ticularly in weighing. The $(Ph_3P)_2N^+BH_4^-$ is not noticeably hygroscopic, is high in molecular weight, permitting greater precision in weighing small quantities of borohydride, is very soluble in organic solvents, and, for the purpose of this study, is adequately soluble in 4:1 water–acetonitrile mixed solvent.

For analysis NAD^+ has several serious disadvantages. Not only is the price high but it has limited shelf life, even when stored in a freezer. At the wavelength of 340 nm, at which the absorbance of NADH is measured, there is not a true absorption maximum but rather a shoulder, so the absorbance is rather sensitive to small changes in the wavelength of measurement. Furthermore, at this wavelength, unreduced NAD^+ has a weak, but measurable, absorbance. Measured absorbances are, therefore, slightly sensitive to the concentration of unreacted NAD^+. The BNA^+ ion suffers from none of these disadvantages. BNA^+Cl^- is inexpensive, easy to make, and stable, at least in the solid state. At 358 nm unreacted BNA^+ does not absorb measurably, and (BNA)H shows a relatively broad absorption maximum, making the measured absorbance independent of unreacted BNA^+ and insensitive to small changes in the wavelength of measurement. At 358 nm the absorptivity of (BNA)H is about 15% higher than that of NADH at 340 nm, a small but significant advantage.

Overall, the change to the more desirable reagents discussed above, together with the careful elimination of catalytic impurities, has resulted both in a substantial reduction in scatter in the kinetic measurements of series I (see Table I) and, over the range of water concentrations used in the study, in an average lowering of about 20% in the magnitude of observed rate constants.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The authors wish to express appreciation to Professor V. J. Shiner, Jr., for a helpful discussion of this isotope effect and the suggestion for the structure of **2**.

Registry No. $(Ph_3P)_2N^+BH_4^-$, 65013-26-5; $(Ph_3P)_2N^+BD_4^-$, 70479-83-3; BH_4^-, 16971-29-2; CH_3COOH, 64-19-7.

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Magnetic Interactions in Exchange-Coupled Pairs of Chromium(III) and Molybdenum(III) Ions in Crystals of $CsMX_3$ Halides

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Trivalent ions tend to cluster in pairs when introduced as impurities into crystals of $CsMX_3$ salts such as $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$. Pairs of this type which contain two paramagnetic trivalent ions behave as magnetic dimers. The EPR spectra of the Cr(III)–Cr(III) and Mo(III)–Mo(III) pairs which are formed in these crystals have been carefully analyzed. The analysis is based on exact solutions of a spin Hamiltonian written for systems which contain two magnetically coupled $S = {}^3/_2$ ions. In all cases accurate spectral descriptions are obtained. The magnetic interactions between metal ions are accurately characterized by two linear exchange terms: $J\vec{S}_i\cdot\vec{S}_j + D_e(3\hat{S}_{iz}\hat{S}_{jz} - \vec{S}_i\cdot\vec{S}_j)$. In these systems the exchange interactions appear to be antiferromagnetic with J values which range from 1 to 6 cm^{-1}.

Introduction

Electron paramagnetic resonance studies indicate that trivalent ions tend to cluster in pairs when doped into crystals of $CsMX_3$ salts which are known to adopt the linear chain $CsNiCl_3$ structure.[1-4] Even at doping levels lower than one part per thousand it appears that a majority of the trivalent impurities enter the $CsMX_3$ cyrstals in pairs. This unusual tendency arises from the rather strict charge compensation requirement of the linear chain lattice. The $CsNiCl_3$ structure can be described as an array of parallel linear chains composed of MX_6^{4-} octahedra sharing opposite faces. These chains are anionic and have the stoichiometry $[MX_3^-]_n$. The cesium ions occupy positions between the chains and balance the anionic charge. When trivalent impurities enter crystals of this type, two impurity ions associate with a divalent ion vacancy within a single $[MX_3^-]_n$ chain (see Figure 1). The combination of the two impurities with a vacancy provides a means by which trivalent ions can be incorporated into the $[MX_3^-]_n$ chains

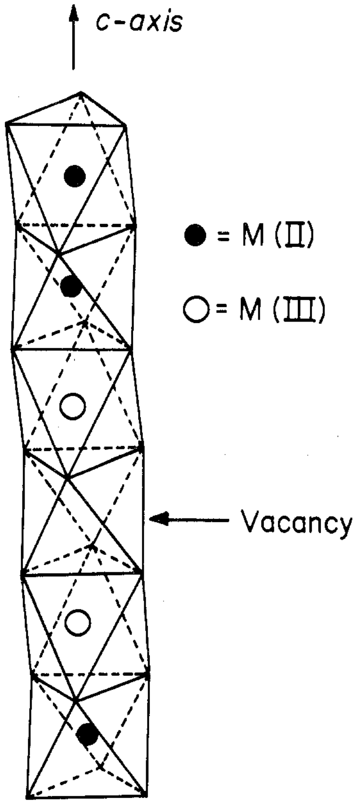

Figure 1. A perspective drawing of a single $[MX_3^-]_n$ chain showing the structure of the change compensation stabilized M(III)–M(III) pair. The corners of the octahedra are occupied by halide ions.

without disrupting the overall charge balance of the host lattice.

