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Correlation between Structure and Circular Dichroism in Ethylenediaminetetraacetatocobaltate(III) and Related Complexes

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Rose and Neal have reported the synthesis and characterization of a novel ligand, (*S*,*S*)-ethylenediamine-*N*,*N*′-dissuccinate (EDDS), and its complexes[1,2] (EDDS contains two (*S*)-aspartic acid units). The ligand, which is an analog of EDTA, exhibits absolute stereospecificity on coordination to Co(III)[1] as has been confirmed by an X-ray crystal structure determination.[3] Although [Co(EDTA)]$^-$ and [Co(EDDS)]$^-$ are structurally similar (Figure 1), the CD spectra are distinctly different.[1,4] Significantly, the isomers with the same absolute configuration of chelate rings[3,5] give dominant CD peaks of opposite sign. It has been suggested that these major changes are due principally to differences in chelate ring size.[6] The EDDS complex has two five-membered rings and two six-membered rings whereas all four amino acid rings of the EDTA complex are five membered (Figure 1). The complex [Co(EDDDA)]$^-$ [7] (EDDDA = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate) shares characteristics of both [Co(EDTA)]$^-$ and [Co(EDDS)]$^-$ (Figure 1). Like [Co(EDDS)]$^-$ it contains two five-membered and two six-membered amino acid chelate rings. Unlike [Co(EDDS)]$^-$, however, and like [Co(EDTA)]$^-$, the amino acid rings branch from the donor nitrogen atoms rather than from asymmetric carbon atoms. The CD spectrum of [Co(EDDDA)]$^-$ [7] is very similar in shape to that of [Co(EDDS)]$^-$, and it was partly on the basis of this similarity that the absolute configuration of [Co(EDDDA)]$^-$ was assigned.[7]

A source of dissymmetry which has not been considered in [Co(EDDS)]$^-$, however, is that associated with the asymmetric nitrogens. Recent studies have shown that the asymmetric nitrogens in closely related chelates make large contributions to the d-d rotatory strengths of the metal ion.[8-10] Maricondi and Douglas[8] found that when methyl and ethyl groups were substituted for the amine hydrogens of *s-cis*-[Co(EDDA)L] (Figure 1), the intensities of the CD peaks were diminished by large values, as much as $\Delta\epsilon = 3.5$.[8,9] It was argued[8] that the vicinal effect due to the chiral nitrogens is large for the secondary amines of *s-cis*-EDDA but very small for the tertiary amines of N-substituted *s-cis*-EDDA so that the difference between the CD curves is due primarily to the vicinal effect. The results of a subsequent study[10] support this argument and indicate that the smallest vicinal contribution to the circular dichroism occurs for methyl-substituted nitrogens.

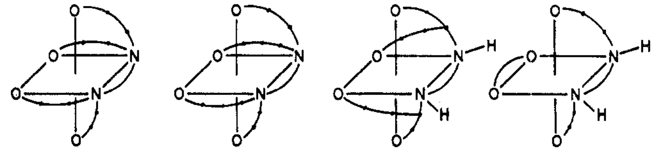
[Co(EDTA)]$^-$ [Co(EDDDA)]$^-$ [Co(EDDS)]$^-$ [Co(EDDA)ox]$^-$

Figure 1. The ΛΛΔ isomers of [Co(EDTA)]$^-$, [Co(EDDDA)]$^-$, and [Co(EDDS)]$^-$ and ΔΔΔ-*s-cis*-[Co(EDDA)ox]$^-$.

The stereochemical arrangement about the nitrogens of [Co(EDDS)]$^-$ is very similar to that of *s-cis*-[Co(EDDA)ox]$^-$ (Figure 1). Therefore, the two complexes might be expected to give rise to similar vicinal effects. In order to evaluate the N-vicinal effect of [Co(EDDS)]$^-$ we have prepared the *N*-methyl (MEDDS) and *N*,*N*′-dimethyl (DMEDDS) derivatives of that complex. Conclusions regarding the role of chelate ring size in the differences among the CD spectra of [Co(EDTA)]$^-$, [Co(EDDS)]$^-$, and [Co(EDDDA)]$^-$ can only be regarded as tentative until the contributions from the asymmetric nitrogens of [Co(EDDS)]$^-$ are known.

