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Natural Solid State Optical Activity of Tris(ethylenediamine)metal(II) Nitrates. II. Single-Crystal Circular and Linear Dichroism Spectra of Tris(ethylenediamine)cobalt(II) Nitrate[1]

Mark Chin-Lan Yang and Richard Alan Palmer*

Contribution from the Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706.
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Abstract: The electronic structure of tris(ethylenediamine)cobalt(II) nitrate has been investigated by measurement of the linear dichroism (LD) and circular dichroism (CD) spectra of cobalt-doped $Zn(en)_3(NO_3)_2$ and of pure $Co(en)_3(NO_3)_2$ single crystals. Spectra have been measured at ambient and cryogenic temperatures in the region from 7 to 35 kK. Cotton effects associated with all ligand field transitions are observed to have the same sign in the axial CD of a given crystal. Polarizations in the orthoaxial LD indicate that the ground state is $^4A_2$ in the trigonal field. The main source of absorption spectral band intensity is a vibronic mechanism, whereas the CD intensity is primarily static in origin. The crystals of both the cobalt and zinc compounds appear to be completely isomorphous with $Ni(en)_3(NO_3)_2$. The CD results show clearly that all three compounds represent unusual instances of spontaneous resolution of tris(bidentate) chelates by crystallization. The absolute configuration of the host crystal is deduced by reference to that of the kinetically inert $Ru(en)_3^{2+}$ ion and from this the chirality and signs of rotational strength of $Co(en)_3^{2+}$ as well as of $Cu(en)_3^{2+}$, $Ni(en)_3^{2+}$, and $Mn(en)_3^{2+}$ in the crystal have been correlated.

Spectroscopic interest in trisethylenediamine complexes has generally centered on the dichroism,[2-4] the source and magnitude of the trigonal field splitting,[5-8] the source of absorption band intensity,[9-11] and/or the optical activity.[3,11-18] Among the first-row transition metal complexes of ethylenediamine, only $Cr(en)_3^{3+}$, $Co(en)_3^{3+}$, $Ni(en)_3^{2+}$, and $Cu(en)_3^{2+}$ have been studied intensively owing to the air sensitivity of the other members of the series. Among these, studies of optical activity have been limited to $Cr(en)_3^{3+}$ and $Co(en)_3^{3+}$ because of the lability of the high spin divalent metal ion complexes, which effectively prevents isolation of the pure enantiomers (except as solid diasteroisomers). $Ru(en)_3^{2+}$ (low spin d^6) appears to be the only divalent trisethylenediamine complex to have been resolved.[17] Besides $Ru(en)_3^{2+}$ and several α-diimine complexes of low spin iron(II), ruthenium(II), and osmium(II),[18] verified natural optical activity measurements of *chiral* divalent transition metal complexes have previously been reported only for tris(1,10-phenanthroline)nickel(II) and tris(2,2′-bipyridine)nickel(II) ions.[19] Natural optical activity measurements have also been made on the intrinsically *achiral* hexaaquo complexes of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) in various enantiomorphous lattices.[20-28]

As part of a continuing study of natural solid state optical activity, we have measured the circular dichroism (CD) and linear dichroism (LD) of the divalent transition metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Ru^{2+} doped into $Zn(en)_3(NO_3)_2$. In the cases of nickel and cobalt, measurements on the isomorphous pure crystals have also been made. Previous reports of the LD of the nickel complex have been made by Karipides[3] and by Dingle and Palmer[10] and of the copper complex by Karipides.[3] LD of the copper complex in the sulfate crystal has also been measured.[29] The solution CD of the kinetically inert complex $Ru(en)_3^{2+}$ has been reported by Elsbernd and Beattie.[17] In this paper we report our results for $Co(en)_3(NO_3)_2$ and $Zn(Co)(en)_3(NO_3)_2$. A preliminary account of this work has been published,[1] and detailed results for nickel, copper, manganese, and ruthenium are reported separately.[30]

The crystals of $Co(en)_3(NO_3)_2$ and $Zn(en)_3(NO_3)_2$ are apparently completely isomorphous with their nickel ana-