If both trivalent ions in the charge compensation stabilized pair are paramagnetic, the system behaves as a magnetic dimer. The EPR spectra of pairs containing trivalent chromium and gadolinium in three $CsMX_3$ salts were characterized in the earlier studies, referred to above. The interpretation of the spectra of the chromium-containing pairs was based on the approximate treatment outlined by Owen.[5,6] It is assumed that two paramagnetic ions couple to give a manifold of states each of which is characterized by a total spin quantum number (Σ). The total spins range from $|S_1 + S_2|$ to $|S_1 - S_2|$ (where S_1 and S_2 are the spins of the two ions which form the pair). Under this formalism a coupled pair of Cr(III) ions ($S = {}^3/_2$) has a four-state manifold, $\Sigma = 0$, 1, 2, and 3. The EPR spectrum of an exchange-coupled pair is analyzed by first assigning the resonances to the different spin states. Each spin state is treated by a separate spin Hamiltonian which describes the behavior of the resonances associated with that spin state. Application of this method to the Cr(III)–Cr(III) pairs in the $CsMX_3$ crystals leads to a reasonable overall spectral interpretation; however, there are some noticeable discrepancies between the observed and predicted behavior. In particular, the resonances assigned to the $\Sigma = 2$ state are not well described by the spin Hamiltonian obtained from this analysis.[4] In order to better characterize these pairs a more complete theoretical treatment of the EPR spectra has been carried out. This treatment is based on exact rather than approximate solutions of the 16 × 16 energy matrix which describes the energy levels of a magnetic dimer containing two $S = {}^3/_2$ ions. This approach gives an accurate fit of the pair spectra and provides a direct determination of the Cr(III)–Cr(III) exchange energy in each host crystal.

In an effort to extend the work to other systems, crystals of $CsMgCl_3$ and $CsMgBr_3$ doped with trivalent molybdenum were prepared and investigated. As expected, the EPR spectra of these crystals contain resonances from exchange-coupled pairs of Mo(III) ions. Although many dimeric systems containing Cr(III) have been described in the literature, examples of well-characterized systems containing coupled pairs of Mo(III) ions are relatively rare. In general, the EPR spectra of Mo(III) complexes have not been extensively studied.[7] Since Mo(III) is also an $S = {}^3/_2$ ion, the spectra of the Mo(III)–Mo(III) pairs can be treated by the exact solution procedure that was applied to the spectra of the Cr(III)–Cr(III) pairs. The procedure does provide accurate characterizations of the Mo(III)–Mo(III) pair spectra. This paper describes the EPR spectra of the Mo(III)-doped crystals and presents the results of the detailed spectral analysis of both the Cr(III)–Cr(III) and Mo(III)–Mo(III) pair systems.

Experimental Section

Preparation of Doped Crystals. The $CsMgCl_3$ and $CsMgBr_3$ were prepared by fusing equimolar amounts of the cesium halide and anhydrous magnesium halide in evacuated Vycor ampules. The doped $CsMgCl_3$ was produced by adding a small amount of $MoCl_3$ to the host material and fusing the mixture. The Mo(III) was introduced into $CsMgBr_3$ by melting samples of the host material with a small amount of $MoBr_2$; the molten samples were then exposed to Br_2 vapor to oxidize the Mo(II) to Mo(III). Single crystals were grown from the melt by the Bridgman method. The apparatus and procedure have been previously described.[8] The presence of Mo(III) imparts a brown color to the crystals of both $CsMgCl_3$ and $CsMgBr_3$. These crystals are extremely hygroscopic.

EPR Measurements. The $CsMgX_3$ crystals have a pronounced tendency to cleave along the [110] face which greatly facilitates mounting and orienting the samples for EPR study. In general the crystals were mounted so that the crystallographic *c* axis was contained in the plane of rotation of the magnetic field. The EPR spectra were recorded at 77 K by using X- and Q-band frequencies. The spectrometers have been previously described.[4]

Computer Calculations. All computations were carried out on an Interdata 7/16 computer operated jointly by the departments of Chemistry and Physics at Tulane University.

Results and Discussion. Theoretical Description of a Coupled Pair of $S = {}^3/_2$ Ions

A complete spin Hamiltonian for a system composed of two interacting paramagnetic centers contains two distinct types of terms. One type describes the magnetic interactions between the two centers while the second type characterizes the properties of each individual center. Such a pair Hamiltonian can be expressed in the following general form:

$$\mathcal{H} = \mathcal{H}^{\mathrm{p}} + \mathcal{H}_i^{\mathrm{s}} + \mathcal{H}_j^{\mathrm{s}}$$

where the pair interactions are contained in $\mathcal{H}^{\mathrm{p}}$ and the individual centers are described by $\mathcal{H}_i^{\mathrm{s}}$ and $\mathcal{H}_j^{\mathrm{s}}$. The charge compensation stabilized pairs in the $CsMX_3$ crystals can be visualized as two octahedral MX_6^{3-} complexes approaching each other along a common threefold axis. The symmetry at both metal ion sites is C_{3v} while the overall point symmetry of the pair is D_{3d}. (In ref 4 the pair symmetry was incorrectly reported as D_{3h}.) The magnetic coupling in pair systems of this type should be relatively weak since the two metal ions are fairly far apart (on the order of 6 Å) and are not connected by direct superexchange pathways. In general, weak exchange can be accurately described by an interaction Hamiltonian which contains only linear coupling terms. The following Hamiltonian is appropriate for a system which has axial symmetry.

$$\mathcal{H}^{\mathrm{p}} = J\vec{S}_i \cdot \vec{S}_j + D_{\mathrm{e}}(3\hat{S}_{iz}\hat{S}_{jz} - \vec{S}_i \cdot \vec{S}_j)$$

The first term corresponds to the isotropic component of the magnetic coupling while the anisotropic component is described by the second term. In homogeneous dimers such as the Cr(III)–Cr(III) and Mo(III)–Mo(III) pairs, the two single ion Hamiltonians, $\mathcal{H}_i^{\mathrm{s}}$ and $\mathcal{H}_j^{\mathrm{s}}$, are identical. An $S = {}^3/_2$ ion

