An Interpretation of the Polarized Crystal Spectra of Mn(II) and Co(II) in D_{2h} Symmetry

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Crystals of TMA$M_xM'_{1-x}$Cl$_3$ · 2H$_2$O where TMA = (CH$_3$)$_3$NH$^+$ and M = Mn^{2+}, M' = Co^{2+} are strikingly pleochroic. The polarized spectra of these highly colored orthorhombic salts are reported and transition assignments are made based on D_{2h} symmetry. Peaks in the Mn(II) spectra are explained as electric dipole transitions while peaks in the Co(II) spectra are explained as magnetic dipole transitions. © 1985 Academic Press, Inc.

Introduction

Crystal spectra of the divalent ions of Mn and Co in various environments have been published. Lawson (*1*) has reported polarized crystal spectra for both MnCl$_2$ · 2H$_2$O and CoCl$_2$ · 2H$_2$O and has attempted to make transitional assignments based on octahedral symmetry. These isomorphous salts are monoclinic and belong to the C2/m space group (*2, 3*); crystal growth is along c with well-developed (110) faces. Neither the spectrum of the Mn nor the Co salt

taken with polarized light incident upon this face can be fully explained assuming a cubic field. Ferguson and Wood (*4*) have also collected polarized crystal spectra for CoCl$_2$ · 2H$_2$O; they defined an orthogonal a', b, c axis system and sectioned crystals to obtain spectra in all three polarizations. These authors made transition assignments based on C_{2h} symmetry, but were still unable to satisfactorily explain all the observed peaks.

In this paper we report the results of a spectroscopic study of TMAMnCl$_3$ · 2H$_2$O, TMACoCl$_3$ · 2H$_2$O and TMAMn$_x$Co$_{1-x}$Cl$_3$ · 2H$_2$O where TMA represents the tri-
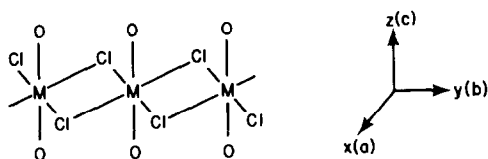
FIG. 1. Location of unit cell axes and polarization directions in orthorhombic salts TMAMCl$_3$ · 2H$_2$O. The morphological needle axis, the chain direction which is the b crystallographic axis and the coordinate axis defined as y all coincide.

methylammonium cation, $(CH_3)_3NH^+$. All three TMA salts are visibly dichroic; that is, they exhibit two different colors even in unpolarized light. For example, the (001) face of the Co containing crystals appears red and the (100) face appears blue. Therefore, the spectra of these compounds must be described utilizing a field with lower than cubic symmetry. Tetragonal symmetry is eliminated as a viable field environment, because three different polarized spectra actually exist for the TMA salts. The highest symmetry point group which fits the observed polarization data is D_{2h} and transition assignments are made based on this symmetry.

Crystal Structure

Caputo, Willett, and Muir (5) have reported the crystal structure of TMAMnCl$_3$ · 2H$_2$O; Losee et al. (6) have reported the structure of TMACoCl$_3$ · 2H$_2$O. Both salts are orthorhombic crystallizing in the Pnma space group. The TMA salts, MnCl$_2$ · 2H$_2$O and CoCl$_2$ · 2H$_2$O all possess the same chromophore, chains of edge-shared MCl$_4$(H$_2$O)$_2$ octahedra. In the TMA salts the crystal habit reflects the internal orthorhombic symmetry which makes orientation of the electric vector of polarized light with the unit cell axes a relatively simple process. Figure 1 illustrates the location of the unit cell axes with respect to the chromophore.

Precession photographs of the mixed-

metal analog TMAMn$_x$Co$_{1-x}$Cl$_3$ · 2H$_2$O indicate that its structure is also orthorhombic, space group Pnma. Cell parameters for the mixed metal crystals are intermediate to those for the pure end members as expected.

