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Circular Dichroism of uns-cis-Trimethylenediamine-N,N′-diacetic Acid Cobalt(III) Complexes with a Carbonate, Oxalato, or Malonate Anion

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The uns-cis complexes $[Co(TMDDA)(CO_3)]^-$, $[Co(TMDDA)(oxalate)]^-$, *and* $[Co(TMDDA)(malonate)]^-$ *(TMDDA = trimethylenediamine-N,N′-diacetate ion) have been prepared and resolved. Their absorption and circular dichroism spectra are reported. Rotational strengths decrease with increasing chelate ring size for the bidentate ligands and for the larger diamine ring of the framework of the TMDDA complexes compared to those of EDDA.*

Introduction

Circular dichroism (CD) studies of Co(III) complexes of ethylenediamine-N,N′-diacetate (EDDA) and related tetradentate ligands have been carried out extensively during the past several years.[1–9] The *s-cis*-[Co(EDDA)L] complexes have been of interest because their CD spectra are quite insensitive to changes in the coordinated atoms or ring size of the bidentate ligand L. Figure 1 shows *s-cis* and *uns-cis* isomers of this type. The complexes of trimethylenediamine-N,N′-diacetic acid (H_2TMDDA) containing a larger diamine backbone, however, have not been so well investigated. Circular dichroism studies of diamine-*uns-cis*-trimethylenediamine-N,N′-diacetatocobalt(III) complexes were reported in the previous paper.[10] It was found that the central chelate ring size of EDDA and TMDDA and the ring size of the bidentate ligands affect the shape of CD spectra in the same fashion. In order to extend the investigation of the effect of chelate ring size on CD spectra, the following three complexes, *uns-cis*-$[Co(TMDDA)(CO_3)]^-$, *uns-cis*-$[Co(TMDDA)(ox)]^-$ (ox = oxalate) and *uns-cis*-$[Co(TMDDA)(mal)]^-$ (mal = malonate) were prepared and their optical isomers resolved. Absorption and CD spectra are discussed in relation to the corresponding EDDA complexes.[11]

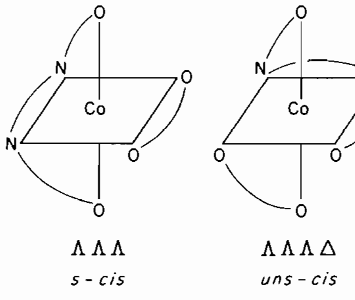

Figure 1. Chirality of *s-cis* and *uns-cis* isomers of the [Co(EDDA)(O–O)]$^-$ type.

Experimental

Preparation and Resolution of Sodium uns-cis-Trimethylenediamine-N,N′-diacetato(carbonato)cobaltate(III), uns-cis-Na$[Co(TMDDA)(CO_3)]$

Fifteen grams of hydrogen dichloro(trimethylenediamine-N,N′-diacetato)cobalt(III) hemihydrate,[10] $H[Co(TMDDA)Cl_2]\cdot 0.5H_2O$, in 300 ml of water was warmed at *ca.* 60° C for 20 min. The color changed from green to blue and finally violet. To the solution was added 10 g of Na_2CO_3, changing the color to more purplish violet. The solution was warmed in a water-bath for 30 min more. After the solution was cooled in a refrigerator, a small amount of insoluble purple complex was filtered off. The filtrate was concentrated to *ca.* 50 ml with a rotary evaporator. Then 100 ml of methanol was added and the solution cooled in a refrigerator. Violet crystals (17.3 g) were separated by filtration, and washed with methanol and then ether. The complex was recrystallized from water by addition of methanol. Yield: 10.2 g. *Anal.* Calcd for $Na[Co(TMDDA)(CO_3)]$ C, 29.10; H, 3.67; N, 8.49. Found: C, 29.35; H, 3.69; N, 8.29. When the complex was dissolved in water for spectral measurements, there was always a very slight turbidity. This could not be avoided by filtration or repeated recrystallization of the complex. The absorption minima are probably higher for the carbonato complex because of the slight turbidity.

For the resolution, 4.2 g of $(-)_{589}$-$[Co(en)_2(ox)]$Br and 2.0 g of silver acetate were combined and stirred for 10 min in 12 ml of water at 50° C. The AgBr which had formed was removed and washed with 10 ml of water. The filtrate and washings were combined and

4.0 g of racemic $Na[Co(TMDDA)(CO_3)]$ in 12 ml of water was added with good stirring. The resulting solution was kept in a refrigerator for several days. Purple diastereomer (3.7 g) was separated by filtration. The material was recrystallized four times until the constant $\Delta\varepsilon_{536} = -3.99$ was obtained. Yield: 2.3 g. *Anal.* Calcd for $[Co(en)_2(ox)][Co(TMDDA)(CO_3)]\cdot 4H_2O$: C, 26.01; H, 5.61; N, 13.01. Found: C, 26.28; H, 5.56; N, 12.53. Since optically active *uns-cis*-$[Co(TMDDA)(CO_3)]^-$ could not be isolated from the diastereomer without racemization, its CD spectrum was obtained by subtracting the CD curve of $(-)_{589}$-$[Co(en)_2(ox)]^+$ from the curve of the diastereomer.[4] Optical activity due to the *uns-cis*-$[Co(TMDDA)(CO_3)]^-$ was found to decrease rapidly for aqueous solutions of the diastereomer. Reproducible CD values were obtained by making measurements on cold solutions of the diastereomer immediately after mixing. A solution was replaced by a fresh one when it no longer gave reproducible data. Six solutions were required to obtain a complete CD curve for 650–350 nm.