Table I. Spin Hamiltonian Parameters for the Cr(III)–Cr(III) and Mo(III)–Mo(III) Pairs

pair	lattice	temp, K	$g_\parallel$	$g_\perp$	J, cm^{-1}	D_e, cm^{-1}	D_c, cm^{-1}
Cr(III)–Cr(III)	$CsMgCl_3$	297	1.984	1.984	+0.80	−0.0079	−0.221
		77	1.984	1.985	+0.96	−0.0081	−0.222
	$CsMgBr_3$	297	2.011	2.011	+1.14	−0.0011	−0.228
		77	2.010	2.010	+1.42	−0.0009	−0.241
	$CsCdBr_3$	297	2.010	2.010	+0.94	−0.0011	−0.251
		77	2.010	2.010	+1.28	−0.0028	−0.275
Mo(III)–Mo(III)	$CsMgCl_3$	77	1.96	1.96	+2.75	−0.0033	−1.139
	$CsMgBr_3$	77	1.99	1.99	+5.6	+0.011	−1.25

in an environment which has C_{3v} symmetry can be described by the spin Hamiltonian given below.

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

The first two terms represent the electron–Zeeman interaction while the third term gives the zero-field splitting associated with a many-electron system in a noncubic environment. (The spin Hamiltonian parameters in these expressions are designated according to the notation used by Owen.[5,6]) In metal complexes, zero-field splitting usually results from the interaction between the spin system centered on the metal ion and the noncubic component of the ligand field. This interaction is brought about by spin–orbit coupling. A basis set of spin functions for a coupled pair is easily constructed by taking products of the single ion functions, $|S_i m_i\rangle |S_j m_j\rangle$. For two $S = 3/2$ ions 16 such product spin functions are obtained. The total pair Hamiltonian can be applied to these product functions in a very straightforward manner. If the spin operators are expanded into three-dimensional Cartesian components and the raising and lowering operators are substituted for the $\hat{S}_x$ and $\hat{S}_y$ components, the complete Hamiltonian for the coupled pair can be written as follows:

$$\mathcal{H} = (J + 2D_e)\hat{S}_{iz}\hat{S}_{jz} + (J - D_e)[1/2(\hat{S}_{i+}\hat{S}_{j-} + \hat{S}_{i-}\hat{S}_{j+})] + g_\parallel \beta (\cos\theta) H (\hat{S}_{iz} + \hat{S}_{jz}) + g_\perp \beta (\sin\theta) H [1/2(\hat{S}_{i+} + \hat{S}_{j+} + \hat{S}_{i-} + \hat{S}_{j-})] + D_c(\hat{S}_{iz}^{\,2} + \hat{S}_{jz}^{\,2} - 5/2)$$

The angle θ is defined as the angle between the applied magnetic field and the principal symmetry axis of the pair (the crystallographic c axis). Application of the Hamiltonian operator to the product spin functions produces a 16 × 16 energy matrix which can be solved numerically by computer diagonalization.

In an EPR spectrum each resonance corresponds to a transition between two of the spin levels associated with the paramagnetic system. Since the frequency of the spectrometer is fixed, it is the resonance fields rather than the energies which must be calculated in a spectral analysis. The following procedure was used to calculate resonance fields in the treatment of the spectra from the Cr(III)–Cr(III) and Mo(III)–Mo(III) pairs. A trial set of spin Hamiltonian parameters was chosen and introduced into the energy matrix along with an observed resonance field and crystal orientation. The matrix was diagonalized to give the energies of the 16 spin levels. The two spin levels were found whose absolute energy difference most closely matched the microwave energy of the spectrometer. The resonance field was then adjusted by an iterative procedure to produce an energy difference between the two levels that was exactly equal (within 0.005 GHz) to the spectrometer energy. The field that was ultimately obtained in this fashion could then be compared to the original observed resonance field. Since each resonance which appears in a spectrum requires a separate computation, a complete spectral analysis using this approach may require a large number of calculations. In particular, this is true if many trial sets of parameters are to be considered. A pair system is assumed to be accurately described only if the spectra at both X- and Q-band frequencies are accurately reproduced by a single set of parameters. This implies good agreement between the observed and calculated resonance fields at all crystal orientations. Although there are five parameters which must be determined in the complete Hamiltonian, some parameters could be established with reasonable certainty beforehand. This simplified, to a great extent, the search for the correct set of parameters. Even so, this trial and error approach proved to be tedious and time consuming in some cases. Ultimately, however, a set of parameters which gave an accurate spectral description was found for each of the Cr(III)–Cr(III) and Mo(III)–Mo(III) systems. The actual procedure by which the correct parameters were found and the resulting fits of the pair spectra are described in detail in the following two sections of the paper.

Spectra of the Cr(III)–Cr(III) Pairs. The EPR spectra arising from the coupled Cr(III)–Cr(III) pairs in the $CsMX_3$ crystals have already been described.[4] The results of the earlier spectral analysis were taken as a starting point for the more exact calculations. The single ion parameters should be reasonably well established by the approximate treatment which leaves only the interaction parameters, J and D_e, to be determined. The single ion parameters given in ref 4 were introduced into the energy matrix along with trial values for J and D_e. The values of J and D_e were varied in order to obtain agreement between the observed and calculated resonance fields. In the initial phase of the analysis, calculations were only carried out for the resonances observed when the magnetic field is directed along the principal symmetry axis of the pair ($\theta = 0°$). Since the off-diagonal Zeeman terms vanish as θ approaches zero, the computer time required to diagonalize the energy matrix is minimized. The fields calculated for the four resonances which had been assigned to the $\Sigma = 2$ state in the earlier treatment were found to be particularly sensitive to the values chosen for J and D_e. By comparison of the observed and calculated fields for these four resonances it was possible to converge fairly quickly on suitable values for the two interaction parameters. Once D_e and J were reasonably well defined, small adjustments in the complete set of parameters produced a very good overall fit of each pair spectrum. The agreement between the observed and calculated resonance fields is satisfactory at all crystal orientations.

