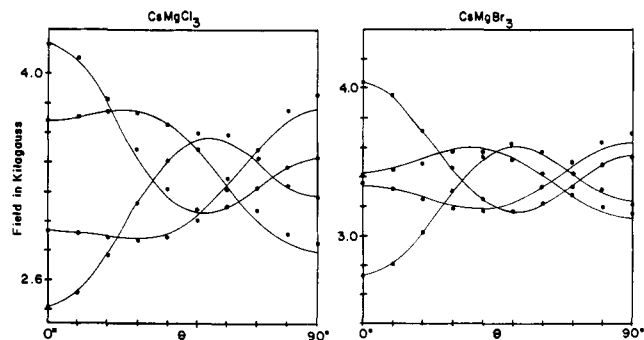
**Figure 3.** Angular dependences of the  $\Sigma = 1$  resonances from the Cr(III)–Cr(III) pairs in CsMgCl<sub>3</sub> and CsMgBr<sub>3</sub>. The resonance fields for the 35-GHz spectra are plotted vertically while the angle  $\theta$  is plotted horizontally. The black dots represent the experimental data while the solid curves are calculated from the spin Hamiltonian parameters in Table II.

of this problem with the  $\Sigma = 2$  state this analysis provides a very rational basis for interpreting the EPR spectra of the Cr(III)–Cr(III) pairs in the three host lattices. There is no question that the major resonances in the spectra of the Cr(III) doped CsMX<sub>3</sub> crystals arise from a single type of exchange coupled pair.

It is possible to determine the energy intervals between the spin states by following the intensities of resonances originating from the different spin states as a function of temperature. This presumes that the populations of the spin states obey Boltzmann statistics and that the relative intensities of the different resonances are directly related to the spin state populations. Unfortunately, the spectra of the Cr(III)–Cr(III) pairs do not exhibit large enough relative intensity changes between room and liquid nitrogen temperature to accurately determine all the energy intervals. The intensities of the resonances from the  $\Sigma = 3$  state show a small but noticeable decrease relative to those from the  $\Sigma = 2$  state as the CsMX<sub>3</sub> crystals are cooled from 298 to 77 K. This decrease is approximately 20% in CsMgCl<sub>3</sub>, 35% in CsMgBr<sub>3</sub>, and 50% in CsCdBr<sub>3</sub>. The changes in the intensities of the  $\Sigma = 2$  resonances relative to those from the  $\Sigma = 1$  states are not large



**Figure 4.** Angular dependences of the  $\Sigma = 3$  resonances from the Cr(III)–Cr(III) pairs in CsMgCl<sub>3</sub> and CsMgBr<sub>3</sub>. The resonance fields for the 35-GHz spectra are plotted vertically while the angle  $\theta$  is plotted horizontally. The black dots represent the experimental data while the solid curves are calculated from the spin Hamiltonian parameters in Table II.



**Figure 5.** Angular dependences of the  $\Sigma = 2$  resonances from the Cr(III)–Cr(III) pairs in CsMgCl<sub>3</sub> and CsMgBr<sub>3</sub>. The resonance fields of the 9.5-GHz spectra are plotted vertically while the angle  $\theta$  is plotted horizontally. The black dots represent the experimental data while the solid curves are calculated from the spin Hamiltonian parameters in Table II.

enough to be determined with any accuracy. (This is partially due to the fact that the intensities of the  $\Sigma = 1$  resonances are difficult to follow as a function of temperature.) These measurements do not provide a complete description of the energy

**Table III.** Analysis of the Second-Order Zero-Field Splitting Parameters

$D_{\Sigma} = 3\alpha D_e - \beta D_c$	$\Sigma$	$\alpha$	$\beta$
	1	17/10	-12/5
	2	1/2	0
	3	3/10	2/5

Results for the CsMX <sub>3</sub> Crystals <sup>a</sup>		
	$D_e, \text{cm}^{-1}$	$D_c, \text{cm}^{-1}$
CsMgCl <sub>3</sub>	-0.0140	-0.224
CsMgBr <sub>3</sub>	-0.0057	-0.230
CsCdBr <sub>3</sub>	-0.0080	-0.254

