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Electronic Structure of the Tris(ethylenediamine)manganese(II) Ion. Circular and Linear Dichroism and Electron Paramagnetic Resonance Spectra of $Mn(en)_3(NO_3)_2$

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Received September 27, 1977

The electronic structure of the tris(ethylenediamine)manganese(II) ion has been investigated by measurement of the orthoaxial linear dichroism (LD), axial absorption, axial circular dichroism (CD), and electron paramagnetic resonance (EPR) spectra of manganese-doped $Zn(en)_3(NO_3)_2$ single crystals. Cotton effects associated with the spin-forbidden ligand field transitions to states derived from $^4T_{2g}(G)$ ((^4E_g, A_{1g})(G)) and $^4T_{2g}(D)$ are observed in the CD spectra at 1.98, 2.36, and 2.65 μm^{-1}, respectively, all with the same sign of $\Delta\epsilon$ in a given crystal. These transitions, as well as the lower quartet level $^4T_{1g}(G)$ (1.50 μm^{-1}), not observed in the CD spectra, are also observed in the LD and axial absorption spectra. The sharp band assigned to the (^4E_g, $^4A_{2g}$)(G) transitions reveals four distinct components at 2.357 ± 0.005, 2.370 ± 0.001, 2.385 ± 0.0005, and 2.395 ± 0.001 μm^{-1} in the absorption spectra. Only the first two of these are prominent in the CD spectra and they are assigned to the origins of the $^4E_g(G)$ and $^4A_{1g}(G)$ transitions, respectively. The ligand field parameters deduced are $Dq = 0.108$, $B = 0.0860$, and $C = 0.301$ μm^{-1}. The EPR data yield $g_\parallel = 2.004 \pm 0.005$ and $g_\perp = 2.021 \pm 0.005$ and $A = 77 \pm 1$, $D = +197 \pm 10$, and $(a - F) = (+15 \pm 10) \times 10^{-4}$ cm^{-1}. The magnitude and sign of D correlate with the magnitude of the trigonal splitting deduced from the electronic spectrum and the trigonally compressed geometry revealed in the crystal structure of the nickel analogue.

Introduction

As previously reported, the crystals of $Zn(en)_3(NO_3)_2$ are enantiomorphous and are isomorphous with the crystals of the analogous nickel compound.[1,2] The enantiomorphous hexagonal crystal with its D_3 metal site symmetry[3] provides an ideal host lattice for study of the electronic spectra of tris(ethylenediamine) complexes of divalent transition-metal ions, including not only the linear dichroism (LD) but also the circular dichroism (CD). Although the pure crystals of the complexes of nickel(II) and cobalt(II) can be grown, other nitrate salts of tris(ethylenediamine)metal(II) ions are best obtained by cocrystallization with the zinc complex. These include the complexes of copper(II), ruthenium(II), and manganese(II). Of these, the manganese(II) complex is particularly interesting, since relatively few tris(bidentate ligand) chelates of manganese(II) are known. The only previous study of the electronic spectra of such a complex is that of the single-crystal absorption and emission spectra of $Mn(OMPA)_3(ClO_4)_2$.[4] Furthermore, natural optical activity of a manganese(II) complex has previously been reported only for manganese-doped α-$Zn(H_2O)_6SeO_4$.[5] Here we report the single-crystal electronic spectra of $Zn(Mn)(en)_3(NO_3)_2$ (orthoaxial LD, axial CD, and axial absorption) along with correlative data on the electron paramagnetic resonance.