In particular, the four resonances associated with the $\Sigma = 2$ spin state were not accurately described in the earlier analysis. While the approximate treatment produced reasonable agreement between observed and calculated resonance fields when the external field was close to the principal axis of the pair, there were serious discrepancies for θ angles greater than 30°. As shown in Figure 2 the discrepancies are much more pronounced in the Q-band spectrum than in the spectrum observed at X band. This problem was encountered with the pair spectra from all three host lattices. In contrast, the more complete treatment gives a very satisfactory fit of the $\Sigma = 2$ resonances at both X and Q band (see Figure 3). It should be mentioned that the other pair resonances also are very well described. The final parameters in the complete Hamiltonian for the Cr(III)–Cr(III) pairs in $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$ are given in Table I.

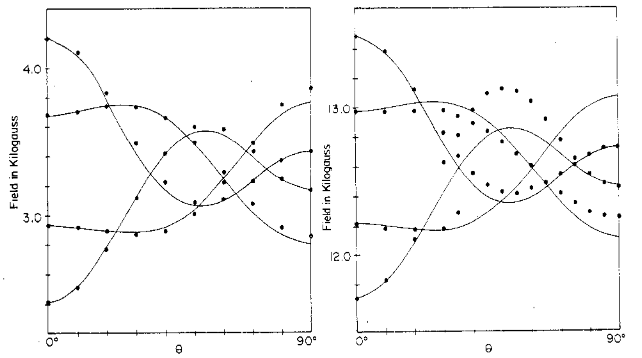

Figure 2. Angular dependence of the $\Sigma = 2$ resonances from the Cr(III)–Cr(III) pairs in $CsMgCl_3$. The angle θ corresponds to the angle between the applied field and the crystallographic c axis. The trace on the left describes the X-band spectrum while that on the right represents the Q-band spectrum. The dots correspond to the observed resonance fields. The solid curves were calculated from the spin Hamiltonian derived in ref 4.

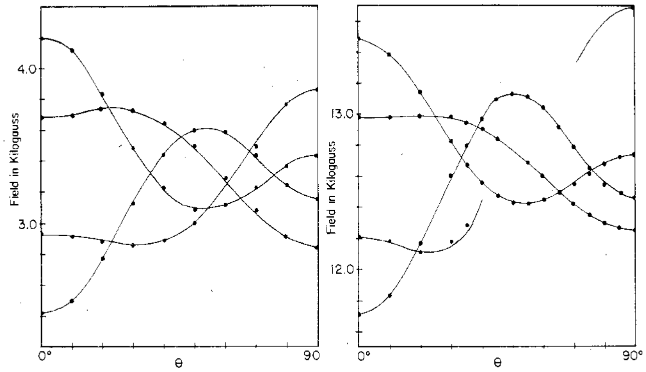

Figure 3. Angular dependence of the $\Sigma = 2$ resonances from the Cr(III)–Cr(III) pairs in $CsMgCl_3$. This is similar to Figure 2 except that the solid curves were calculated from the complete pair Hamiltonian by using the parameters in Table I.

The successful analysis of the pair spectra strongly suggests that the change compensation stabilized chromium(III) pairs are accurately described by the rather simple and straightforward total Hamiltonian. The solutions of this Hamiltonian provide a complete description of energy level systems associated with these magnetic dimers. The energy levels of the Cr(III)–Cr(III) pairs at zero field (no external magnetic field) are shown in Figure 4. When an external field is applied, the degeneracy in the system is completely removed so that there are 16 distinct energy levels. The levels of these pairs, even in zero field, are significantly more complex than the simple four-state system ($\Sigma = 0$, 1, 2, and 3) pictured in the approximate treatment.

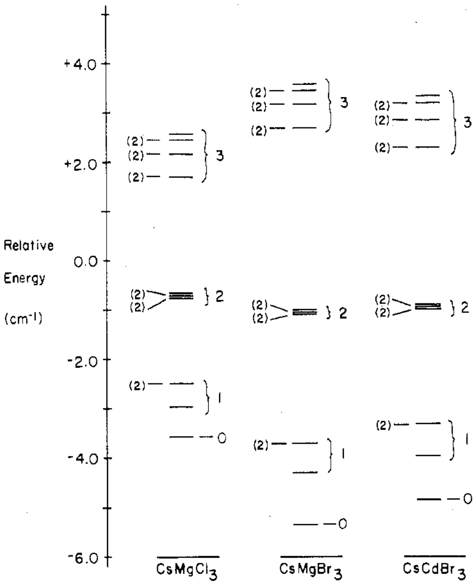

Figure 4. The energy levels of the Cr(III)–Cr(III) pairs in $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$ at 77 K with no external magnetic field. The levels which are doubly degenerate are designated by "(2)".

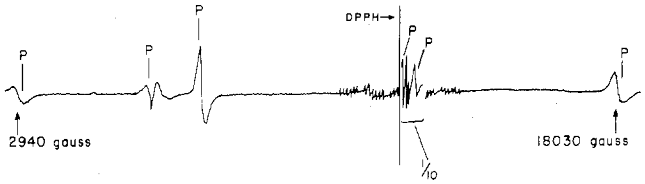

Figure 5. The Q-band EPR spectrum of a $CsMgCl_3$ crystal doped with Mo(III) taken at 77 K with the field directed along the crystallographic c axis. The central portion of the spectrum marked by "1/10" was recorded with the spectrometer gain reduced by a factor of 10. The resonances labeled by "P" arise from the Mo(III)–Mo(III) pairs.