Calculated Parameters			
	$D_1, \text{cm}^{-1}$	$D_2, \text{cm}^{-1}$	$D_3, \text{cm}^{-1}$
CsMgCl <sub>3</sub>	+0.466	-0.0210	-0.102
CsMgBr <sub>3</sub>	+0.523	-0.0086	-0.0971
CsCdBr <sub>3</sub>	+0.569	-0.0120	-0.109

<sup>a</sup> The signs are determined on the basis that  $D_e$  is negative.

level system of the Cr(III)-Cr(III) pairs but the observations do suggest that the  $\Sigma = 3$  state is above the  $\Sigma = 2$  state by about 15 cm<sup>-1</sup> in CsMgCl<sub>3</sub>, 30 cm<sup>-1</sup> in CsMgBr<sub>3</sub>, and 50 cm<sup>-1</sup> in CsCdBr<sub>3</sub>. While these energies are at best qualitative, it seems reasonably certain that the  $\Sigma = 3$  state is higher in energy than the  $\Sigma = 2$  state in all three CsMX<sub>3</sub> crystals. This indicates that the exchange interactions are antiferromagnetic. It is unfortunate that intensity measurements could not be carried out at temperatures below that of liquid nitrogen. At sufficiently low temperatures the thermal depopulation of the higher energy spin states will cause dramatic relative intensity changes in the pair spectra. Thus, it should be possible to accurately determine the energy intervals for the complete four-state manifold of the Cr(III)-Cr(III) pair.

In addition to relative intensities there are other small but noticeable changes in the spectra of the Cr(III)-Cr(III) pairs as the CsMX<sub>3</sub> crystals are cooled from room to liquid nitrogen temperature. These changes reflect the fact that the zero-field splitting parameters are slightly temperature dependent (see Table II). Since the variations in the parameters are small, it is reasonable to assume that the observed temperature dependence results from the minor structural changes which take place in the host lattice as a crystal is cooled. Relative to other systems containing coupled pairs of d<sup>3</sup> ions, the most unusual feature of the pairs in the CsMX<sub>3</sub> crystals is the large fourth-order zero-field term in the Hamiltonian for the  $\Sigma = 2$  resonances. Analyses of the spectra from V(II)-V(II) pairs in MgO<sup>11</sup> and KMgF<sub>3</sub>,<sup>12</sup> Cr(III)-Cr(III) pairs in Al<sub>2</sub>O<sub>3</sub><sup>13</sup> and ZnGa<sub>2</sub>O<sub>4</sub>,<sup>14</sup> and salts of the dimeric Cr<sub>2</sub>Cl<sub>9</sub><sup>3-</sup> ion<sup>15,16</sup> have not required the use of a fourth-order term. It would appear that the pairs in the CsMX<sub>3</sub> crystals differ from these other pair systems in some significant aspect. Unfortunately, we have no insight into the physical significance of the large fourth-order term.

Unlike the fourth-order terms an analysis of the second-order zero-field terms ( $D_{\Sigma}$ ) does provide useful information. According to the theoretical treatment of Owen the second-order zero-field splittings of a coupled pair of paramagnetic ions are the result of contributions from two distinct effects (see Table III).<sup>8,9</sup> One contribution arises from the anisotropic magnetic interactions between the two ions ( $D_e$ ), while the other results from distortions in the crystal lattice ( $D_c$ ) which affect the zero-field splittings of the individual ions. For a given  $\Sigma$  state the zero-field parameter,  $D_{\Sigma}$ , is determined by  $D_e$ ,  $D_c$ , and the mixing coefficients  $\alpha$  and  $\beta$ . The mixing coefficients for a coupled pair of  $S = 3/2$  ions are included in Table III. Since