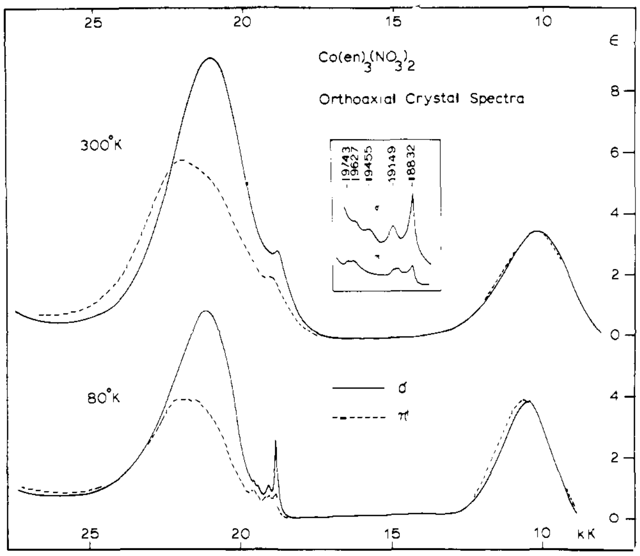

Figure 1. Linear dichroism spectrum of $Co(en)_3(NO_3)_2$. Insert shows expansion of 80° spectrum in the region of the $^2T_{1g}(P)$ levels.

log. The structure of the nickel complex was determined by Swink and Atoji[31] as hexagonal, with space group $D_6{}^6$-$P6_322$, $a = 8.87$ Å, $c = 11.41$ Å, and $Z = 2$. Using a polarizing microscope these authors failed to observe optical rotation or the conoscopic properties which have been cited as characteristic of uniaxial enantiomorphous crystals[32] and suggested that some sort of domain structure existed. The domains were hypothesized to be of dimensions large with respect to the X-ray wavelength but present in equal extent left and right handed so as to produce an optically inactive crystal. Recently Mason et al.[18] have explained their observation of the CD of nickel-doped $Zn(en)_3(NO_3)_2$ as due to nickel occupying only domains of one chirality. Our results reported here and elsewhere[1,30] show conclusively that, contrary to Swink and Atoji's hypothesis, $Ni(en)_3(NO_3)_2$, as well as its zinc and cobalt analogs, is truly enantiomorphous.

Apparently because of the lability of the complexes (expected to be high for spin-free octahedral d^5, d^7, and d^9 and moderate for d^8) these crystals fall experimentally into the same class as the hexaaquo metal sulfates, selenates, sulfites, etc.,[20-28] in that the detection of optical activity is limited to the crystalline state (with the single exception of $Ru(en)_3{}^{2+}$). However, the intrinsic chirality of the chromophore structure places them in that rare class of compounds which are spontaneously resolved (in the sense of Pasteur's tartrate crystals) by crystallization of the racemate.[34] As noted by Yamanari et al.[34] only a very few metal complexes have been reported which spontaneously resolve. The verified examples have been almost entirely confined to the inert configurations d^3 and low spin d^6. Several additional cobalt(III) examples have also been reported recently.[35,36] Apparently the only other case in which CD measurements have been made on labile chelates resolved by cocrystallization in a spontaneously resolving host crystal is that reported by Norden and Grenthe for a series of rare earth carboxylates.[37] The CD spectra of these complexes were measured using randomized powders of single crystals in KCl disks. The availability of relatively large, easily cut and polished, nonbiaxial crystals has made single-crystal CD measurements possible in the case of the $M(en)_3(NO_3)_2$ compounds.

Experimental Section

Large single crystals of $Co(en)_3(NO_3)_2$ (3 × 2 × 5 mm) and of $Zn(Co)(en)_3(NO_3)_2$ (5 × 2.5 × 8 mm) were grown from aqueous solutions of the metal nitrates and ethylenediamine under oxygen-free conditions by slow evaporation. This was accomplished by using a small flow of dry nitrogen gas through a plastic glove bag. The mole per cent of cobalt in the doped crystals varied from 5 to 50. The packing of the $M(en)_3{}^{2+}$ and $(NO_3)^-$ groups in the unit cell is such that the metal ions are at sites of 32 (D_3) symmetry and the nitrogen atoms at 3 (C_3) sites.[31] The C_3 axes of the complex ions are aligned with the c axis of the crystal. The circular dichroism and axial absorption spectra were obtained from sections of crystals cut and polished perpendicular to the hexagonal c axis of the crystal. Orientation of these sections was verified by conoscopic examination. To the eye, orthoaxial sections of pure and doped crystals showed only weak LD, orange to yellow-orange with the plane of polarization perpendicular or parallel, respectively, to the unique axis. The σ, π, and axial absorption spectra, as originally defined by McClure,[38] were obtained using instrumentation, cryogenic equipment, and techniques previously described.[39] The techniques and instrumentation used for axial circular dichroism measurements have also been reported earlier.[21,23] A baseline, determined by substituting for the sample a crystal of $Zn(en)_3(NO_3)_2$ of approximately the same thickness, was subtracted from each spectrum. The absolute and relative strengths of the transitions giving rise to the spectral bands were determined in terms of the oscillator strength, $f = 4.32 \times 10^{-9} \int \epsilon d\bar{\nu}$; the integrated band intensity, $I = (\int \epsilon d\bar{\nu})/\bar{\nu}_{max}$; the dipole strength, $D = (91.8 \times 10^{-40} \int \epsilon d\bar{\nu})/\bar{\nu}_{max}$; the rotational strength, $R = (22.9 \times 10^{-40} \int \Delta\epsilon \, d\bar{\nu})/\bar{\nu}_{max}$; and the anisotropy factor, g, given by $4R/D$. Magnetic susceptibilities were measured by the Faraday method. Pascal's constants[40] were used in calculating the corrected magnetic susceptibility.