Spectra of the Mo(III)–Mo(III) Pairs. The molybdenum resonances from the doped $CsMgCl_3$ and $CsMgBr_3$ crystals are very broad and unresolved at room temperature, but these resonances sharpen considerably when the crystals are cooled. At 77 K the spectra are sufficiently resolved that an analysis is possible, although the resonances are still much broader (5–10 times) than those observed in the Cr(III)-doped crystals. The spectrum of Mo(III) in $CsMgCl_3$ is very similar in overall appearance to that of Mo(III) in $CsMgBr_3$. As expected, there are prominent features in the spectra which can be assigned to exchange-coupled pairs. Figure 5 shows the spectrum observed in $CsMgCl_3$ at Q-band frequency. The resonances from the Mo(III)–Mo(III) pairs occur over an enormous span of magnetic field. This primarily reflects the large single ion zero-field splitting associated with trivalent molybdenum. It is clear that the complete pair spectrum in either $CsMgCl_3$ or $CsMgBr_3$ greatly exceeds the experimentally available field range (0–18500 G). Many of the resonances which are observed are extremely dependent on crystal orientation. In some cases a few degrees change in θ produces a shift of more than 1000 G in a resonance field. This, along with broadness of the resonances, makes it impossible to determine a complete angular dependence for every pair line. Although the experimental observations do not cover the entire pair spectra, the data are more than sufficient to characterize the magnetic properties of the Mo(III)–Mo(III) dimers.

The general procedure that was used in the analysis of the Cr(III)–Cr(III) systems was applied to the spectra of the Mo(III)–Mo(III) dimers. It was, however, considerably more difficult to converge on a suitable set of parameters for the total pair Hamiltonian. A great number of calculations was carried out before parameters were found which produced good agreement between the observed and calculated resonance fields. Eventually it was possible to obtain sets of parameters which accurately reproduced the X- and Q-band spectra of both dimer systems. The final parameters for the Mo(III)–Mo(III) pairs in $CsMgCl_3$ and $CsMgBr_3$ are given in Table I. Although the angular dependences of the Mo(III)–Mo(III) pair spectra are extremely complex, the agreement between observed and calculated behavior is quite good. The theoretical fits of the observed X- and Q-band spectra of the pairs in $CsMgCl_3$ are shown in Figures 6 and 7. It appears that the Mo(III)–Mo(III) dimers as well as Cr(III)–Cr(III) systems are accurately described by the total pair Hamiltonian. The zero-field energy levels of the Mo(III)–Mo(III) pair are shown in Figure 8. These levels qualitatively resemble those of the Cr(III)–Cr(III) pairs but cover a significantly wider span in energy.

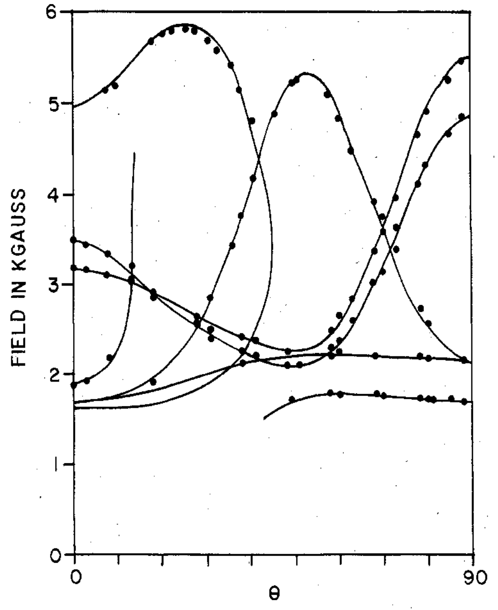

Figure 6. Angular dependence of the X-band spectrum of the Mo(III)–Mo(III) pairs in $CsMgCl_3$. The dots correspond to the observed resonance fields while the solid curves were calculated from the complete pair Hamiltonian by using the parameters in Table I.

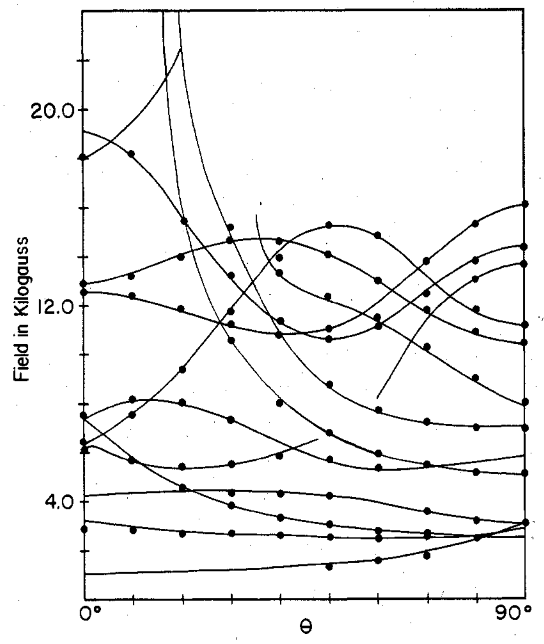

Figure 7. Angular dependence of the Q-band spectrum of the Mo(III)–Mo(III) pairs in $CsMgCl_3$. The dots correspond to the observed resonance while the solid curves were calculated from the complete pair Hamiltonian by using the parameters in Table I.