$\beta$  is zero for the  $\Sigma = 2$  state the value of  $D_e$  can be calculated directly from the experimentally determined parameter,  $D_2$ . The value of  $D_c$  can then be computed from the observed zero-field parameters of either the  $\Sigma = 1$  or the  $\Sigma = 3$  states. Unfortunately, it is not possible to obtain an exact fit of the observed  $D_{\Sigma}$  terms from all three spin states with the theoretical expression. The  $D_e$  and  $D_c$  values in Table III represent an average fit to the experimental data. The  $D_{\Sigma}$  parameters which are calculated from these  $D_e$  and  $D_c$  values differ from the observed  $D_{\Sigma}$  parameters by about 5%. A possible explanation for these discrepancies is the phenomenon of exchange striction. In a detailed study of Mn(II)-Mn(II) pairs in MgO,<sup>17</sup> Harris also found that the zero-field parameters could not be precisely described by the treatment outlined by Owen. Harris suggested that this behavior was the result of exchange striction. In the presence of exchange striction the separation between the magnetic ions of a pair varies as a function of spin state. For states of low total spin, exchange striction produces an attraction between the two paramagnetic ions while a repulsion results in states of high total spin. These forces can be likened to weak bonding and antibonding interactions. Thus, the interionic separation is shortest for the  $\Sigma = 0$  state and increases with increasing spin. Since the values of both  $D_e$  and  $D_c$  may depend quite critically on the separation between the two ions, the failure to precisely fit the observed zero-field splittings with the theoretical expressions given by Owen is quite understandable. Harris was able to show that the energy separations between spin states of the Mn(II)-Mn(II) pairs deviate significantly from Landé rule behavior which was cited as strong evidence for the presence of exchange striction. We cannot make the same argument since the exchange energies for the Cr(III)-Cr(III) pairs are not accurately known. Thus, it is not really certain that exchange striction is a significant factor in the behavior of the Cr(III)-Cr(III) pairs. In any case the treatment given by Owen does provide a reasonable approximate description of zero-field parameters of the Cr(III)-Cr(III) pairs. The results indicate that the lattice distortion produces a much larger zero-field effect than the anisotropic magnetic interactions.

**"Chemistry" of Trivalent Ions in the CsMX<sub>3</sub> Lattice.** It is quite clear that in the doped CsMX<sub>3</sub> crystals the Cr(III) ions cluster in pairs far more frequently than would be expected from purely statistical considerations. This certainly indicates that when a linear chain CsMX<sub>3</sub> lattice is doped with trivalent impurities there is an inherent stability associated with an impurity center containing two trivalent ions. The spin Hamiltonian parameters of the Cr(III)-Cr(III) pairs provide some significant insights into the structure of this impurity center. The angular dependences of the pair resonances show that all of the pairs have axial symmetry with the principal axis coincident with the crystallographic  $c$  axis. This observation is best explained by assuming that the two Cr(III) ions enter Mg(II) or Cd(II) ion sites within the same  $[\text{MX}_3^-]_n$  chain. An estimate of the Cr(III)-Cr(III) separation in the pairs can be obtained from the analysis of the second-order zero-field terms. For a pair which has a nearly isotropic  $g$  tensor the anisotropic magnetic interactions result primarily from dipolar effects. If the two ions are treated as point dipoles the magnetic anisotropy can be calculated from the following simple expression.

$$D_e = -g^2\beta^2/R^3$$

The distance between the two dipoles is represented as  $R$ . From the  $D_e$  values determined in the previous section the Cr(III)-Cr(III) separations for the pairs in the three host materials can be easily computed. The separations are calculated to be 5.0, 6.5, and 6.0 Å in CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub>, respectively. Although these calculations are based on a series of

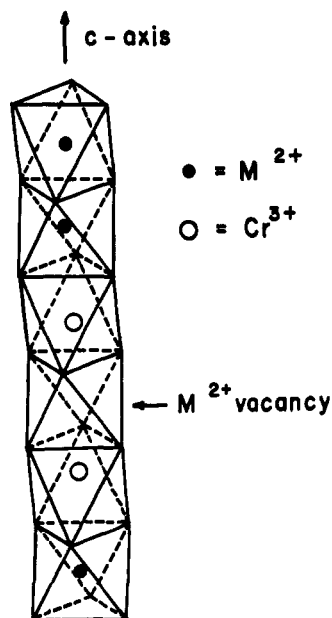


Figure 6. A perspective view of a  $[MX_3^-]_n$  chain showing the proposed structure of the Cr(III)-Cr(III) pair. The corners of the octahedra are occupied by halide ions.