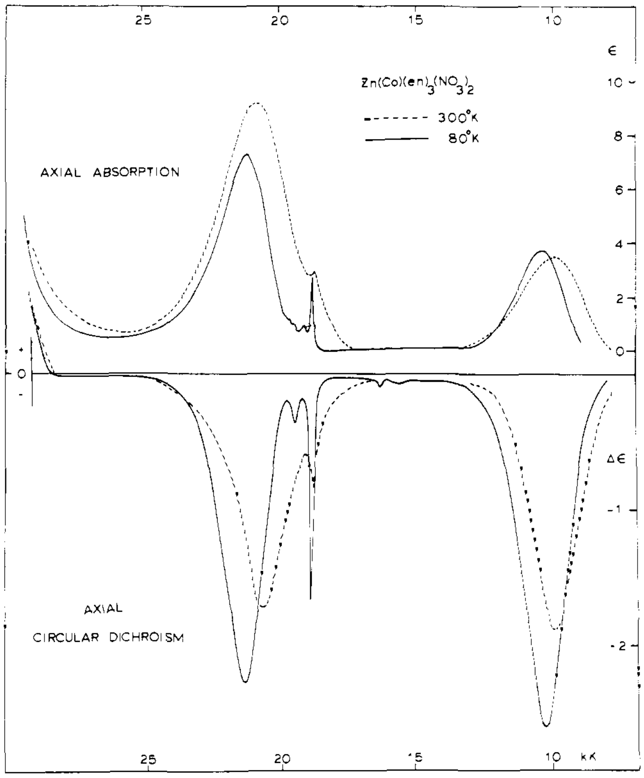

Figure 2. Axial absorption and axial circular dichroism spectra of $Zn(Co)(en)_3(NO_3)_2$.

Results

The orthoxial LD and the axial absorption and CD of $Co(en)_3{}^{2+}$ at 300 and 80 K are shown in Figures 1 and 2. No additional resolution of fine structure was observed in spectra measured at 5°K. Band maxima, molar absorptivities, oscillator strengths, and integrated band intensities are summarized in Table I. The rotational strengths, dipole strengths, and anisotropy factors obtained from the CD and axial absorption spectra are given in Table II. Orthoaxial

Table I. Orthoaxial Absorption Spectral Data for $Co(en)_2(NO_3)_2$

Excited state O_h	D_3	Polarization	ν_{max} (kK) 300°K	ν_{max} (kK) 80°K	ϵ 300°K	ϵ 80°K	10^5f 300°K	10^5f 80°K	I 300°K	I 80°K
$^4T_{2g}(F)$	^4E	σ	10.0	10.4	3.6	4.0	3.7	3.9	0.86	0.86
	$^4A_1$	π	10.0	10.5	3.6	4.1	3.7	3.9	0.86	0.86
$^2T_{1g}(P)$	^2E	σ	18.8	18.83		2.0		0.17		0.02
	$^2A_2$	π	18.8	18.83		0.8		0.05		0.007
$^4T_{1g}(P)$	^4E	σ	20.8	21.1	9.3	6.7	12.1	7.2	1.3	0.80
	$^4A_2$	π	21.7	21.8	5.9	3.8	9.4	5.0	1.0	0.54

Table II. Axial Absorption and CD Spectral Data for $Co(en)_3(NO_3)_2$

Excited state O_h	D_3	ν_{max} (kK) Absorption 300°K	ν_{max} (kK) Absorption 80°K	ν_{max} (kK) CD 300°K	ν_{max} (kK) CD 80°K	$10^{40}D$ (cgs) 300°K	$10^{40}D$ (cgs) 80°K	$10^{40}R$ (cgs) 300°K	$10^{40}R$ (cgs) 80°K	g ($4R/D$) 300°K	g ($4R/D$) 80°K
$^4T_{2g}(F)$	^4E	10.0	10.4	10.0	10.2	79.3	77.7	9.07	11.6	0.46	0.59
$^2T_{1g}(G)$	^2E			15.3	15.3						
$^2T_{1g}(G)$	^2E			16.3	16.3						
$^2T_{1g}(P)$	^2E	18.70	18.83	18.80	18.83		2.68		0.48		0.70
$^4T_{1g}(P)$	^4E	20.9	21.1	20.62	21.0	123	72.8	4.44	5.0	0.14	0.27

LD spectra measured in either pure or cobalt doped zinc crystals are the same within experimental error as regards band maxima and integrated band intensities; i.e., normal Beer–Lambert law behavior obtains. The room temperature orthoaxial spectra summed to average out orientation effects correspond closely to the aqueous solution spectrum.[41] The magnetic susceptibility ($\chi_{300} = 1.21 \times 10^{-2}$ cgs), when corrected, yields a μ_{eff} of 5.4 μ_B, as expected for a high-spin octahedral d^7 ion.