Experimental Section

Crystals of $Zn(en)_3(NO_3)_2$ doped to as much as 10 mol % with manganese(II) were obtained from a N_2-purged, saturated aqueous solution of the zinc compound innoculated with a few drops of concentrated manganese nitrate solution. A small excess of ethylenediamine was present. Crystal growth was by slow evaporation in a glovebag under N_2. The percent manganese in the crystals was determined by atomic absorption. The crystals were cut and polished as previously described.[2]

Absorption spectra and CD spectra were measured using a Cary 14R spectrophotometer and JASCO ORD/CD-5 (SS-20 modification) instrument, respectively. The detailed description of the instrumentation and techniques of recording and treating the data have been given earlier.[1,2] Spectral bandwidth for the Cary 14R was 0.83 Å (slit width 0.025 mm), whereas the minimum for the JASCO instrument was 2.8 A (slit width 0.020 mm). The slit width on the JASCO instrument in the region of the sharp 2.36-μm^{-1} band was adjusted manually to the above value in order to resolve the fine structure more completely. Maximum time constant (64 s) and minimum scan speed were necessary in order to achieve a CD S/N of ≥10 using this reduced slit width. Both the Cary and JASCO instruments were wavelength calibrated using the 4460- and 3608-Å lines of a Ho_2O_3 filter. EPR spectra were measured on a Varian V-4502-15 X-band spectrometer system equipped with frequency- and power-monitoring devices. The concentration of manganese in the crystals used for EPR spectra was ≤1 mol %.

Results

Room-temperature axial absorption and CD spectra are shown in Figure 1. The CD spectrum of the enantiomer with negative Cotton effects for the ligand field bands is chosen for illustration. The assignments of the bands in terms of their octahedral parentages and spectral results in terms of dipole

Table I. Axial Absorption and Circular Dichroism Spectral Data for $Zn(Mn)(en)_3(NO_3)_2$

	ν_{max}, μm^{-1}					
Excited state	Abs	CD	Calcd[a]	$10^{40}D$, cgsu	$10^{44}R$, cgsu	g ($4R/D$)
$^4T_{1g}(G)$	1.50		1.50	$0.6\bar{5}$		
$^4T_{2g}(G)$	1.99	1.98	1.99	$0.6\bar{0}$	$9.\bar{4}$	0.006
$(^4E_g, {}^4A_{1g})(G)$	2.36	2.36	2.36	$0.1\bar{4}$	$2\bar{3}$	$0.06\bar{6}$
$^4T_{2g}(D)$	2.65	2.65	2.72	$0.1\bar{0}$	$8.\bar{1}$	$0.03\bar{2}$

[a] $Dq = 0.108$, $B = 0.0860$, and $C = 0.301$ μm^{-1}.

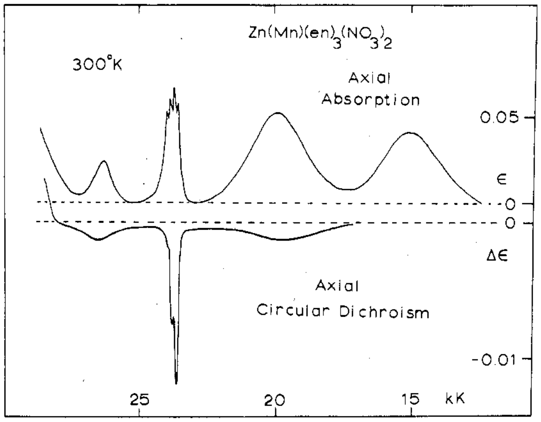

Figure 1. Single-crystal axial absorption and axial circular dichroism of manganese-doped $Zn(en)_3(NO_3)_2$ at room temperature.

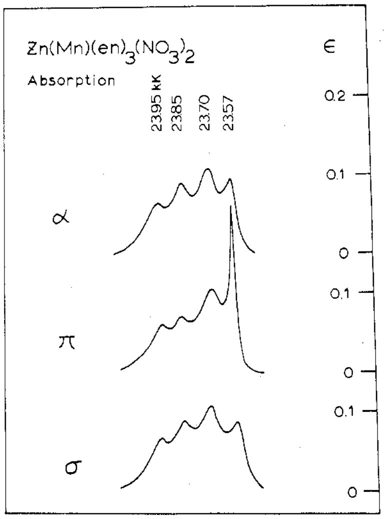

Figure 2. Single-crystal (α) and orthoaxial π ($\parallel C_3$) and σ ($\perp C_3$) absorption spectra of manganese-doped $Zn(en)_3(NO_3)_2$ in the region of the $(^4E_g, {}^4A_{1g})(G) \leftarrow {}^6A_{1g}$ transitions at room temperature.