assumptions which are not entirely justified, it seems likely that the computed Cr(III)-Cr(III) separations are at least qualitatively accurate. In the unperturbed host lattices the distance between adjacent metal ions within the same  $[MX_3^-]_n$  chain ranges from 3.09 Å in CsMgCl<sub>3</sub> to 3.35 Å in CsCdBr<sub>3</sub>. (In the CsNiCl<sub>3</sub> structure the M(II)-M(II) separation is equal to one-half of the lattice constant,  $c$ .) These distances are approximately half as large as the calculated Cr(III)-Cr(III) separations. Thus, it appears that two Cr(III) ions enter next-nearest-neighbor sites in a  $[MX_3^-]_n$  chain to form the coupled pair. A reasonable explanation is obtained if it is assumed that the metal ion site between the two Cr(III) ions is vacant. This produces a linear Cr(III)-vacancy-Cr(III) system (see Figure 6). The overall symmetry of this system is  $D_{3h}$ , which is consistent with the observed axial symmetry of the pair resonances. The stability of this arrangement almost certainly arises from the charge compensation requirement of the linear chain CsMX<sub>3</sub> lattice. By combining two trivalent ions with a vacancy it is possible for trivalent impurities to be incorporated into the  $[MX_3^-]_n$  chains without disrupting the overall charge balance.

If the distribution of the Cr(III) ions is determined primarily by electrostatic factors, it should be possible to alter the situation by introducing other impurity ions into the Cr(III) containing CsMX<sub>3</sub> crystals. If a second trivalent ion is present one would expect that "mixed" as well as homonuclear pairs would be formed during crystallization. This appears to be the case, since the EPR spectra of CsMgCl<sub>3</sub> and CsCdBr<sub>3</sub> crystals doped with trivalent indium and chromium contain an intense new resonance. This resonance exhibits the three-line fine structure characteristic of a single Cr(III) ion and is not observed in crystals doped only with chromium (see Figure 7). This resonance almost certainly arises from a Cr(III)-vacancy-In(III) system structurally analogous to the Cr(III)-Cr(III) pair. The symmetry of this type of mixed pair system is  $C_{3v}$ . The angular dependence is well described by the spin Hamiltonian which is normally used to interpret the spectra of axially symmetric Cr(III) complexes.

$$\mathcal{H} = g_{\parallel}\beta H_z \hat{S}_z + g_{\perp}\beta(H_x \hat{S}_x + H_y \hat{S}_y) + D(\hat{S}_z^2 - 5/4)$$

It is interesting to note that the zero-field splitting parameters

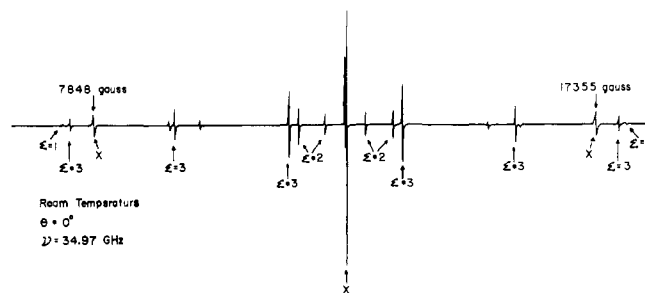


Figure 7. EPR spectrum of a CsMgCl<sub>3</sub> crystal doped with Cr(III) and In(III). The resonances marked by X arise from the Cr(III)-In(III) center. The spectrum was recorded with an 8-min scan, 10 000-G sweep, 0.1-s time constant, 10-G modulation amplitude, and 50 reviewer gain.

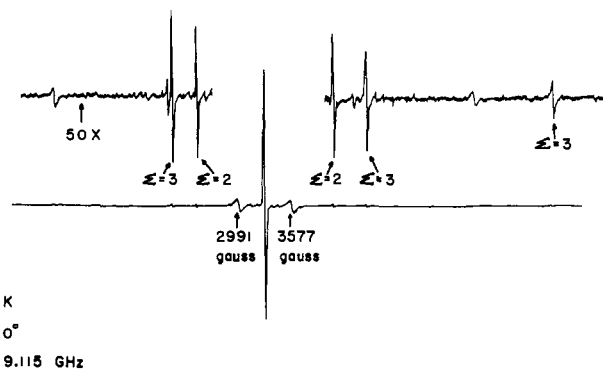


Figure 8. EPR spectrum of a CsMgCl<sub>3</sub> crystal doped with Cr(III) and Li(I). The raised portion of the spectrum was recorded with the spectrometer sensitivity increased by a factor of 50. The spectrum was recorded with a 4-min scan, 10 000-G scan, 0.1-s time constant, 0.63-G modulation amplitude, and 800 receiver gain.