The distribution of trivalent molybdenum in the $CsMX_3$ crystals appears to be governed by the same electrostatic considerations that were observed with other trivalent impurities.[2,4] The formation of pairs is suppressed by the presence of small monovalent ions such as lithium. The spectrum of a crystal of $CsMgCl_3$ doped with Li(I) and Mo(III) shows no pair resonances. Instead, strong resonances from single isolated Mo(III) ions are observed. These resonances, which almost certainly arise from the Mo(III)–Li(I) centers, are accurately described by the usual axial spin Hamiltonian:

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

The parameters are consistent with those of Mo(III) in an axial environment (at 77 K: $g_{\parallel} = g_{\perp} = 1.96$, $|D| = 0.75$ cm^{-1}).

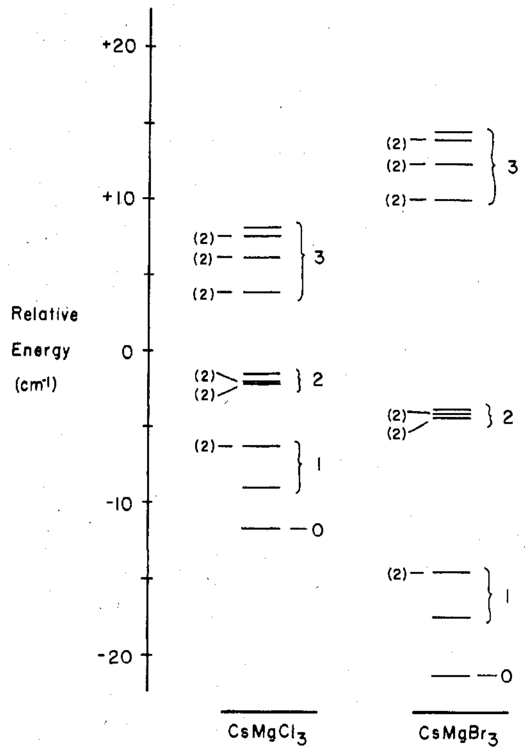

Figure 8. The energy levels of the Mo(III)–Mo(III) pairs in $CsMgCl_3$ and $CsMgBr_3$ at 77 K with no external magnetic field. The levels which are doubly degenerate are designated by "(2)".

Properties of the Exchange-Coupled Pairs. The exchange-coupled pairs which have been characterized in this study represent uniquely favorable systems in the sense that their EPR spectra are well resolved and that all the magnetic parameters can be evaluated directly from the spectra. Under these conditions it is possible to completely describe the energy level systems associated with these magnetic dimers. It appears that the magnetic interactions between the metal ions are accurately defined by a Hamiltonian which contains only linear exchange terms. There is no evidence that higher order effects such as biquadratic exchange are important in these systems. From a conceptual point of view it is pleasing that the rather complex EPR spectra can be accurately interpreted in terms of a simple theoretical model.

According to the signs of the parameters in Table I the exchange coupling in all of the pairs is antiferromagnetic. The treatment of the pair spectra establishes with certainty only the relative signs of the spin Hamiltonian parameters. Thus, an equally good fit of each pair spectrum would result if all the parameters for the system were given opposite signs. It is then appropriate to comment on the considerations which led to this choice of signs. It seems certain that the structures of the charge compensation stabilized pairs are very nearly the same in all the $CsMX_3$ crystals. Thus, the immediate environment of the trivalent ions in the pair should not change significantly from one host crystal to another. This implies that the single ion zero-field splitting (D_c) for a given trivalent ion should be the same sign and approximately the same magnitude in each of the crystals. Since Cr(III) and Mo(III) are both d^3 systems, it seems likely that the electron distributions are similar in the Cr(III)–Cr(III) and Mo(III)–Mo(III) pairs. Although the magnitudes may differ, the signs of the principal magnetic parameters, J and D_c in particular, should be the same in the chromium and molybdenum systems. In an ionic lattice the anisotropic exchange interactions between two octahedrally coordinated d^3 ions is primarily the result of dipolar coupling. This requires D_e to be negative. (If the unpaired electrons associated with the two metal ions are extensively delocalized onto the ligands, the origin and sign of D_e is much less certain.[9]) Of the hexachloro and hexabromo complexes of Cr(III) and Mo(III), the $CrCl_6^{3-}$ cluster should be most ionic. The observed value of D_e for the Cr(III)–Cr(III) pairs in $CsMgCl_3$ is very close to that which is calculated from the simple point dipole expression ($D_e = -g^2\beta^2/R^3$). If the two dipoles are separated by 6 Å (a reasonable estimate for $CsMgCl_3$), D_e is computed to be −0.0078 cm^{-1}. In this case the anisotropic interaction appears to be of dipolar origin which implies that D_e is negative. The choice of parameter signs shown in Table I follows directly from the initial assignment of a negative D_e for the Cr(III)–Cr(III) pairs in $CsMgCl_3$. In a number of other pair systems containing Cr(III) the sign of D_e has been assumed to be determined by the dipolar coupling.[6,10–13] For a group of structurally similar magnetic dimers the signs and magnitudes of the parameters in Table I seem quite reasonable. The conclusion that the isotropic exchange is antiferromagnetic is consistent with the observed temperature dependence of the pair resonance intensities.[4] Only in the case of the Mo(III)–Mo(III) pairs in $CsMgBr_3$ is the sign of D_e inconsistent with dipolar interactions. Of the hexahalo complexes, the $MoBr_6^{3-}$ system should have the greatest covalent character. Thus, the anisotropic interactions in this pair system should be least accurately described by a point dipole model. Although the evidence is not unequivocal, our choice is by far the most reasonable of the possible sign combinations.