Discussion

Band Assignments. The correspondence of the absorption data and circular dichroism of $Co(en)_3(NO_3)_2$ in pure and doped crystals and the linear dependence of dipole and rotational strengths on concentration in the doped crystals indicate that an oriented gas model may safely be assumed in analyzing these spectra.[42] The magnetic susceptibility and the spectral band structure are consistent with high spin Co^{2+} in a field of near octahedral symmetry, as would be expected from the previous analysis of the $Ni(en)_3^{2+}$ spectrum.[10] The electronic structure of octahedral cobalt(II) has been extensively studied[43-47] and several detailed theoretical calculations have been reported for O_h d^7 ions.[47-50] Consideration of these results clearly leads to the assignments of the major band manifolds at ca. 10 and 21 kK as associated with the $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions in the parent octahedral field. These assignments allow the estimation of the parameters Dq and B as 1130 and 810 cm^{-1}, respectively, and permit the assignment of the spin forbidden octahedral transitions to $^2T_{1g}(G)$, $^2T_{2g}(G)$, and $^2T_{1g}(P)$ states to the bands at 15.3 and 16.3 kK in the CD and 18.8 kK in the absorption and CD spectra, respectively (Tables I and II).

The moderately strong linear polarization of the bands is consistent with the axial symmetry of the D_3 site occupied by the metal ion. The similarity of the pure and doped crystal data for both nickel and cobalt suggest that the same trigonally compressed octahedral structure obtains in the zinc and cobalt lattices as in the nickel analog, and that D_3 effective symmetry should be assumed. The correspondence of the σ and axial spectra indicates that the intensities in the absorption are principally electric dipole in origin.[38] However, the substantial temperature dependence of intensity, particularly of the $^4T_{1g}(P)$ manifold, which decreases in dipole strength by 40–50% in both σ and π spectra between 300 and 80°K, shows that vibronic effects are significant in the cobalt spectrum as well as the nickel.[10] Magnetic dipole effects, though of minor importance in the LD, appear to be appreciable in the CD, as might be expected from the magnetic dipole allowed character of transitions to $^4T_{2g}(F)$ and $^4T_{1g}(P)$. Vibronic and magnetic dipole interactions are discussed further below.

Turning now to the effects of the trigonal field, the first question to be settled is that of the identity of the ground state. States of T_{1g} and T_{2g} symmetry will split into $E + A_2$ and $E + A_1$, respectively, in a D_3 field. The sense and type of trigonal distortion should determine whether the ground state is $^4A_2$ or ^4E. If ^4E lies lower, transitions to excited states of $^4A_1$, $^4A_2$, and ^4E are allowed in the σ spectrum by a first-order electric dipole mechanism, whereas those to ^4E are also allowed in the π spectrum. Therefore, reasonably strong intensity might be anticipated in σ and π spectra in both spin allowed band manifolds. This situation should also be reflected in weak polarization of the nearby spin forbidden bands. On the other hand, a ground symmetry of $^4A_2$ should produce intensity only in the σ spectrum of the second band manifold ($^4T_{1g}(P)$) if D_3 electric dipole selection rules are obeyed. In this case, doublet transitions mixing with this quartet should also be strongly polarized in their no-phonon components. The extensive polarization of the sharp band at 18.8 kK, which may confidently be assigned to the 0-0 component of an intraconfigurational spin forbidden transition to a D_3 level arising from $^2T_{1g}$, suggests that the ground state is in fact $^4A_2$. In this analysis the no-phonon transition is presumed to reflect the first-order electric dipole character of the spin allowed transitions from which it borrows its intensity. Since the orbital symmetries of the quartet and doublet levels are the same in this case, spin-orbit mixing is possible with both ^4E and $^4A_2$. The very weak relative intensity in the π spectrum at 18.8 kK confirms the vibronic nature of the major portion of the π intensity in the quartet manifold. The lack of complete polarization of the $^2T_{1g}(P)$ no-phonon line (in contrast to the $^1A_{1g}(G)$ band of $Ni(en)_3(NO_3)_2$)[10] may be due to the complication of spin and orbital degeneracy of the doublet level in the cobalt case. The spectrum of $Co(OMPA)_3^{2+}$ shows a similar effect.[51]

The possibility of a significant magnetic dipole contribution to the dipole strength of the $^2T_{1g}(P)$ band, accounting for the π intensity, is suggested by the relatively high g values of both the $^4T_{1g}(P)$ and $^2T_{1g}(P)$ bands. With this in mind, the integrated band intensities from the σ, π, and axial spectra of this band were carefully compared. With a significant magnetic dipole contribution the intensity of the axial spectrum should be greater than that of either the σ or π spectra. However, within experimental error, the axial and σ spectra are identical. Apparently the magnetic dipole strength, though important for the CD spectrum, is, as predicted,[43] at least two orders of magnitude smaller than the electric dipole strength.