Table IV. Spin Hamiltonian Parameters<sup>a</sup> of Various Isolated Cr(III) Ion Species at Room Temperature

Host lattice	Species	$g_{\parallel}$	$g_{\perp}$	$D, \text{cm}^{-1}$
CsMgCl <sub>3</sub>	Cr(III)-Li(I)	1.991 (4)	1.991 (4)	0.0088 (2)
	Cr(III)-In(III)	1.984 (4)	1.983 (4)	0.220 (1)
CsMgBr <sub>3</sub>	Cr(III)-Li(I)	2.012 (6)	2.012 (6)	0.0171 (5)
CsCdBr <sub>3</sub>	Cr(III)-Li(I)	2.014 (6)	2.014 (6)	0.0329 (8)
	Cr(III)-In(III)	2.015 (4)	2.010 (4)	0.246 (4)

<sup>a</sup> The numbers in parentheses represent the estimated maximum error in the last place of the reported parameter.

for the Cr(III)-In(III) pairs in CsMgCl<sub>3</sub> and CsCdBr<sub>3</sub> are quite similar to the lattice contributions to the zero-field splitting ( $D_c$ ) calculated for the Cr(III)-Cr(III) pairs. This seems quite reasonable since the immediate environment of the individual Cr(III) ions in the Cr(III)-Cr(III) and Cr(III)-In(III) pairs should be almost identical.

The distribution of Cr(III) in the CsMX<sub>3</sub> crystals can also be altered by the presence of small monovalent ions. The introduction of a small amount of lithium ion to a Cr(III)-containing crystal causes dramatic changes in the EPR spectrum. As can be seen from Figure 8 a small amount of Li(I) ion causes a drastic reduction in the intensity of the pair resonances. A new resonance appears which is characteristic of a species containing a single Cr(III) ion. This resonance is well described by the same axial spin Hamiltonian as that used to treat the Cr(III)-In(III) system. The spin Hamiltonian parameters for the Cr(III)-In(III) and Cr(III)-Li(I) centers in the CsMX<sub>3</sub> crystals are given in Table IV. It is quite evident

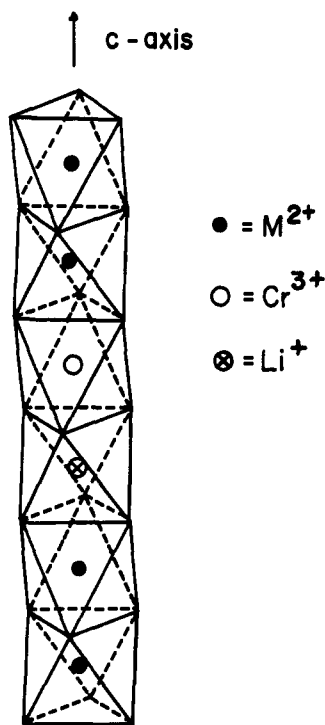


Figure 9. A perspective view of a  $[MX_3^-]_n$  chain showing the proposed structure of the Cr(III)-Li(I) center.