Experimental Section

Preparation of the *N*-Methyl and *N*,*N*′-Dimethyl Derivatives of (*S*,*S*)-Ethylenediaminedisuccinic Acid, MEDDS and DMEDDS. Sodium hydroxide, 2.4 g (0.060 mol), was added to 4.1 g (0.010 mol) of H_4EDDS[1] in 75 ml of water and the mixture was stirred until all solid had dissolved. The solution was transferred to a bomb which was sealed after adding 3.2 g (0.023 mol) of methyl iodide. The mixture was stirred for 5 hr in a water bath at 75° and then cooled to room temperature. The solution was adjusted to pH 7 with HCl and then stirred for *ca.* 10 min with excess AgCl to precipitate all iodide. The filtrate contained a mixture of EDDS, MEDDS, and DMEDDS.

Preparation of Sodium ((*S*,*S*)-*N*-Methylethylenediaminedisuccinato)cobaltate(III), Na[Co(MEDDS)], and Sodium ((*S*,*S*)-*N*,*N*′-dimethylethylenediaminedisuccinato)cobaltate(III), Na[Co(DMEDDS)]. $CoCl_2 \cdot 6H_2O$ (2.4 g, 0.010 mol) was added to the above mixture of ligands. The solution was neutralized with NaOH and 2 g of blood charcoal was added. A stream of air was passed through the mixture for *ca.* 12 hr. The charcoal was removed by filtration and the filtrate was concentrated to a volume of *ca.* 5 ml in a rotary evaporator. The solution was eluted on a column (4 × 90 cm) of Sephadex G-15 with chloroform-saturated water to separate NaCl from the violet band containing Co(III) complexes. The violet fraction was then chromatographed on a column (4 × 38 cm) of 200–400 mesh Dowex 1-X8 anion-exchange resin in the chloride form. This material separated cleanly into three violet bands during elution with 0.0064 *M* NaCl over a 2-week period. Each fraction was collected, concentrated, and passed through a Sephadex column, as described above, to remove NaCl. Each solution was then evaporated to dryness under vacuum. The solid, in each case, was transferred to a filter with the aid of ethanol and washed with ethanol and acetone. It was then dried, first on the filter and then under vacuum at 80° for 4 hr. For fraction 1, [Co(DMEDDS)]$^-$: $\Delta\epsilon_{604} = +0.18$, $\Delta\epsilon_{540} = -1.88$, $\Delta\epsilon_{380} = +0.56$. For fraction 2, [Co(MEDDS)]$^-$: $\Delta\epsilon_{604} = +0.39$, $\Delta\epsilon_{542} = -2.17$, $\Delta\epsilon_{380} = +0.83$. For fraction 3, [Co(EDDS)]$^-$: $\Delta\epsilon_{607} = +0.39$, $\Delta\epsilon_{548} = -2.31$, $\Delta\epsilon_{390} = +0.95$. The values obtained for fraction 3 agree with those previously reported for [Co(EDDS)]$^-$.[1,6]

Anal. Fraction 1: Calcd for $Na[Co(C_{12}H_{16}N_2O_8)] \cdot H_2O$: C, 34.62; H, 4.36; N, 6.73. Found: C, 34.31; H, 4.16; N, 6.54. Fraction 2: Calcd for $Na[Co(C_{11}H_{14}N_2O_8)] \cdot H_2O$: C, 32.81; H, 4.01; N, 6.96. Found: C, 32.70; H, 4.01; N, 6.88. Fraction 3: Calcd for $Na[Co(C_{10}H_{12}N_2O_8)] \cdot 1.5H_2O$: C, 30.24; H, 3.55; N, 7.05. Found:

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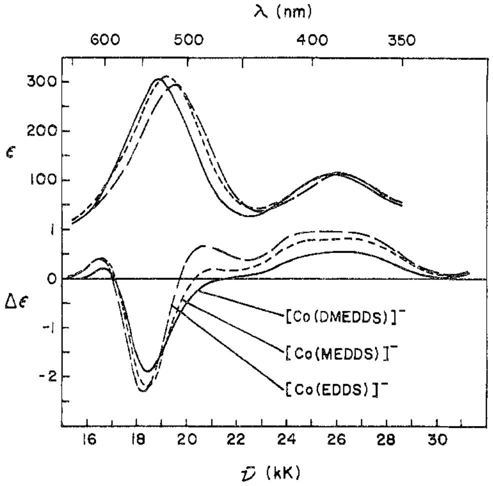

Figure 2. The visible absorption and circular dichroism spectra of Na[Co(EDDS)], Na[Co(MEDDS)], and Na[Co(DMEDDS)].