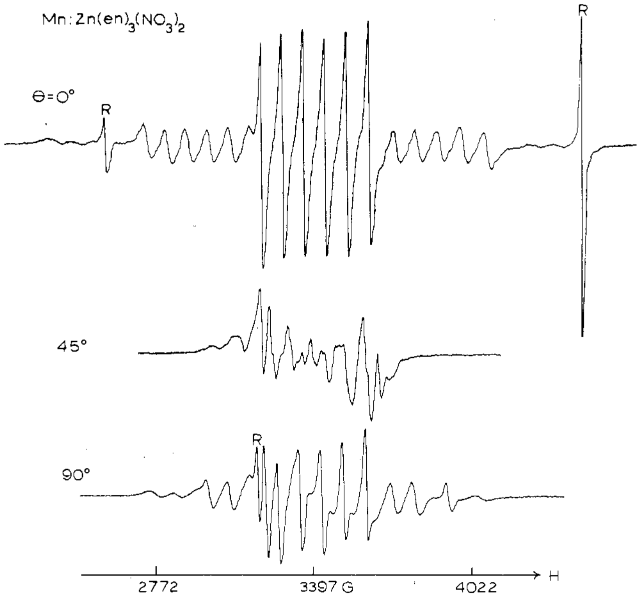

Figure 3. Single-crystal EPR spectra of manganese-doped $Zn(en)_3(NO_3)_2$ at room temperature with θ = 0, 45, and 90°.

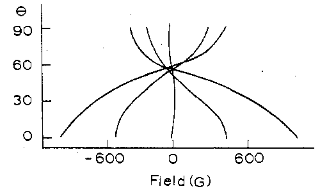

Figure 4. Field variation in the centers of the fine-structure sextets as a function of θ in a manganese-doped $Zn(en)_3(NO_3)_2$ single crystal.

strengths, rotational strengths, and anisotropy factors are given in Table I. The dipole strengths are very small, and the rotational strength is vanishingly small in the first quartet level. Because of the low concentration of manganese(II) ion in the crystal and relatively small thickness of the crystal in the orthoaxial direction, it was difficult to obtain the detailed absorption spectra of the broader and lower energy bands in the 15–20-μm^{-1} region. However, the results at higher energy are much clearer and reveal, unmistakably, an unusual splitting of the sharp bands at 2.36 μm^{-1} into four components. The first one at 2.357 ± 0.0005 μm^{-1} is strongly π polarized. The spectra obtained in this region (axial, σ, and π)[6] are shown in Figure 2. The molar absorptivities of these bands are very low ($\epsilon < 0.1$), but the $\Delta\epsilon$ is relatively large, at least for the 2.357 ± 0.0005 and 2.370 ± 0.001 μm^{-1} maxima. Only weak shoulders in the CD spectra are associated with the absorption maxima at 2.385 ± 0.0005 and 2.395 ± 0.001 μm^{-1}. These components must have R of at least one order of magnitude smaller than the first two. The tail of the NO_3^- Cotton effect centered at 3.25 μm^{-1} with sign opposite to that of the ligand field bands is seen at 2.8 μm^{-1}.[1]

Unfortunately, it was not possible to measure manganese-doped $Zn(en)_3(NO_3)_2$ crystal spectra at low temperature. It was found that at lower temperatures the doped crystals slowly become opaque. Interestingly, the crystals become transparent again upon warming. This phenomenon is presently unexplained. Ligand field transitions at energy higher than 2.7 μm^{-1} are masked by the NO_3^- absorption. As expected for the relatively strong ligand field, no *emission* associated with $Mn(en)_3^{2+}$ could be detected at 300 or 80 K at wavelengths shorter than 800 nm.