that the presence of small monovalent ions during crystallization provides an alternate mode by which the Cr(III) ions can be incorporated into the  $CsMX_3$  lattice. It seems likely that a chromium and a lithium ion enter adjacent metal ion sites within the same  $[MX_3^-]_n$  chain (see Figure 9). The resulting Cr(III)-Li(I) center has a symmetry of  $C_{3v}$ , and would be expected to follow an axial spin Hamiltonian. Since the combination of a trivalent and a monovalent ion is equivalent in total charge to two divalent ions, the charge balance of the  $CsMX_3$  lattice is maintained. Apparently the lithium ion is small enough to readily enter sites normally occupied by magnesium or cadmium ions. When  $CsMgCl_3$  is doped with both chromium and sodium similar behavior is observed except that the "quenching" of the Cr(III)-Cr(III) pair resonances is not as pronounced. It is possible that the larger size of sodium prevents the ion from entering a Mg(II) site as readily as the lithium ion. The zero-field splittings for the Cr(III)-Li(I) centers are considerably smaller in magnitude than those of the Cr(III)-In(III) centers. This indicates that the coordination sphere of the Cr(III) ion in the Cr(III)-Li(I) system is much less distorted than that in the Cr(III)-In(III) system.

Although it is always difficult to establish the structures of impurity centers in crystals with absolute certainty, all of the available evidence supports the correctness of our proposed structures. It appears that the "chemistry" of the Cr(III) impurities can be satisfactorily explained in terms of the charge compensation requirement of the linear chain lattice. Charge compensation has been shown to play an important role in the distribution of Cr(III) impurities in other crystals in which the Cr(III) ions enter sites normally occupied by divalent ions. The phenomenon has been studied previously in crystals of  $MgO$ <sup>18,19</sup> and  $KMgF_3$ .<sup>20</sup> The  $CsMX_3$  lattice, however, seems to be unique in that charge compensation leads to the almost exclusive formation of pairs. Recently it has been found by studying the EPR spectra of  $CsCdBr_3$  crystals doped with trivalent gadolinium that Gd(III) behaves in exactly the same manner as Cr(III).<sup>21</sup> The fact that similar behavior is observed with trivalent ions as different in size and chemical properties as Cr(III) and Gd(III) strongly supports the assertion that the

distribution of trivalent impurities in the  $CsMX_3$  lattices is primarily determined by localized electrostatic effects.

**Magnetic Properties of the Cr(III)-Containing Centers.** The magnetic properties of a number of the Cr(III) species which are observed in the  $CsMX_3$  crystals are rather interesting and deserve further comment. The principal  $g$  values of all the centers (pairs and single ion species) which occur in  $CsMgBr_3$  and  $CsCdBr_3$  are noticeably greater than the spin only value of 2.0023 while those for the centers in  $CsMgCl_3$  are somewhat lower than 2.0023. In  $d^3$  ion complexes, the spin-orbit interaction associated with the metal ion normally produces a reduction in the  $g$  values. The vast majority of Cr(III) complexes have  $g$  values which are measurably lower (1.95-2.00) than the spin only value. According to the structures proposed in the previous section the coordination spheres of the individual Cr(III) ions in each type of center consist of approximately octahedral arrangements of halide ions. Thus, it appears that the anomalously high  $g$  values observed in the bromide host lattices are characteristic of the octahedral  $[CrBr_6^{3-}]$  complex. It has been pointed out that a complete theoretical treatment of the  $g$  factors of  $d^3$  ion complexes must consider ligand contributions. These contributions have the opposite sign as central metal contribution and arise from the delocalization of the unpaired electrons from the metal ion onto the ligands.<sup>22,23</sup> The magnitude of the ligand contribution to the  $g$  factors increases not only as the metal to ligand delocalization becomes more extensive but as the spin-orbit constant for the ligand atoms increases. Since the spin-orbit constants of light atoms are quite small, the ligand contribution to the  $g$  values is smaller in magnitude than that from the central metal ion in complexes composed of ligands which have atoms such as O, N, F, Cl, etc., as donors. In the case of the  $[CrBr_6^{3-}]$  complex it appears that the spin-orbit constant for bromine is large enough to produce a ligand contribution which is larger than that of the central metal ion.