Experimental

Sample Preparation

Single crystals of TMAMnCl$_3$ · 2H$_2$O, TMACoCl$_3$ · 2H$_2$O, and TMAMn$_x$Co$_{1-x}$Cl$_3$ · 2H$_2$O were grown by slow evaporation of aqueous solutions containing stoichiometric amounts of trimethylamine hydrochloride and the divalent metal chlorides. Crystals tended to grow parallel to [010] with well-developed (100) faces. Larger crystals, in which the principal directions are not so easily located, may be grown from solutions containing concentrated HCl. Metal and chloride content were determined by titration; structural information was obtained from precession photographs.

Single Crystal Absorption Spectroscopy

Polarized spectra were collected on single crystals of the TMA salts at room temperature utilizing a Cary 14 spectrophotometer. Measurements were made on TMA MnCl$_3$ · 2H$_2$O and TMAMn$_x$Co$_{1-x}$Cl$_3$ · 2H$_2$O with polarized light incident on the (100) and (001) faces; specra of TMACoCl$_3$ · 2H$_2$O were taken on the (100) and (010) faces. Both color and precession photographs were used as a check on orientation and polarization directions.

Spectra were collected for the mixed-metal crystal at reduced temperatures using a homemade Dewar flask which permitted a stream of cold nitrogen gas to envelope the crystal. A thermocouple was attached to the crystal mount to determine the temperature of the crystal while recording. Spectra were taken at 130, 180, and 250 K in addition to room temperature (295 K).

When referring to the polarization directions in the following discussion, the notation $\hat{x}$-L is used to designate light in which the electric vector is parallel to the x coordinate or a crystallographic axis, similarly for y- and z-polarized light.

Results and Discussion

The Hamiltonian for a many-electron wavefunction includes several terms which are combined as H_0 and form the ground state of the $3d$ transition metal ion. The Hamiltonian then is

$$\hat{H} = \hat{H}_0 + V_c$$

where V_c is the perturbation introduced by the crystal field and which must transform according to local site symmetry. The environment of the metal ion in the TMA salts suggests that V_c should transform under D_{4h} symmetry, but the observed polarized spectra require an even lower symmetry as noted earlier. An orthogonal coordinate axis system has been defined in which the x, y, and z polarization directions correspond to the a, b, and c crystallographic axes of the orthorhombic unit cell. An important feature of the structure of the TMA salts is that each chromophore within the unit cell is oriented in almost the same direction. If this were not true, the dichroic effect would cancel in the same way as optical activity in a racemate.

Manganese(II) Spectra

For a static complex containing high-spin Mn(II) all electric dipole transitions are both spin- and parity-forbidden. Inclusion of vibronic coupling, however, removes the parity restriction for some transitions, but because they remain spin-forbidden, such peaks should be narrow and relatively weak in intensity. The transition moment is given by $\langle \psi'_e \psi'_v | \hat{M} | \psi_v \psi_e \rangle$ where ψ_e and ψ_v are the electronic and vibrational wavefunctions, respectively, and $\hat{M}$ is either the electric or

TABLE I

NORMAL MODES OF VIBRATION FOR AN ML_6 COMPLEX IN D_{2h} SYMMETRY

$3A_g$	B_{1g}	B_{2g}	B_{3g}
	$3B_{1u}$	$3B_{2u}$	$3B_{3u}$

magnetic dipole moment operator. For this integral to be nonzero the direct product must contain the totally symmetric representation. In D_{2h} both the electronic ground state, ψ_e, for Mn(II) and the vibrational ground state, ψ_v, belong to the A_g representation. Therefore a transition is vibronically allowed only if the direct product of the representations of the operator and the excited electronic state, ψ'_e, is one of the normal modes of vibration. For electric dipole transitions in D_{2h} symmetry the representations of the moment operators for $\hat{x}$-L, $\hat{y}$-L, and $\hat{z}$-L are B_{3u}, B_{2u}, and B_{1u}, respectively. The corresponding magnetic dipole moment operator representations are B_{3g}, B_{2g}, and B_{1g}. The 15 normal modes of vibration for an ML_6 complex in D_{2h} are listed in Table I. Because A_u is not one of these modes, any product with this representation corresponds to a forbidden symmetry transition.