C, 30.28, H, 3.69; N, 7.18. Elemental analyses were obtained from the Materials Chemistry Section, Washington State University.

Spectra. The absorption spectra were measured on a Cary 14 spectrophotometer using a tungsten lamp. The CD spectra were recorded on a JASCO ORD-UV5 instrument equipped with a xenon source and CD attachment and calibrated with *d*-10-camphorsulfonic acid (Aldrich, recrystallized from acetic acid and dried over P_2O_5 at *ca.* 80° under vacuum); $\Delta\epsilon_{290} = +2.34$. The spectra were obtained at room temperature at concentrations of *ca.* 10^{-3} *M.*

Results and Discussion

The CD and visible absorption spectra of $[Co(EDDS)]^-$, $[Co(MEDDS)]^-$, and $[Co(DMEDDS)]^-$ are shown in Figure 2. Like EDDS,[1,3] the N-methylated derivatives show absolute stereospecificity. The chromatographic behavior of the Co(III) complexes indicated only one geometrical isomer in each case. That $[Co(MEDDS)]^-$ and $[Co(DMEDDS)]^-$ have the same absolute configuration as $[Co(EDDS)]^-$ (six-membered rings in the plane, Figure 1)[3] is apparent from the similarity of the CD spectra. The alternate arrangement (five-membered rings in the plane) would require the opposite chiral configuration of chelate rings and thus near-enantiomeric (to $[Co(EDDS)]^-$) CD curves.

As expected the CD curve for $[Co(MEDDS)]^-$ is intermediate between those of the EDDS and DMEDDS complexes. Whereas very large changes occur in the CD spectra of *s-cis*-EDDA complexes on *N*-methyl substitution, the changes in the CD of $[Co(EDDS)]^-$ are small. If the major differences between the CD spectra of $[Co(EDDS)]^-$ (Figure 2) and $[Co(EDTA)]^-$ (Figure 3) were due to the N-vicinal effect, then the spectrum of the DMEDDS complex (Figure 3) would be expected to be quite similar to that of $[Co(EDTA)]^-$ since the nitrogens in these two compounds have similar immediate environments (three alkyl groups bonded to each nitrogen in $[Co(EDTA)]^-$ and $[Co(DMEDDS)]^-$ compared to two alkyl groups and one hydrogen in $[Co(EDDS)]^-$). To the contrary, the CD spectrum of $[Co(DMEDDS)]^-$ is similar to that of $[Co(EDDS)]^-$ (Figure 2) and quite different from that of $[Co(EDTA)]^-$ (Figure 3).

Once the N-vicinal effect has been accounted for, the remaining circular dichroism is the sum of the configurational effect due to the dissymmetric arrangement of chelate rings, the C-vicinal effect due to the asymmetric carbon atoms at which the five- and six-membered chelate rings join, and the conformational effect. The C-vicinal and conformational contributions to the CD of $[Co(EDDS)]^-$ should be quite similar to those observed for cobalt(III)-(*S*)-aspartate complexes since EDDS contains two (*S*)-aspartic acid units. For the complex $[Co(NH_3)_3(S\text{-asp})]^+$, the C-vicinal and conformational effects associated with *S*-asp are the only sources of rotatory strength. It is, therefore, possible to obtain an estimate of the combined vicinal–conformational effect in $[Co(EDDS)]^-$ (allowing for a change in ligand field strength) by doubling the CD observed for $[Co(NH_3)_3(S\text{-asp})]^+$.[11] By this procedure, it is found that the C-vicinal–conformational effect is both too small and of the wrong sign to account for the large differences between the CD curves of $[Co(EDDS)]^-$ and $[Co(EDTA)]^-$.

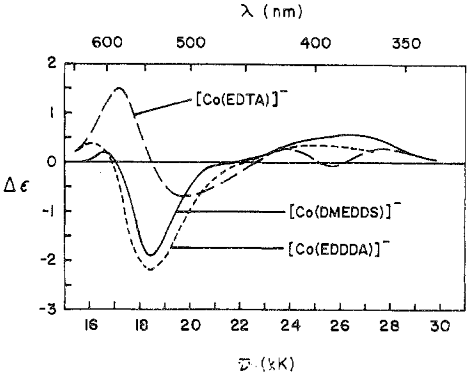

Figure 3. The circular dichroism spectra of $[Co(EDTA)]^-$ (from ref 4), $[Co(EDDDA)]^-$ (from ref 7), and $[Co(DMEDDS)]^-$. The CD curves correspond to the isomers shown in Figure 1.