The deduction of $^4A_2$ as the ground state is entirely consistent with the predictions of the crystal field model of Lever and Hollebone.[52] In this analysis the order and magnitude of splitting of the one-electron orbitals e and a_1 arising from the t_{2g} level in O_h is correlated with the polar angle ϕ. A second factor is the ratio, G, of the second- and fourth-order radial parameters. For first-row transition metal complexes, a G value of somewhat less than one has been assumed[52] and this seems probably to be the case of all trisethylenediamine complexes.[8] If this G value is valid, the assignments in the spectra of $Co(en)_3(NO_3)_2$ can be fitted to an energy level diagram such as that computed by Gerloch and Quested[53] as a function of ϕ with $Cp = 1000$ cm^{-1}, $Dq = 1000$ cm^{-1}, and $B = 850$ cm^{-1}. From the available crystal structure results, $\phi = 57.2°$ may be assumed. Thus K, the trigonal field splitting parameter, is negative, the ordering of the t_{2g} orbitals is $e < a_1$, and the ground state is $^4A_2$, as previously deduced from the polarization data.

Empirical evidence for the *magnitude* of the trigonal splitting of the ground and excited states is somewhat more difficult to obtain. Even the sense of splitting of the bands is questionable. Splitting of the π and σ allowed components of the $^4T_{2g}(F)$ levels ($^4A_1$ and ^4E, respectively) is negligible. However, the linear dichroism in the $^4T_{1g}(P)$ manifold would seem to indicate a trigonal splitting of ca. 700 cm^{-1} with $^4A_2$ above ^4E. Although this is consistent with the model for the splitting of the one-electron orbitals, it seems unusually large considering the vanishingly small excited state splitting observed in $Ni(en)_3(NO_3)_2$. The effects of first- and second-order (with $^4A_2$ ($^4A_{2g}$)) spin-orbit coupling may be important in the case of $Co(en)_3(NO_3)_2$, in addition to trigonal field effects.

The transition to the $^4A_{2g}(F)$ state is a two-electron jump in the strong-field limit and thus should be broad and weak. Its calculated energy is 21.66 kK, virtually degenerate with the $^4T_{1g}$ manifold. In addition, with a $^4A_2$ ground state in D_3 symmetry, this transition is also symmetry forbidden. Thus it is not surprising that we see no evidence of a band assignable to it in either the absorption or CD measurements.

Some further clue to the electronic structure may be obtained from consideration of the structure in the region of the $^2T_{1g}(P)$ band (Figure 1). The two most prominent components in the absorption spectra, the no-phonon band at 18.83 kK and a second maximum at 19.45 kK, are the only ones observed in the CD. The 0.62 kK between these two σ allowed bands might be spin-orbit and/or trigonal field splitting, a vibronic interval, or the distance between the origins of the $^2E(^2T_{1g}(P))$ and the $^4E(^4T_{1g}(P))$ transitions. The other structure in the absorption spectrum, consisting of closely spaced doublets 310 ± 20 cm^{-1} on the high side of each of the stronger components, seems clearly to be vibronic and probably involves metal ligand vibrations associated with the t_{1u} octahedral mode, as observed in the spectrum of $Co(en)_3{}^{3+}$.[9,11]

Circular Dichroism. Turning now to the CD results, we note first that, since the ground state is $^4A_2$ in D_3, all transitions observed with light propagated along the unique axis in both CD and absorption should be to states of E symmetry. It has not been possible to observe the $^4A_1 \leftarrow {}^4A_2$ transition in the $^4T_{2g}(F)$ manifold, although it should be seen in a suitable mull. However, since its rotational strength should be equal in magnitude but opposite in sign to that of the E band,[14,15] the small splitting observed in the linear dichroism spectra would predict a very small residual $\Delta\epsilon$ in this region in the mull spectrum.