The relative ordering of the d^5 energy levels in an octahedral environment may be determined from a Tanabe–Sugano diagram (7). In D_{2h} symmetry the splitting arrangement proposed in Fig. 2 yields the best correlation of the observed polarized spectra with group theoretical predictions. The lowest energy peak seen in the Mn(II) spectra presented in Fig. 3 occurs at 580 nm. Because it disappears in $\hat{x}$-L, it is assigned as the $A_g \rightarrow B_{3g}$ transition. The band centered around 530 nm shows definite changes in shape and intensity in various polarizations. It is most intense in $\hat{x}$-L, but is also present in $\hat{y}$-L and $\hat{z}$-L. While both the $A_g \rightarrow B_{1g}$ and $A_g \rightarrow B_{2g}$ transitions are allowed in $\hat{x}$-L, the former is forbidden in $\hat{z}$-L, the latter in $\hat{y}$-L. These transition assign-

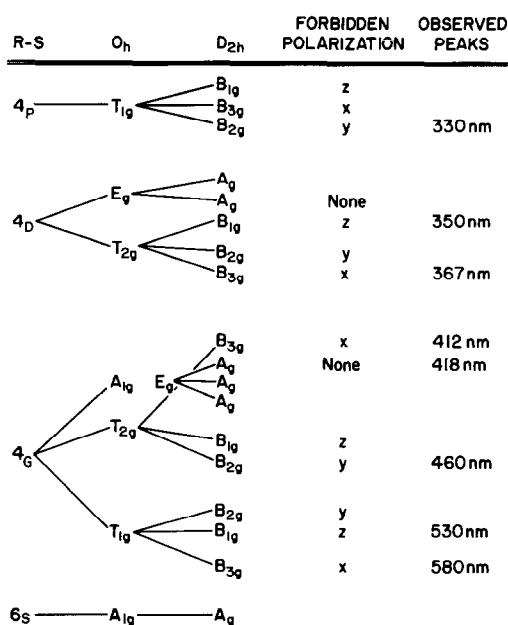| R-S	O_h	D_{2h}	FORBIDDEN POLARIZATION	OBSERVED PEAKS
^4P	T_{1g}	B_{1g}	z	
		B_{3g}	x	
		B_{2g}	y	330nm
^4D	E_g	A_g	None	
		A_g		
		B_{1g}	z	350nm
	T_{2g}	B_{2g}	y	
		B_{3g}	x	367nm
^4G	A_{1g} E_g	B_{3g}	x	412nm
		A_g	None	418nm
		A_g		
		A_g		
	T_{2g}	B_{1g}	z	
		B_{2g}	y	460nm
	T_{1g}	B_{2g}	y	
		B_{1g}	z	530nm
		B_{3g}	x	580nm
^6s	A_{1g}	A_g		

FIG. 2. Proposed energy level diagram for Mn(II).

ments account for the behavior of the peak at 530 nm.

The sharp peak at 412 nm disappears completely in $\hat{x}$-L while the broader, less intense peak at 418 nm displays no polarization effects. The three A_g levels arising from E_g and A_{1g} (^4G) could yield the unpolarized band at 418 nm. The proposed splitting of T_{2g} (^4G) suggests that the $A_g \rightarrow B_{3g}$ transition is the source of the peak at 412 nm. This leaves the $A_g \rightarrow B_{1g}$ and $A_g \rightarrow B_{2g}$ transition to be explained.

The peak at 460 nm cannot be assigned solely as an electric dipole transition. If $A_g \rightarrow B_{1g}$ were an extremely weak electric dipole transition, it could be assigned as the peak seen in $\hat{x}$-L. It is forbidden in $\hat{z}$-L and is lost beneath the larger band present in $\hat{y}$-L. The behavior of this larger peak suggests that $A_g \rightarrow B_{2g}$ may be a magnetic dipole transition. The operator for such transitions has even symmetry, and in D_{2h} symmetry magnetic dipole transitions are allowed in just those polarizations in which electric dipole transitions are forbidden. This implies

that $A_g \rightarrow B_{2g}$ is allowed only in $\hat{y}$-L which fits the observed data. This peak is too weak to be observed in the mixed crystal, so its behavior as a function of temperature has not been observed.