Having eliminated the N-vicinal, C-vicinal, and conformational effects as structural sources responsible for the major differences between the CD curves for $[Co(EDDS)]^-$ and $[Co(EDTA)]^-$, only the configurational effect remains. It can be seen from Figure 1 that the arrangement of chelate rings is the same for the two complexes. However, $[Co(EDDS)]^-$ and $[Co(EDTA)]^-$ should have different dissymmetric distributions of donor atoms due to the different constraints imposed on the donor atoms by the chelate rings. Specifically, the bond angle spanned by the six-membered amino acid rings of EDDS[3] is almost certainly greater than the bond angle spanned by the corresponding glycinate rings of EDTA.[12] Dissymmetric donor atom distortions have been shown to have a major effect on the CD spectra of tris(diamine)- and tris(dicarboxylato)cobalt(III) complexes.[13] It is concluded, then, that the major differences between the CD spectra of $[Co(EDTA)]^-$ and $[Co(EDDS)]^-$ are due to changes in chelate ring size as postulated by Legg and Neal.[6]

While *N,N'*-dimethyl substitution of $[Co(EDDS)]^-$ does not cause the CD spectrum to approach that of $[Co(EDTA)]^-$, the spectrum does become even more similar to that of $[Co(EDDDA)]^-$ (Figure 3). This is consistent with the above deductions since $[Co(DMEDDS)]^-$ and $[Co(EDDDA)]^-$ not only have similar environments about the nitrogens but have a similar arrangement of like-sized chelate rings. The absolute configuration assignment of the $[Co(EDDDA)]^-$ optical isomers by Byers and Douglas[7] is also supported.

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Contribution from the Inorganic Chemistry Laboratory,
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Valence Delocalization Coefficients for $[(NH_3)_5Ru^{II}(pyr)Ru^{III}(NH_3)_5]^{5+}$

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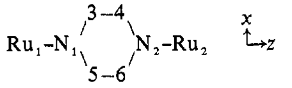
The electronic absorption[1] and Mossbauer spectra[2] of $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{5+}$ (pyr = pyrazine) suggest very strongly that, despite the fact that the ligands surrounding them are identical, the environments of the two Ru atoms differ in such a way that one may be considered to a first approximation as Ru^{II} and the other as Ru^{III}; *i.e.*, the complex is a class II[3] mixed-valence system. We recently pointed out[4] that this apparently surprising observation is capable of rationalization if the resonance interaction between the two equivalent valence structures ($Ru_1^{II}Ru_2^{III}$) and (Ru_1^{III}-Ru_2^{II}), where 1 and 2 are the two sites, is smaller than the energy needed to transfer an electron adiabatically from one site to the other. It is thus a matter of some interest to calculate rough values for the resonance interaction and hence the valence delocalization coefficients for this important model compound.

It is reasonable to suppose that since 1 and 2 are usually separated by quite a large distance in class II mixed-valence compounds (6.9 Å in the Ru dimer), they do not interact directly but only through higher order perturbations involving nonorthogonal $\pi \rightarrow Ru^{III}$ and $Ru^{II} \rightarrow \pi^*$ charge-transfer states. This simple idea was recently set out within the general formalism of perturbation theory[5,6] and applied with some sucess to Fe^{II}-Fe^{III} interactions in cyanides and silicates. The purpose of the present note is to apply it to the Ru^{II}-Ru^{III}-pyr dimer.