EPR spectra of $Zn(Mn)(en)_3(NO_3)_2$ with the magnetic field parallel, perpendicular, and at 45° to the c axis of the crystal (θ = 0, and 90, and 45°, respectively) are shown in Figure 3. The field variation of the centers of the five sextets as a function of θ is shown in Figure 4. The principal g values were calculated by the usual method using the g value of a strong-pitch sample (2.0028) as reference: $g_\parallel = 2.004 \pm 0.005$ and $g_\perp = 2.021 \pm 0.005$.

Discussion

The ground state of the high-spin d^5 electronic configuration of manganese(II) ion is ^6S in the free ion and $^6A_{1g}$ in an

Table II. Spin-Hamiltonian Parameters for Three Trigonally Distorted Manganese(II) Complexes

Complex	g	10^4A^d	10^4D^d	$10^4(a-F)^d$
$Mn{:}Zn(en)_3(NO_3)_2$[a]	∥ 2.004 ± 0.005 ⊥ 2.021 ± 0.005	−77 ± 1	+197 ± 10	+15 ± 10
$Mn{:}Zn(OMPA)_3(ClO_4)_2$[b]	∥ 2.011 ± 0.005 ⊥ 2.0100 ± 0.0005	−99	+146	+7.5
$Mn{:}Mg(Apy)_6(ClO_4)_2$[c]	2.008	−87	−44	−6.6

[a] This work. [b] Reference 33. [c] Reference 35 (g isotropic). [d] Units of cm^{-1}.

octahedral field. Since this is the only sextet state, all ligand field transitions are spin as well as parity forbidden. Consequently, the source of the small but finite intensities of observed bands has been the subject of numerous studies. Low-symmetry fields,[7-10] spin–orbit coupling,[7,9,10] odd-parity vibronic coupling,[11,12] and magnetic-exchange interaction[13-16] may relax the selection rules to make the ligand field transitions weakly allowed. Since five to seven transitions are usually observed in the readily accessible visible region of the spectrum, an excellent testing ground for theoretical calculations is provided. Several energy-level diagrams of the d^5 system in O_h and lower symmetry fields have been given.[7,19-24]

Band Assignments and Cubic Field Parameters. Since all of the ligand field transitions in manganese(II) are spin forbidden, normal spin-allowed D_3 selection rules do not necessarily apply to the bands observed for $Mn(en)_3{}^{2+}$. Therefore, polarizations in the LD spectra give no reliable clue for assignments and it is reasonable to make initial assignments of transitions in terms of the parent octahedral states. In the absorption and CD spectra of $Zn(Mn)(en)_3(NO_3)_2$, the prominent sharp bands at 2.36 μm^{-1} can confidently be assigned to the intraconfigurational, accidently degenerate $({}^4A_{1g}, {}^4E_g)(G) \leftarrow {}^6A_{1g}$ transitions, which are independent of O_h crystal field strength and occur around 2.3–2.6 μm^{-1} in most six-coordinate manganese(II) complexes.[4,7,9,13-22,25,26] From the energy-level diagram, we expect transitions to two other quartet levels (${}^4T_{1g}(G)$ and ${}^4T_{2g}(G)$) on the long-wavelength side of these sharp bands. The broad band centered at 1.98 μm^{-1} in the absorption and CD spectra is assigned as the transition to the ${}^4T_2(G)$ state. However, the exact energy of the transition to the first excited state (${}^4T_{1g}(G)$) is less well defined. It is also expected to give a weak broad band. Its rotational strength is very small and no definite maximum can be observed in the CD spectrum. However, the absorption spectrum reveals this transition clearly at 1.5 μm^{-1}.