The peak at 367 nm is visible in all polarizations, but it is most intense in $\hat{z}$-L. It is assigned as the superimposed $A_g \rightarrow B_{2g}$ and $A_g \rightarrow B_{3g}$ transitions. The former is present in $\hat{x}$-L, the latter in $\hat{y}$-L, and both are allowed in $\hat{z}$-L. The B_{1g} (^4D) level is superimposed on the two A_g (^4D) levels. Thus, the peak at 350 nm is drastically reduced in intensity in $\hat{z}$-L, but does not completely disappear due to the presence of the unpolarized $A_g \rightarrow A_g$ transitions.

Because the peak at 330 nm disappears in $\hat{y}$-L, it may be assigned as the $A_g \rightarrow B_{2g}$ (^4P) transition. Higher energy peaks were not seen as the polarizers absorb strongly in the UV region.

Peaks in the spectra of the TMA salt coincide with those reported by Lawson for $MnCl_2 \cdot 2H_2O$ which contains the same chromophore. Lawson's spectral data could not be fully explained assuming octahedral symmetry. However, the proposed energy level diagram based on D_{2h} symmetry accounts for the observed polarized spectra of $TMAMnCl_3 \cdot 2H_2O$.
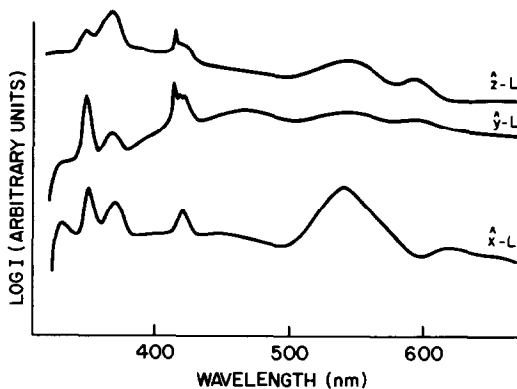
FIG. 3. Polarized crystal spectra of $TMAMnCl_3 \cdot 2H_2O$. Light in which the electric vector is parallel to x is designated $\hat{x}$-L; similarly for $\hat{y}$-L and $\hat{z}$-L.

R-S	O_h	D_{4h}	D_{2h}	FORBIDDEN POLARIZATION CALCULATED	TMACoCl$_3$·2H$_2$O PEAKS	FORBIDDEN POLARIZATION OBSERVED
			A_{2g}—B_{1g}	None	425 nm	?
^4P	T_{1g}		B_{2g}	x	515 nm	y,z
		E_g	B_{3g}	y	545 nm	x,z
			A_{2g}—B_{1g}—A_g	z	610 nm	x,y
			B_{3g}	y	830 nm	x,z
	T_{2g}	B_{2g} E_g	B_{1g}	None		
^4F			B_{2g}	x		
	T_{1g}	E_g	B_{2g} B_{3g}			
			A_{2g}—B_{1g}			

FIG. 4. Proposed energy level diagram for Co(II).

Cobalt(II) Spectra

The spin allowed transitions in the Co(II) complex yield observed peaks which are much more intense than those in the Mn(II) spectra. In the visible region of the TMACo Cl$_3$ · 2H$_2$O spectra the broad band between 500 and 550 nm is so intense that it was impossible to obtain crystals thin enough to keep the recorder on scale in $\hat{x}$-L and $\hat{y}$-L. Crystals of TMAMn$_x$Co$_{1-x}$Cl$_3$ · 2H$_2$O can be chosen in which the mole fraction of Co is low enough so that all peaks remain on scale in all polarizations. Since there is apparently no interaction between the different metal ions in the mixed salt (*vide infra*), the spectra of the mixed metal crystals are utilized in the discussion of the transitions in the Co(II) ion.

Cobalt(II) Spectra in the Presence of Manganese(II)

If the polarized spectra of TMAMn$_x$ Co$_{1-x}$Cl$_3$ · 2H$_2$O are compared to those of TMAMnCl$_3$ · 2H$_2$O, it is noted that the peaks due to Mn(II) map on both except for the two lowest-energy transitions which are lost beneath the more intense spin allowed transitions of the Co(II) ion. A similar correspondence is observed for the peaks due to Co(II), if the spectra of the Mn–Co and pure Co salts are compared. If the unavoidable intensity differences are neglected, the spectra of the mixed-metal crystal are simply the sum of the Mn(II) and Co(II) individual spectra.