Within this series of structurally related dimers it is interesting to compare the magnitudes of the various magnetic interactions from the different pair systems. (While the signs of the magnetic interactions are not absolutely certain, the magnitudes are well defined by the EPR analysis.) Certain general trends are apparent which are readily explained in terms of rather straightforward chemical and physical principles. Since the single ion zero-field splitting (D_c) arises by a mechanism which involves spin–orbit coupling, the magnitude of the splitting should be much larger in the systems containing Mo(III) than in those which contain Cr(III). The spin–orbit coupling constant (λ) of Mo(III) is about 3 times that of Cr(III) (272 vs. 91 cm^{-1}).[14] The measured values of D_c for the Cr(III)–Cr(III) and Mo(III)–Mo(III) systems are in qualitative agreement with this consideration. It seems clear that the exchange interaction in these pairs must take place through indirect superexchange pathways. The magnitude of the interaction should increase as the unpaired electrons become more delocalized from the central metal ions to the halide ligands. The isotropic exchange parameters (J) of the Mo(III)–Mo(III) systems are significantly larger than those of the Cr(III)–Cr(III) dimers. In any given chemical environment the 4d electrons of Mo(III) should be more delocalized than the 3d electrons of Cr(III), since the 4d orbitals are larger and more diffuse than the 3d orbitals. Also the exchange interactions seem to be somewhat stronger in $CsMgBr_3$ and $CsCdBr_3$ than in $CsMgCl_3$ which is consistent with the view that a metal–bromine bond has greater covalent character than a metal–chlorine bond. The magnetic interactions in the d^3 ion pairs are an interesting contrast to those of the previously studied Gd(III)–Gd(III) systems.[2,3] The isotropic exchange interactions in the rare earth dimers are approximately 3 orders of magnitude smaller (less than 0.001 cm^{-1}) than in the Cr(III) and Mo(III) systems. The anisotropic interactions in the Gd(III)–Gd(III) pairs are dipolar in origin and are accurately described by the simple point dipole expression. This contrast clearly reflects the fact that 4f electrons behave as inner-shell electrons and are much more localized than 4d or 3d electrons.

General Approach to Pair Spectra. The procedure based upon the computer diagonalization of the complete Hamiltonian matrix is quite successful in treating this series of pairs and seems to have a potential for general use. The fact that exact rather than approximate solutions to the complete spin Hamiltonian are obtained is an important advantage of this method. Although the Hamiltonian used in our treatment is rather simple, the procedure is readily adopted to more complex situations. For example, the spectrum of a coupled Cr(III)–Mo(III) pair has been successfully analyzed by the diagonalization procedure using an appropriately modified spin Hamiltonian.[15] The heterogeneous Cr(III)–Mo(III) dimer was observed in $CsMgCl_3$ crystals which were doped with both trivalent ions. While each resonance which appears in a pair spectrum requires a separate computation, the computer time consumed by each resonance field calculation is small. The complete angular dependence of a pair spectrum can be computed relatively quickly once the values of the Hamiltonian parameters are determined. A complete calculation requires between 1 and 2 h on the Interdata 7/16. The computation time should be significantly less on a larger and faster computer.

The most serious weakness in the procedure used in our analysis is the difficulty of finding the correct Hamiltonian parameters. The trial and error approach was extremely tedious, particularly in the case of the Mo(III)–Mo(III) pairs. During the course of our work, however, Edgar reported that the spectra of the Cr(III)–Cr(III) pairs in the $CsMX_3$ crystals could be accurately analyzed by a perturbation treatment carried to second order.[16] The exchange parameters, J and D_e, obtained in the perturbation treatment are in close agreement (within 10%) with those obtained by direct diagonalization. The important advantage of the perturbation procedure is that the Hamiltonian parameters can be determined from a pair spectrum in a straightforward manner. The parameters obtained in the perturbation procedure are sufficiently accurate that refinement by the exact diagonalization method is fairly easy. Edgar's perturbation method also gives reasonably good results when applied to the spectra of the Mo(III)–Mo(III) pairs. A great deal of time and effort could have been saved in our analysis of Mo(III)–Mo(III) spectra by the use of the perturbation expressions.

It appears that the combination of the perturbation treatment with direct diagonalization could be quite effective in the analysis of EPR spectra from magnetic dimers. Two conditions, however, must prevail in order for the approach to be completely successful. The first condition requires that the spectrum be sufficiently well resolved that the angular variation of a number of pair resonances may be followed. It is advantageous to obtain data at more than one microwave frequency. The second condition requires that the absolute value of the isotropic exchange (J) not exceed that of the single ion zero-field splitting (D_c) by more than 2 orders of magnitude. Edgar has shown that the second-order effects are proportional to the ratio, $(D_c)^2/J$. If $|J| \leq 100|D_c|$, it is possible to make a fairly accurate determination of J from this type of treatment. The fact that the exchange interactions are determined directly from the spectrum is an important advantage. Values determined in this manner should be considerably more accurate than those determined by the more traditional method of following the temperature dependence of the pair spectrum.

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Registry No. $CsMgCl_3$, 13845-09-5; $CsMgBr_3$, 38994-50-2; $CsCdBr_3$, 16593-55-8; Cr(III), 16065-83-1; Mo(III), 22541-86-2.