Empirical parameters developed by Jørgensen[27] indicate that values of $B = 0.0860$ and $Dq = 0.110$ μm^{-1} should be appropriate for $Mn(en)_3{}^{2+}$, presuming an essentially O_h field. From the strong-field functions of Tanabe and Sugano $E[({}^4E_g, {}^4A_{1g})(G) \leftarrow {}^6A_{1g}(S)]$ is $10B + 5C$.[19] Setting this equal to 2.36 μm^{-1} and assuming $B = 0.0860$ μm^{-1} lead to a value of C very close to the $3.5B$ observed in the free ion.[19] Fitting the diagonalized ${}^4T_{1g}$ and ${}^4T_{2g}$ matrices to the other three bands as assigned, using these values of B and C, yields a Dq of 0.108 μm^{-1}. This procedure fits the bands arrising from ${}^4G$ exactly, with somewhat less success for the ${}^4T_{2g}(D)$ level, as shown in Table I. However, this is not surprising since the apparent reduction in term energy for ${}^4D$ has previously been observed to be greater than for ${}^4G$.[28] Reducing B and C by 12.5% (as opposed to 11.6% for the fit of the ${}^4G$ levels) while holding Dq at 0.108 μm^{-1} fits the ${}^4T_{2g}(D)$ level much better, according to expectation. The values of $Dq = 0.108$, $B = 0.0860$, and $C = 0.301$ μm^{-1} are consistent with the corresponding parameters obtained from fitting the spectra of $Co(en)_3{}^{2+}$ and $Ni(en)_3{}^{2+}$.[11,21]

Trigonal-Field Splitting. The structure observed in the 2.36-μm^{-1} band can be related to spin–orbit, vibronic, or trigonal-field splitting and can also be partially explained by a model which takes into account the difference in interelectron repulsion energies for the ${}^4E_g(G)$ and ${}^4E_g(D)$ states.[29] However, the separations of the maxima (100–150 cm^{-1}) are considerably larger than expected for spin–orbit coupling.[7,24] (For example, the high-resolution single-crystal MCD spectrum of $KMg(Mn)F_3$ shows three spin–orbit components of the ${}^4E_g(G)$ state to have a spacing of less than 20 cm^{-1}.[29] The possibility that the structure is entirely vibronic also seems unlikely in view of the marked contrast in the $\Delta\epsilon$ of the lower two components with respect to the higher two (Figure 1). On the other hand, the strong π polarization of the first component and lack of polarization of the other three (Figure 2) argue for assignment of special status to the 2.357-μm^{-1} peak. However, as previously pointed out,[4] no currently available theory predicts the frequently observed[4,9,10,26] π polarization of the $({}^4E_g, {}^4A_{1g})(G)$ transitions in trigonal symmetry, and so, at present, this polarization offers no specific help in making assignments.

If we interpret the CD results as indicating that both the 2.357- and 2.370-μm^{-1} maxima represent electronic origins (vide infra), then the 130-cm^{-1} interval between them can be viewed as the splitting of ${}^4E_g(G)$ and ${}^4A_{1g}(G)$ induced primarily by the trigonal field and by differences in orbital expansion or interelectronic repulsion energies of the ${}^4E_g(G)$ and ${}^4E_g(D)$ states. Since it is found that the ${}^4E_g(G)$ state is always lower in energy than ${}^4A_{1g}(G)$, regardless of the sign of the trigonal field,[24] the 2.357-μm^{-1} peak is assigned as the origin of the ${}^4E_g(G)$. The magnitude of the observed splitting is about what would be expected, considering that the corresponding interval in $Mn(OMPA)_3{}^{2+}$ is 70 cm^{-1} [4] and that the trigonal distortion of the ligand field in that case is somewhat less than in $Mn(en)_3{}^{2+}$. In this assignment, the other two components must be considered as vibronic maxima built on the two origins and based on a mode of ca. 270 cm^{-1}.

Although the *sign* of the trigonal distortion is not clearly indicated by the ${}^4E_g$–${}^4A_{1g}$ splitting, the EPR spectrum is more informative in this regard. When $H \parallel z$ ($\theta = 0°$), the splittings between the centers of the outer pairs of hyperfine sextets ($\pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ and $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$) and inner pairs ($\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ and $+{}^1/_2 \leftrightarrow -{}^1/_2$) are set equal to $2D - 3(a - F)$ and $2D + {}^5/_3(a - F)$, respectively, as appropriate for manganese(II) in a trigonal field.[30] From these relationships the absolute values of D and $a - F$ may be calculated. Further, the fact that the hyperfine splittings increase from the low- to the high-field sextet indicates that D is positive[31] (and thus also $a - F$). The absolute value of A is determined from the average of the hyperfine splittings of the five sextets[32] and is assumed to have a negative sign for manganese(II).[33-35] The parameters of the spin Hamiltonian for $Mn(en)_3{}^{2+}$ derived as described above, along with those of two other related manganese(II) complexes, are given in Table II.[36]