The results of this work also apply to the spectra of CoCl$_2$ · 2H$_2$O reported by Ferguson and Wood (*4*). Careful comparison of actual polarization directions with respect to the CoCl$_4$(H$_2$O)$_2$ octahedra indicates that the spectra in all polarizations at 10 K are very similar to those of the Co containing TMA salts at room temperature. The proposed energy level diagram in Fig. 4 thus provides a consistent explanation of the spectral data for both Co salts.

The Russell–Saunders ground state for Co(II), a d^7 ion, is ^4F; Tanabe–Sugano diagrams (*7*) show that in an octahedral field this term splits into A_{2g} + T_{2g} + T_{1g}, the latter of which is the ground state. When the degeneracy of the T_{1g} level is removed by lowering the symmetry to D_{2h}, three new energy levels arise, B_{1g} + B_{2g} + B_{3g}, any of which could be the new ground state. These splitting patterns are shown in Fig. 4; the relative ordering in D_{4h} is based on data for CoCl$_2$ · 6H$_2$O reported by Ferguson and Wood (*8*).

The visible spectra of Co(II) complexes have generally been explained as electric dipole transitions. In the spectra of the TMA salt most of the observed peaks decrease in intensity in two polarizations, behavior indicative of magnetic dipole transitions in D_{2h} symmetry. The magnetic moment is given by $\langle \psi_e | \hat{M} | \psi_e \rangle$ where $\hat{M}$ has even symmetry, B_{1g}, B_{2g}, or B_{3g} as noted previously. The electronic wavefunctions also have even symmetry. Therefore, magnetic dipole transitions are Laporte-allowed for Co(II) whereas electric dipole transitions are Laporte-forbidden because the
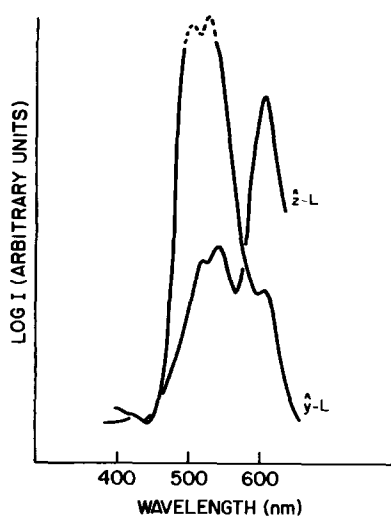
FIG. 5. Polarized crystal spectra of TMACoCl$_3$ · 2H$_2$O. In $\hat{x}$-L and $\hat{y}$-L the band between 500 and 550 nm is offscale. The peak shape here is inferred from the $\hat{z}$-L spectrum.

electric dipole operators possess odd symmetry. A magnetic dipole transition is considerably weaker than an electric dipole transition. Similarly, a Laporte-forbidden transition is much weaker than a Laporte-allowed transition. Therefore, it is reasonable to assume that a Laporte-allowed magnetic dipole transition and a Laporte-forbidden electric dipole transition are of comparable intensity.

Selecting B_{1g} as the ground state yields the splitting arrangement shown in Fig. 4. This energy level diagram adequately explains the observed spectral data shown in Figs. 5 and 6. Superimposed on the broad band between 500 and 550 nm are two peaks which are assigned as the $B_{1g} \rightarrow B_{2g}$ and $B_{1g} \rightarrow B_{3g}$ magnetic dipole transitions. They occur at 515 and 545 nm, respectively, and the former is allowed only in $\hat{x}$-L while the latter is allowed only in $\hat{y}$-L. The peak at 610 nm, the lowest energy transition in the visible region, is assigned as the $B_{1g} \rightarrow A_g$ transition allowed only in $\hat{z}$-L. The highest energy band in the near IR re-

gion is found at 830 nm. Visible only in $\hat{y}$-L, it represents the $B_{1g} \rightarrow B_{3g}$ magnetic dipole transition. The two remaining IR peaks seen in the low-temperature spectra of Co Cl$_2$ · 2H$_2$O were never observed in the TMA salt. The highest energy spin-allowed transition, $B_{1g} \rightarrow B_{1g}$ (^4P), is magnetically forbidden in all polarizations. No such peak appears in the Co(II) spectra.