According to Moffitt's criterion,[54] the magnitude of the rotational strengths of g factors of both ^4E bands and of the $^2E(^2T_{1g}(P))$ band would clearly class them as magnetic dipole allowed. However, the source of this allowed character is ambiguous. It is consistently observed in the CD of nickel compounds, both intrinsically chiral compounds[30] as well as the chiral crystalline hexaaquonickel salts,[20-28] that the octahedral parentage of states is a significant factor in determining rotational strength. Thus, the transitions to states arising from $^3T_{2g}(F)$ always have significantly larger R than those associated with $^3T_{1g}(F)$ or $^3T_{1g}(P)$ in nickel(II) complexes, apparently because of the first-order magnetic dipole character of the former as opposed to the latter. In the case of cobalt(II), transitions to both $^4T_{2g}(F)$ and $^4T_{1g}(P)$ from the octahedral ground state $^4T_{1g}(F)$ are magnetic dipole allowed. Furthermore, rotational strengths of the two ^4E transitions observed in $Co(en)_3(NO_3)_2$ are the same order of magnitude. Like the $^3T_{2g}(F)$ band in nickel(II) complexes, the spin allowed bands in $Co(en)_3{}^{2+}$ have $R > 2 \times 10^{-40}$ and show an increase in R with decreasing temperature. In both respects this is opposite to the behavior of the $^3T_{1g}$ transitions of nickel(II) complexes (at least in the hexaaquonickel crystals). Thus, it is possible that some of the rotational strength of $Co(en)_3(NO_3)_2$ is derived from the magnetic dipole character of the parent octahedral transitions. Further theoretical consideration of this point is beyond the scope of this paper.

The temperature dependence of the rotational strengths of both spin allowed manifolds is relatively small as might be expected for first-order magnetic dipole allowed bands which are also electric dipole allowed (in D_3). The increase in R with decreasing temperature may be seen as due to the depopulation of nontotally symmetric ground state vibrational modes which rob the magnetic dipole of its strength. The effect should be most pronounced in the no-phonon components, but vibronic structure has not been observed on either of the quartet-quartet bands. However, the striking increase in R for the $^2E(^2T_{1g}(P))$ band is clear evidence of this phenomenon. This effect has been discussed in more detail elsewhere.[55]

As observed in Figure 2, all bands in the axial CD of $Co(en)_3(NO_3)_2$ have the same sign of R. This is in contrast to the results for $Co(H_2O)_6{}^{2+}$ in the $Zn(H_2O)_6SeO_4$ lattice where a band of opposite sign is observed in the $^4T_{1g}(P)$ manifold.[23] However, it is consistent with the fact that, owing to the alignment of the chromophores in the trisethylenediamine nitrate, only the E component should be observed. This is also true for $Co(H_2O)_6{}^{2+}$ in $Mg(H_2O)_6SO_3$, where the C_3 metal sites are also aligned.[28,55] In the selenate apparently a mixture of several low symmetry transitions is observed, because of the lack of alignment of the chromophores, and at least one of these transitions has the opposite sign of R to the rest of the band manifold.

Spontaneous Resolution. It can be easily confirmed that in a given enantiomer of $Zn(en)_3(NO_3)_2$ the signs of all the ligand field transitions observed, not only in $Co(en)_3{}^{2+}$ but also $Ni(en)_3{}^{2+}$, $Cu(en)_3{}^{2+}$, and $Mn(en)_3{}^{2+}$, are all the same.[30] This is possible even without multiple doping experiments because of the internal standard provided by the lowest energy $NO_3{}^-$ transition at 32.5 kK.[1] This transition has been observed in the CD of both pure $Zn(en)_3(NO_3)_2$ and of crystals doped with each of the above metal ions. In the crystals containing transition metal ions it invariably has the opposite sign of R to the ligand field bands. Its assignment has been previously discussed.[1]

The fact that the $NO_3{}^-$ band is seen in the CD of pure $Zn(en)_3(NO_3)_2$ is clear evidence of the enantiomorphism of the crystal. Both left- and right-handed crystals, doped and undoped, are found with roughly the same frequency, though no strict statistical test was attempted. Except for the observation of CD in the pure crystals $M(en)_3(NO_3)_2$ ($M = Zn^{2+}$, Ni^{2+}, and Co^{2+}), it might be argued that the domain hypothesis of Swink and Atoji[31] was valid. It might be argued that in the doped crystals the various guest ions preferentially occupied domains of one chirality leaving an excess of zinc ions in the domains of opposite handedness. The current evidence shows conclusively that the domain hypothesis is without foundation and that in fact $Zn(en)_3(NO_3)_2$, $Ni(en)_3(NO_3)_2$, and $Co(en)_3(NO_3)_2$ are spontaneously resolved by crystallization. However, all attempts to observe optical activity in solutions made from single crystals have produced negative results. This is not surprising considering the predicted lability of the complexes.