The points of interest are the sign and magnitude of the zero-field splitting parameter D. It has been previously predicted[24,37] that the sign of D should relate to the sense of the trigonal distortion and to the identity of the first excited state (i.e., ${}^4E$ or ${}^4A_1$ in D_3). Hempel[24] has demonstrated that a positive D corresponds to a trigonal-compression geometry of the complex and a negative D, to elongation. Both $Mn(en)_3(NO_3)_2$ and $Mn(OMPA)_3(ClO_4)_2$[33,34] have a positive sign of D. In agreement with theory, the structure[6] of these two complexes may be inferred from the crystal structures of analogous complexes to involve trigonal compression.[3,38,39] The trigonally elongated structure of Mn(Apy)$_6$(ClO$_4$)$_2$ has a negative *D*,[35] also consistent with the prediction. We note also that *D* is greater for the en complex than for the OMPA complex and that the **g** tensor is more anisotropic. Both observations are consistent with a somewhat more distorted geometry for the en complex than for the OMPA complex.

Circular Dichroism. Previous natural CD results for manganese(II)-doped α-Zn(H$_2$O)$_6$SeO$_4$ reported by Katô and Tsujikawa[5] were restricted to the region of the sharp ^{4}E$_g$, ^{4}A$_{1g}$ $\leftarrow$ ^{6}A$_{1g}$ intraconfigurational transitions. These authors observed two extremes in this region which they assigned to spin–orbit components.

The four maxima in the absorption spectrum of manganese-doped Zn(en)$_3$(NO$_3$)$_2$ (2.357, 2.370, 2.385, and 2.395 μm^{-1}) give rise to CD extremes at exactly these same energies (within experimental error). However, only the first two of these are clearly defined, the others being only weak shoulders with *R* values at least one order of magnitude less than the prominent components. The CD spectrum of the hexaaquoselenate is similar in appearance except that the intensity distribution between the two observed components is reversed. Little can be made of this comparison, however, since lack of parallel orientation of the chromophoric axes in the selenate crystal (isomorphous with α-hexaaquonickel sulfate) scrambles the polarization.[40] In the ethylenediamine complex the splittings of the components (130 cm^{-1}) and the intensity distribution in the CD, as well as the EPR analysis (above), support the assignment of the first two components of this band as the ^{4}E$_g$ and ^{4}A$_{1g}$ origins.

Another interesting comparison between the hexaaquomanganese data and those of the tris(ethylenediamine) complex is seen in the relative *R* values. Whereas the total rotational strength of the (^{4}E$_g$, ^{4}A$_{1g}$) band in the former is reported to be 4×10^{-44}, it is more than 5 times that for the latter ($2\bar{3} \times 10^{-44}$). A similar ratio is found for the rotational strengths of Co(H$_2$O)$_6$SeO$_4$[41] and Co(en)$_3$(NO$_3$)$_2$.[2] This apparently reflects the more pronounced chirality of the tris chelate structure as opposed to that of the hydrogen-bonded lattice structure of the selenate, although the lack of alignment of axes in the selenate may also contribute to reduction of observed *R*.

It is also worth noting that, although neither the manganese-doped hexaaquozinc selenate or tris(ethylenediamine)zinc nitrate crystals will yield optically active solutions, the tris chelate structure is intrinsically chiral, whereas the hexaaquometal ion is not. Thus the cocrystallization of the Mn(en)$_3^{2+}$ ion in the enantiomorphous Zn(en)$_3$(NO$_3$)$_2$ lattice represents a unique spontaneous resolution of a manganese(II) complex.

Registry No. Mn(en)$_3$(NO$_3$)$_2$, 65651-13-0; Zn(en)$_3$(NO$_3$)$_2$, 62571-30-6.

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