Ferguson and Wood (4) reported a charge transfer band at 395 nm which increases in intensity as temperature decreases and is polarized perpendicular to the chain direction. This peak is not seen in the spectra of the TMA salts. However, a very weak band appears at 425 nm in the latter spectra which is not seen in the Co Cl$_2$ · 2H$_2$O spectra. Although most intense in $\hat{z}$-L, it is also visible in $\hat{y}$-L and $\hat{x}$-L. Because of its weak intensity, its absence in the spectra of the mixed Mn–Co crystal would not be surprising. Close examination of the mixed metal spectra in Fig. 6 reveals evidence of a shoulder on the 418-nm peak of Mn(II) which may be this transition. This peak may be explained in two ways: as the $B_{1g} \rightarrow B_{1g}$ electric dipole transition or as a
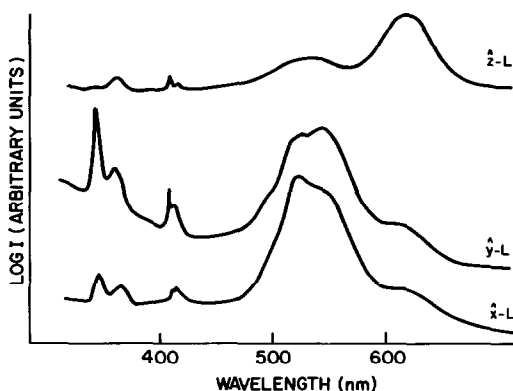

FIG. 6. Polarized crystal spectra of TMAMn$_x$Co$_{1-x}$ Cl$_3$ · 2H$_2$O. Spectra for $\hat{x}$-L and $\hat{y}$-L polarizations have been run at several temperatures down to 130 K. Changes in the spectra as a function of temperature are too small to be plotted on the scale of the figure. For details see discussion in text.

spin-forbidden transition to one of the ^2G energy levels. Because of intensity considerations, the latter interpretation is preferred.

The low-temperature spectra of the Co–Mn mixed system support this explanation. The three major Co(II) bands in the visible region, at 610, 545, and 515 nm, are essentially temperature-independent, as would be expected of magnetic dipole transitions. In contrast, the vibronic transitions of Mn(II) which can be observed in the mixed crystal all show an enhancement of intensity as the temperature is lowered; the band at 417 nm, which contains several components in the proposed assignment scheme, resolves into two components, at 415 and 420 nm.

Description of the Co(II) spectra in the TMA salt as magnetic dipole transitions leaves only one peak unexplained. This broad, intense band at 510–550 nm present in $\hat{x}$-L and $\hat{y}$-L almost completely disappears in $\hat{z}$-L. Although one would expect it to be an electric dipole transition since it persists in two polarizations, no choice of ground state in either D_{2h} or D_{4h} symmetry can account for its polarization. Ferguson and Wood (4) have described this peak as an "anomalous" band, utilizing water vibrations to induce intensity for transitions to some of the spin-forbidden doublet terms. However, it is difficult to accept this peak as a spin-forbidden transition because of its intensity, particularly in comparison to the peak observed at 425 nm. The peak is well-documented, appearing in all Co(II) spectra, but only in polarized spectra of lower symmetry such as D_{2h} does its interpretation become a problem. It has been described in the literature as the T_{1g} (^4F) → T_{1g} (^4P) electric dipole transition in octahe-

dral symmetry or A_{2g} → E_g in tetragonal symmetry. Without polarization data, no conflict arises in these assignments based on an octahedral energy level diagram. More spectral work needs to be done utilizing polarized light in complexes of lower symmetry in order to fully explain the origin of this peak.

Conclusion

The polarized crystal spectra of TMAMCl$_3$ · 2H$_2$O where M = Mn or Co have been studied. The chromophore in these salts, MCl$_4$(H$_2$O)$_2$, suggests that the observed peaks can be explained based on tetragonal symmetry. However, because three different polarized spectra actually exist, transition assignments were ultimately made utilizing D_{2h} symmetry. The proposed energy level diagram for Mn(II) is adequately explained by assuming that the observed peaks are electric dipole transitions whereas the behavior of the Co(II) peaks in polarized light require that they be described as magnetic dipole transitions.

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