The inability reported by Swink and Atoji[31] to observe the expected rotation and conoscopic properties[32] in tris(ethylenediamine)nickel(II) nitrate crystals has been confirmed by us using crystals up to 1 cm thick. However, crystals this thick of α-$Ni(H_2O)_6SO_4$ and of α-$Zn(H_2O)_6SeO_4$, both undisputedly enantiomorphous, also fail to show either the expected interference figures or optical rotation detectable by a regular polarizing microscope. Tutton's conoscopic observations[32] were made on plates of quartz 3.75 mm thick, for which the rotation would be ca. 79° at the sodium D line. In contrast it would take a plate of α-$Ni(H_2O)_6SO_4$ ca. 60 mm thick to produce the same effect. Tutton also observes that a plate of quartz 1 mm thick shows the interference figure expected for an inactive uniaxial crystal and that disappearance of the centers of the isogyres is obvious only for much thicker crystals. The rotational strength of the $Ni(en)_3(NO_3)_2$ crystal is comparable to that of α-$Ni(H_2O)_6(SO_4)$ in the d-d bands and from this it can be inferred that its specific rotation (per millimeter of crystal) in the visible is, like that of α-$Ni(H_2O)_6SO_4$, less than one-tenth that of quartz. For these reasons it is not surprising that the $M(en)_3(NO_3)_2$ crystals appear under the polarizing microscope to be optically inactive.

Absolute Configuration. Finally, it has been possible to correlate the signs of rotational strength of the ligand field transitions in $Co(en)_3^{2+}$ (and its analogs as well) with the absolute configuration of the complex ions. This has been accomplished by comparing the axial CD spectra of single crystals of ruthenium(II)-doped $Zn(en)_3(NO_3)_2$ with the spectra of solutions made by dissolving those single crystals. Unlike $Co(en)_3^{2+}$ and the analogous complexes of manganese, nickel, copper, and zinc, $Ru(en)_3^{2+}$ is inert to racemization.[17] Furthermore, as shown by Elsbernd and Beattie,[17] the enantiomer with the Λ configuration gives a positive $\Delta\epsilon$ in solution for the lowest energy band (λ_{max} 402 nm). Single crystals of $Zn(en)_3(NO_3)_2$ doped with ruthenium(II) which have a positive $\Delta\epsilon$ for the 385-nm band in the axial CD have a negative NO_3^- band and dissolve to give a positive solution $\Delta\epsilon$ at 402 nm.[56]

Therefore, it can be concluded that $Zn(en)_3(NO_3)_2$ crystals with a negative $\Delta\epsilon$ for the NO_3^- band must contain $M(en)_3^{2+}$ ions of the $\Lambda(C_3)$ configuration (IUPAC convention[37]). As noted above, when $\Delta\epsilon$ for the NO_3^- band in the doped crystals is *negative*, the ligand field bands observed in the axial CD spectra (of $Ru(en)_3^{2+}$ and $Co(en)_3^{2+}$ as well as $Mn(en)_3^{2+}$, $Ni(en)_3^{2+}$, and $Cu(en)_3^{2+}$) have *positive* $\Delta\epsilon$. That all the transitions have the same sign is not as unusual as at first it might appear, since in the axial CD spectra all the spin allowed transitions in all the complex ions, $M(en)_3^{2+}$ (M = Mn, Co, Ni, Cu, and Ru), may be assigned as $E \leftrightarrow A_{1,2}$ and as such are both electric dipole and magnetic dipole allowed in the D_3 field.

It is interesting to note that positive $\Delta\epsilon$ for these transitions in the $\Lambda(C_3)M(en)_3^{2+}$ ions is consistent with theoretical prediction based either on a chirality,[58] distortion,[13] or sector rule[59] model. Further discussion of this aspect of this work will appear elsewhere.

Summary and Conclusions

This paper has reported the linear and circular dichroism spectra of $Co(en)_3(NO_3)_2$ in single crystals. The results have been analyzed to indicate a $^4A_2$ ground state for the complex ion with a negative trigonal field parameter K. Another interesting conclusion drawn from this work is that of the spontaneous resolution of $Co(en)_3^{2+}$ (as well as $Ni(en)_3^{2+}$ and $Zn(en)_3^{2+}$) by crystallization of the nitrate salt. By comparison with the single-crystal axial circular dichroism and solution circular dichroism of $Zn(Ru)(en)_3(NO_3)_2$ it has been determined that $\Lambda(C_3)$ $Co(en)_3^{2+}$ has $\Delta\epsilon > 0$ for all ligand field bands observed in the axial CD of $Co(en)_3(NO_3)_2$ and $Zn(Co)(en)_3(NO_3)_2$. It is worth emphasizing that the combination of the circular dichroism with linear dichroism spectra of the single crystal has allowed deductions of electronic structure details not possible with linear dichroism alone. Analogous results for $Ni(en)_3(NO_3)_2$, $Mn(en)_3(NO_3)_2$, $Cu(en)_3(NO_3)_2$, and $Ru(en)_3(NO_3)_2$ will be published separately.