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Ligand Field Photolysis of Some *cis*-β-1,4,8,11-Tetraazaundecane Complexes of Cobalt(III) and Rhodium(III): Evidence for Stereochemical Control in d^6 Photochemistry

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The ligand field photolysis of *cis*-β-[M(2,3,2-tet)ClX]$^{n+}$ (M = Co, Rh; X = Cl, H_2O) and the thermal aquations of *cis*-α- and *cis*-β-[Rh(trien)Cl_2]$^+$ and *cis*-β-[Rh(2,3,2-tet)Cl_2]$^+$ were studied in acidic aqueous solution. Photolysis of *cis*-β-[Co(2,3,2-tet)Cl_2]$^+$ and *cis*-β-[Co(2,3,2-tet)Cl(H_2O)]$^{2+}$ leads to *trans*-[Co(2,3,2-tet)Cl(H_2O)]$^{2+}$ as the only photoproduct at efficiences ($\phi_{Cl_2} = 0.0083$, $\phi_{Cl(H_2O)} = 0.0053$) typical for cobalt(III) amine complexes. Photolysis of *cis*-β-[Rh(2,3,2-tet)Cl_2]$^+$ generates *cis*-β-[Rh(2,3,2-tet)Cl(H_2O)]$^{2+}$ and *trans*-[Rh(2,3,2-tet)Cl(H_2O)]$^{2+}$ with a total chlorine-release efficiency of $\phi = 0.26$ and a trans/cis photoproduct ratio of about 3/1. *cis*-β-[Rh(2,3,2-tet)Cl(H_2O)]$^{2+}$ photoisomerizes to *trans*-[Rh(2,3,2-tet)Cl(H_2O)]$^{2+}$ ($\phi = 0.13$). A kinetic study of the chloride aquation of *cis*-α- and *cis*-β-[Rh(trien)Cl_2]$^+$ and *cis*-β-[Rh(2,3,2-tet)Cl_2]$^+$ showed that all three ions aquated with retention of the cis configuration and with pH-independent (pH 1–4) pseudo-first-order rate constants (at pH 2, $\phi = 0.15$, and $T = 25$ °C, $k_{Cl^-} = 1.8 \times 10^{-4}$, 16.7×10^{-4} and 3.7×10^{-4} s^{-1}, respectively). The photochemical behavior of *cis*-β-[M(2,3,2-tet)ClX]$^+$ ions is compared to the photochemistry of the analogous trien complexes, and the increased percentage of photoisomerization is justified in terms of a dissociative mechanism.

Introduction

The stereochemical consequences of the ligand field photolysis of Rh(III) and Co(III) complexes have become quite perplexing, as stereoretentive photolyses[1] as well as photoinduced isomerizations[2] have been observed for both metals. Until recently, the only models which dealt with photoinduced stereochemical change in transition-metal complexes were (a) an edge-displacement model,[2d,3] based on the semiempirical photolysis rules,[4] and (b) a mechanism involving distortion of the excited state toward a five-coordinate species with a geometry dependent upon the ligands remaining in the primary coordination sphere.[5] The fundamental difference between these empirical models is the former's retention of at least six-coordinate geometry throughout the reaction, while the latter path assumes the existence of a coordinatively unsaturated species at some point along the reaction coordinate.

A more theoretical analysis of the stereochemical consequences of ligand field excitation of d^6 complexes, recently presented by Vanquickenborne and Ceulemans,[6] also postulated the existence of five-coordinate species during the photolysis. They used an additive point ligand model[7] (APLM) to analyze the orbital energies of the five-coordinate species which would remain following photoinduced ligand labilization. For the d^6 haloammine complexes analyzed, the square-pyramid (SP) structure was calculated to be significantly more stable than the trigonal-bipyramid (TBP) structure, with the photoproduct resulting from stereospecific water attack at the vacant coordination site (trans to the axial ligand) in the SP structure. The stereochemical path of a photochemical reaction can thus be predicted by the calculation of the specific SP species which would predominate.

A tacit assumption in the Vanquickenborne analysis is that the photogenerated five-coordinate species would have a sufficient lifetime to allow intramolecular rearrangement to the lowest energy configuration. For cationic complexes in a tenaciously solvating and highly nucleophilic medium such as water, the existence of coordinatively unsaturated di- and trivalent cations for a finite period is open to question.

In an effort to probe the importance of coordinatively unsaturated species in the photochemistry of d^6 haloamine complexes, we have studied the ligand field photochemistry of *cis*-β-[M(2,3,2-tet)ClX]$^{n+}$ (M = Co, Rh; X = Cl, H_2O).[8]

As shown in Figure 1, the 2,3,2-tet complexes differ only marginally from the previously studied[3,5] *cis*-β-[M(trien)ClX]$^{n+}$ ions, where photolysis leads to mixtures of *cis*-β- and *trans*-[M(trien)Cl(H_2O)]$^{2+}$. By use of the edge-displacement model, the formation of these two photoproducts results from the photoinduced labilization of the ligands at either end of the axis defined by a primary amine and a coordinated chloride. The isomeric composition of the photoproduct then reflects the discrimination between amine and chloride loss along the photoreactive axis, as chloride loss would lead directly to *cis*-β-[M(trien)Cl(H_2O)]$^{2+}$ and amine labilization would lead to edge-displacement and formation of *trans*-[M(trien)Cl(H_2O)]$^{2+}$.

The factors which affect the degree of discrimination between chloride and amine labilization are unknown, but the addition of a methylene group in the central chelate ring would not affect the reactivity pattern of an excited state formed upon the population of metal-centered orbitals. Thus, if the edge-displacement model is valid, photolysis of *cis*-β-[M(2,3,2-tet)ClX]$^{n+}$ ions should closely mimic that of the corresponding *cis*-β-[M(trien)ClX]$^{n+}$ ions.

In contrast, if the photochemical reaction proceeds via a species of reduced coordination number, addition of a methylene group into the chelated amine could have profound effects upon the stereochemistry of the photoproducts. The trien ligand forms transition-metal complexes almost exclu-

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