Consider the system



and assume that valence delocalization between the low-spin metal ions occurs only *via* the π, π^* molecular orbitals of the bridging pyrazine. The component of the zeroth-order ground state in which the unpaired electron on Ru occupies d_{yz} may be written

$$\psi_0 = |yz_1\overline{yz}_1\pi y\overline{\pi y}yz_2|\psi_0' \tag{1}$$

where ψ_0' takes account of the remaining electrons in the d shells of Ru_1 and Ru_2 and the π MO's of the pyrazine. The $Ru_1^{II} \rightarrow Ru_2^{III}$, $Ru_1^{II} \rightarrow \pi^*$ and $\pi \rightarrow Ru_2^{III}$ configurations are then

$$\psi_1 = |yz_1\overline{yz}_2\pi y\overline{\pi y}yz_2|\psi_0' \tag{2}$$

$$\psi_2 = |yz_1\overline{\pi y^*}\pi y\overline{\pi y}yz_2|\psi_0' \tag{3}$$

$$\psi_3 = |yz_1\overline{yz}_1\pi y\overline{yz}_2yz_2|\psi_0' \tag{4}$$

The ground and $Ru^{II} \rightarrow Ru^{III}$ charge-transfer states are then formed as linear combinations of ψ_0 and ψ_1

$$\Psi_G = \psi_0 + \gamma_1\psi_1 \tag{5}$$

$$\Psi_{E1} = \psi_1 + \gamma_0'\psi_0 \tag{6}$$

Taking into account all the pyrazine π, π^* MO's, the valence delocalization coefficients are now given[5] by

$$\gamma_1 = \sum_{i=1,3}\frac{(yz_1|H|\pi i^*)(yz_2|H|\pi i^*)}{(E_{i+1}-E_0)(E_1-E_0)} - \sum_{i=1,3}\frac{(yz_1|H|\pi i)(yz_2|H|\pi i)}{(E_{i+4}-E_0)(E_1-E_0)} \tag{7}$$

$$\gamma_0' = -\sum_{i=1,3}\frac{(yz_1|H|\pi i^*)(yz_2|H|\pi i^*)}{(E_{i+1}-E_1)(E_1-E_0)} + \sum_{i=1,3}\frac{(yz_1|H|\pi i)(yz_2|H|\pi i)}{(E_{i+4}-E_1)(E_1-E_0)} \tag{8}$$

where the πi label occupied π MO's of pyrazine in order of decreasing energy and πi^* the vacant π MO's in order of increasing energy. $(E_1 - E_0)$ is the energy of the $Ru_1^{II} \rightarrow Ru_2^{III}$ configuration, $(E_{i+1} - E_0)$ that of $Ru_1^{II} \rightarrow \pi i^*$, and $(E_{i+4} - E_0)$ that of $\pi i \rightarrow Ru_2^{III}$. We express the integrals $(yz_1|H|\pi i^*)$, $(yz_2|H|\pi i^*)$, $(yz_1|H|\pi i)$, and $(yz_2|H|\pi i)$ in terms of MO coefficients C_{ia} and C_{ia}^* for pyrazine and Ru^{II}-N, Ru^{III}-N resonance integrals and then estimate the coefficients from a Pariser-Parr-Pople[7] calculation[6] on the pyrazine molecule.

The integral $\beta(Ru^{II}\text{-}N)$ is chosen so that the application of first-order perturbation theory and the dipole length operator to the $Ru^{II} \rightarrow \pi i^*$ charge-transfer excitation yields the observed transition moment as

$$\mu(\Psi_G \rightarrow \Psi_{E2}) = -\frac{2^{1/2}C_{11}^*\beta(Ru^{II}\text{-}N)R(Ru^{II}\text{-pyr})}{E_2 - E_0} \tag{9}$$

From Creutz and Taube's work[1] we estimate that μ_{obsd}-$(\Psi_G \rightarrow \Psi_{E2})$ is about 1.12 e Å while $(E_2 - E_0)$ is set as the energy of the excitation $\Psi_G \rightarrow \Psi_{E2}$, again estimated from ref 1 as 17.7 kK. Finally, $R(Ru^{II}\text{-pyr})$ is taken from structural data for related compounds[8] as 3.45 Å. Applying eq 9 then yields a value of $\beta(Ru^{II}\text{-}N) = 7.75$ kK, and for simplicity $\beta(Ru^{III}\text{-}N)$ is assigned the same value.

The configuration energy terms, $(E - E_0)$, are chosen by reference to both experimental and theoretical data. $(E_1 - E_0)$ and $(E_2 - E_0)$ are equated to the energies of the $Ru^{II} \rightarrow Ru^{III}$ and $Ru^{II} \rightarrow \pi 1^*$ charge-transfer bands in the spectrum of the mixed-valence ion, while $(E_3 - E_0)$ and $(E_4 - E_0)$ are calculated from $(E_2 - E_0)$ using the approximate formula

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