NOTE ADDED IN PROOF: Several additional maxima on the high energy side of the $^4T_{1g}(P)$ manifold have been observed in our reexamination of the 5 K LD spectra. These bands are extremely weak ($\epsilon < 0.05$), but sharp ($\Delta_{1/2} < 10$ cm^{-1}), characteristic of intraconfigurational spin forbidden transitions. The lowest energy of these peaks (24.69 kK) may be assigned to the origin of the $^2T_{2g}(H)$ state. This band is strongly σ polarized, which supports our earlier argument, concerning the $^2T_{1g}(P)$ transition (see text). Both transitions borrow their intensities from the near-by quartet manifold and reflect the polarization of the quartet state. Additional weak peaks at 24.84 and 24.93 kK (σ spectrum) and 24.94 and 25.97 kK (π spectrum) may tentatively be attributed to vibronic structure and/or spin-orbit components.

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Preparation and Nuclear Magnetic Resonance Studies of the Stereochemically Nonrigid Anions $B_4H_9^-$, $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$ Improved Syntheses of B_5H_{11} and B_6H_{12}

R. J. Remmel, H. D. Johnson, II, I. S. Jaworiwsky, and S. G. Shore*

Contribution from the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

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Abstract: Using KH or NH_3 as a deprotonating agent, $B_4H_9^-$ is prepared on a practical basis from B_4H_{10}. Addition of BH_3 to $B_4H_9^-$, $B_5H_8^-$, and $B_6H_9^-$ results in polyhedral expansion, yielding $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$. The $B_5H_{12}^-$ ion is the only known binary hydride species that is a member of the newly recognized class of hypho boranes. Variable temperature boron-11 and proton NMR spectra are presented and discussed in terms of dynamic properties of the anions and their static structures. Syntheses of B_5H_{11} and B_6H_{12} in 60–70% yield are achieved by addition of liquid HCl to $B_5H_{12}^-$ and $B_6H_{11}^-$. Relative Brönsted acidities of B_4H_{10} and B_6H_{12} are established by proton competition reactions.

Although the Brönsted acidity of $B_{10}H_{14}$ was first demonstrated in 1956,[1] leading to the prediction[2] that lower boron hydrides could also function as Brönsted acids, it was not until 1967 that definitive evidence for the Brönsted acidity of a lower boron hydride, B_5H_9,[3a-c] was offered. Over the past several years evidence has been accumulated which shows that many of the lower boron hydrides can function as monoprotic Brönsted acids with a bridging hydrogen serving as the proton source.[4-6] Each of the resulting conjugate bases possesses a boron–boron bond which is susceptible to insertion of an electrophillic reagent.[3b,7-9] Thus deprotonation of B_4H_{10}, B_5H_9, and B_6H_{10} yields conjugate bases to which the electrophile BH_3 can be added, resulting in polyhedral expansion of the boron frameworks to give the new anions $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$.

In the present article we consider the acidities of B_4H_{10} and B_6H_{12} and provide detailed boron-11 and proton NMR spectra of the anions $B_4H_9^-$, $B_5H_{12}^-$, and $B_6H_{11}^-$, and $B_7H_{12}^-$, which allow consideration of static and dynamic forms. Detailed procedures are provided for good yield syntheses of B_5H_{11} from $B_5H_{12}^-$ and B_6H_{12} from $B_6H_{11}^-$. Observations and procedures which were not discussed in detail in earlier communications[4d,7b] are fully presented herein.

Results and Discussion

Reactions of Tetraborane(10). At −78° deprotonation of B_4H_{10} in ether solvents can occur according to the following reaction. The $B_4H_9^-$ ion is formed in essentially quantitative yield.[4d,5]

$$B_4H_{10} + ML \rightarrow M^+ B_4H_9^- + LH \qquad (1)$$

where ML = KH,[4d] NaH,[10] and $LiCH_3$.[5] We have found the reaction to be very sensitive to solvent, deprotonating agent, and concentration of reactants. The cleanest reactions were consistently obtained in dimethyl ether using potassium hydride as the deprotonating agent with concentrations of reactants being at least 1 *M*. Solutions of KB_4H_9 in ether solvents are colorless and appear to be stable for periods of several months at −78°. At room temperature the solutions indicate decomposition after 30–40 min. A white, unidentified solid precipitates and new, unidentified resonances appear in the boron-11 NMR spectrum, but $B_4H_9^-$ is still visible in the boron-11 NMR spectrum even after the solution has been at room temperature for 12–14 hr. Ether solutions of LiB_4H_9 give evidence for much more rapid decomposition than those of KB_4H_9 under equivalent conditions.