It is interesting to speculate on the origin of the magnetic exchange interactions in the Cr(III)-Cr(III) pair systems. According to the proposed structure, the pair can be described as two approximately octahedral  $[CrX_6^{3-}]$  complexes interacting along a common threefold (trigonal) axis. It seems very unlikely that the magnetic exchange results from direct metal-metal interaction, since the Cr(III)-Cr(III) distances are on the order of 5-6 Å. A superexchange or through-ligand mechanism seems much more likely. The fact that the exchange interactions appear to be larger in  $CsMgBr_3$  and  $CsCdBr_3$  than in  $CsMgCl_3$  even though the Cr(III)-Cr(III) separation is smaller in  $CsMgCl_3$  tends to support this conclusion. One would expect superexchange interactions to increase as the metal-ligand bonding becomes more covalent. The  $[CrBr_6^{3-}]$  complex almost certainly has more covalent character than the  $[CrCl_6^{3-}]$  complex.

Since the two Cr(III) ions share no common ligands, the magnetic interactions must be transmitted through pathways involving at least two intervening halide ions. It is interesting that these indirect superexchange pathways actually lead to fairly substantial exchange energies. Although the exchange energies are not precisely known, it seems reasonably certain that the exchange parameter,  $J$ , is at least  $1 \text{ cm}^{-1}$  or more in all three  $CsMX_3$  crystals. This is in sharp contrast to the Cr(III)-Cr(III) pairs observed by Davis and Belford in chromium-doped crystals of  $Al(\text{urea})_6I_3$  for which  $J$  was found to be approximately  $0.005 \text{ cm}^{-1}$ .<sup>24</sup> The pairs in  $Al(\text{urea})_6I_3$  are structurally similar to those which occur in the  $CsMX_3$  crystals to the extent that they result by the interaction of two octahedral Cr(III) complexes along a common threefold axis. The Cr(III)-Cr(III) separation is slightly less than 7.0 Å, which is comparable to those determined for the pairs in the  $CsMX_3$  crystals. The only explanation which we can offer is that the chloride and bromide ligands provide a much more

efficient indirect superexchange pathway than does urea. The fact that relatively strong exchange interactions may be transmitted through two halide ions is not without precedent. Indirect pathways of the type  $[M-X\cdots X-M]$  have been shown to produce fairly strong exchange ( $J \sim 5-10 \text{ cm}^{-1}$ ) in the Ir(IV)-Ir(IV) pairs observed in iridium-doped crystals of  $K_2PtCl_6$  and  $(NH_4)_2PtCl_6$ .<sup>25,26</sup> In this case the dimer is formed from two octahedral  $[IrCl_6^{2-}]$  complexes which interact along a common twofold axis. It is unfortunate that a more quantitative discussion of the magnetic interactions in Cr(III)-Cr(III) pairs is prevented by the lack of accurately determined exchange energies.

### Conclusions

It is clear that the Cr(III) impurities in the doped  $CsMX_3$  crystals are incorporated into the lattice in a highly selective manner. The selectivity appears to arise from the rather strict charge compensation requirement of the host lattices. The charge compensation requirement is primarily an electrostatic effect and is not greatly dependent on the chemical properties of the impurity ions. It is reasonable to conclude that within rather broad limits any trivalent ion will behave like Cr(III) when doped into crystals which adopt the linear chain  $RMX_3$  structure. From a spectroscopic point of view these systems are unique in that magnetically coupled pairs are produced in high relative concentrations, even at low doping levels. The fact that the distribution of a given trivalent ion can be manipulated by the introduction of other impurity ions makes it possible to control the nature of the spectroscopic species present in the doped crystals.

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### References and Notes

- (1) G. L. McPherson, L. J. Sindel, H. F. Quarls, C. B. Frederick, and C. J. Doumit, *Inorg. Chem.*, **14**, 1831 (1975).
- (2) G. L. McPherson, T. J. Kistenmacher, and G. D. Stucky, *J. Chem. Phys.*, **52**, 815 (1970).
- (3) G. L. McPherson, A. M. McPherson, and J. L. Atwood, to be published.
- (4) G. L. McPherson and K. O. Devaney, *Inorg. Chem.*, **16**, 1565 (1977).
- (5) H. Rinneberg and H. Hartmann, *J. Chem. Phys.*, **52**, 5814 (1970).
- (6) G. L. McPherson, R. C. Koch, and G. D. Stucky, *J. Chem. Phys.*, **60**, 1424 (1974).
- (7) G. L. McPherson and W. Heung, *Solid State Commun.*, **19**, 53 (1976).
- (8) J. Owen, *J. Appl. Phys.*, **32**, 213S (1961).
- (9) J. Owen and E. A. Harris, "Electron Paramagnetic Resonance", S. Geschwind, Ed., Plenum Press, New York, N.Y., 1972, pp 427-492.
- (10) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Metal Ions", Clarendon Press, Oxford, 1970.
- (11) A. J. B. Codling and B. Henderson, *J. Phys. C*, **4**, 1409 (1971).
- (12) S. R. P. Smith and J. Owen, *J. Phys. C*, **4**, 1399 (1971).
- (13) M. J. Berggren, G. F. Imbusch, and P. L. Scott, *Phys. Rev.*, **188**, 675 (1969), and references cited therein.
- (14) J. C. M. Hennling, J. H. DenBoef, and G. G. P. van Gorkom, *Phys. Rev. B*, **7**, 1825 (1973).
- (15) J. R. Beswick and D. E. Dugdale, *J. Phys. C*, **6**, 3326 (1973).
- (16) P. C. Benson and D. E. Dugdale, *J. Phys. C*, **8**, 3872 (1975).
- (17) E. A. Harris, *J. Phys. C*, **5**, 338 (1972).
- (18) J. E. Wertz and P. Auzins, *Phys. Rev.*, **106**, 484 (1957).
- (19) J. E. Wertz and P. Auzins, *J. Phys. Chem. Solids*, **28**, 1557 (1967).
- (20) J. L. Patel, J. J. Davies, B. C. Cavenett, H. Takeuchi, and K. Horai, *J. Phys. C*, **9**, 129 (1976).
- (21) G. L. McPherson and L. M. Henling, *Phys. Rev. B*, **16**, 1889 (1977).
- (22) B. R. McGarvey, *J. Chem. Phys.*, **41**, 3743 (1964).
- (23) B. B. Garrett, K. DeArmond, and H. S. Gutowsky, *J. Chem. Phys.*, **44**, 3393 (1966).
- (24) P. H. Davis and R. L. Belford, *ACS Symp. Ser.*, **5**, 51 (1974).
- (25) J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, *Proc. R. Soc. London, Ser. A*, **250**, 84 (1959).
- (26) E. A. Harris and J. Owen, *Proc. R. Soc. London, Ser. A*, **289**, 122 (1965).

## Electronic Selection Rules in the Photochemical Substitution Reactions of Cr(III) Complexes

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**Abstract:** The stereochemistry of photoinduced substitution reactions of Cr(III) complexes has been analyzed by using orbital and state correlation diagrams. The experimentally observed stereomobility was considered to be the result of several steps: initiated by the selective loss of a ligand, the complex fragment undergoes an isomerization, followed by the nucleophilic attack of an entering ligand. Both isomerization and association reactions are shown to occur in a stereospecific way, controlled by the electronic structure of the complex. The analysis was carried out by means of a general computer program, incorporating both the effects of the ligand field potentials and of the interelectronic repulsion. The conclusions of this study point to the existence of electronic selection rules in the photochemical reaction pathways of transition metal complexes. These rules can be restated either in terms of the frontier orbital concept or in terms of the conservation of orbital symmetry.

### Introduction

The experimental data on the photochemistry of Cr(III) complexes have been accumulating increasingly fast over the last years.<sup>1,2</sup> The first effort to systematize the photostitution behavior has led to Adamson's empirical rules.<sup>3</sup> These rules suggest that the relative spectrochemical strength of the different ligands is the main factor determining which ligand is exchanged.

From a more theoretical point of view, a number of authors<sup>4,5</sup> have attempted to explain, or at least to rationalize, Adamson's rules. Recently, we have developed a model that

allows the prediction of the leaving ligand while using only simple ligand field considerations;<sup>6</sup> at the same time, the model provides an alternative to the original rules.

During the last few years, it became clear that the oriented labilization represents only *one* facet of the Cr(III) photochemistry. Another feature, almost equally clear cut, shows up in the stereochemical aspects of the substitution reactions. Kirk summarized the photostereochemistry as follows: "the entering ligand will stereospecifically occupy a position corresponding to entry into the coordination sphere trans to the leaving ligand".<sup>7</sup>