Preparation and Resolution of Sodium uns-cis-Trimethylenediamine-N,N′-diacetato(oxalato)cobaltate (III), uns-cis-Na[Co(TMDDA)(ox)]

Fifteen grams of the dichloro complex in 300 ml of water was warmed at *ca.* 60° C for 20 min in a water-bath. To the solution was added 12.6 g of sodium oxalate, changing the color from violet to more purplish violet. The solution was warmed for 25 min more at *ca.* 70° C. The color changed to purple during this time. Then the solution was concentrated to 100 ml under an air stream. After a white substance was filtered off (presumably sodium oxalate), the filtrate was further concentrated under an air stream to 75 ml. To the solution was added 150 ml of methanol and kept in a refrigerator. The purple complex (15.4 g) was filtered, washed with methanol and then ether. Purple crystals were obtained by recrystallization from water by addition of methanol. Yield: 13.9 g.

For the resolution, 3.9 g of $(-)_{589}$-$[Co(en)_2(ox)]Br$ and 1.9 g of silver acetate were combined and stirred for 10 min in 12 ml of water at 50° C. The AgBr which had formed was removed and washed with 12 ml of warm water. The filtrate and washings were combined. Four grams of racemic $Na[Co(TMDDA)(ox)]$ in 12 ml of water was added to the above solution with good stirring. Addition of 10 ml of methanol to the solution and cooling resulted in precipitation of purple–red diastereomers. The diastereomers were separated by filtration and then dissolved in 100 ml of warm water and then 50 ml of methanol was added. After the solution was cooled in a refrigerator, the first fraction (2.0 g) was removed by filtration. This purple red material was recrystallized from water by addition of methanol, followed by cooling in a refrigerator. The recrystallization did not change the $\Delta\varepsilon$ value ($\Delta\varepsilon_{520} = -1.81$, assuming an anhydrous 1 : 1 diastereomer). To the filtrate, after the removal of the first fraction, was added 120 ml of methanol and the solution was cooled in a refrigerator. From this was isolated the other diastereomer (1.6 g) with $\Delta\varepsilon_{530} = -3.06$ (assuming an anhydrous 1 : 1 diastereomer). Recrystallization of this diastereomer from water by addition of methanol did not change the $\Delta\varepsilon$ value. The diastereomer with $\Delta\varepsilon_{520} = -1.81$ was dissolved in a small amount of water and passed through a cation-exchange column (Dowex 50W–X8, K^+ form). To the eluate (30 ml) was added 70 ml of ethanol and the solution was cooled in a refrigerator. Purple crystals were separated by filtration and washed with ethanol–water (1 : 1) mixture, ethanol, and then ether. Recrystallization from water by addition of ethanol did not change the $\Delta\varepsilon_{564}(+1.25)$. Yield: 0.29 g. The other enantiomer was obtained from the diastereomer with $\Delta\varepsilon_{530} = -3.06$ in the same way as for the plus isomer. Recrystallization did not change $\Delta\varepsilon_{564}(-1.25)$. Yield: 0.31 g. *Anal.* Calcd for $K[Co(TMDDA)(ox)]\cdot H_2O$: C, 27.56; H, 3.60; N, 7.14. Found: C, 28.03; H, 3.65; N, 7.31.

Preparation and Resolution of Silver uns-cis-Trimethylenediamine-N,N′-diacetato(malonate)cobaltate(III), uns-cis-Ag[Co(TMDDA)(mal)]

Twelve grams of the dichloro complex in 225 ml of water was warmed at *ca.* 65° C for 45 min in a water-bath. To the solution was added an aqueous solution containing 7.9 g of malonic acid and 6.0 g of NaOH in 15 ml of water, changing the color from violet to purple. The solution was warmed for 25 min more at *ca.* 70° C. After the reaction solution was concentrated to *ca.* 40 ml in a rotary evaporator, 19.2 g of $AgNO_3$ in 12 ml of water was added to it. The AgCl precipitate, which formed immediately, was filtered and washed with a small amount of water. To the combined filtrate and washings was added 20 ml of methanol little by little and the solution was cooled in a refrigerator. Purple complex (3.7 g) was separated by filtration and washed with methanol and then ether. To the filtrate was added 15 ml of methanol and the solution was kept in a refrigerator overnight. Another 20 ml of methanol was added to the solution containing the product and this was kept in a refrigerator overnight. Another 50 ml of methanol was added and again the solution was kept in a refrigerator (gradual addition of methanol was performed in order to prevent the sudden precipitation of a gummy solid). Purple complex (8.2 g) was separated by filtration and washed with methanol and then ether. The combined two fractions were recrystallized from water by addition of methanol. Yield: 7.2 g.

For the resolution, 4.6 g of $Ag[Co(TMDDA)(mal)]$ and 3.5 g of $(-)_{589}$-$[Co(en)_2(ox)]Br$ were combined and stirred for 10 min in 30 ml of water at

50° C. The AgBr which had formed was removed and washed with 5 ml of warm water. To the combined filtrate and washings was added 25 ml of ethanol and this solution was cooled in a refrigerator. The first fraction (3.0 g) was separated by filtration. The second (2.7 g) and the third (0.6 g) fractions were also obtained by addition of ethanol and subsequent cooling. After one recrystallization of the first fraction, the diastereomer was dissolved in a small amount of water and passed through a cation (Na^+) exchange column. The eluate was concentrated to *ca.* 6 ml using a rotary evaporator, and then 3 ml of an aqueous solution containing 1.7 g of $AgNO_3$ was added to it. After the addition of 1 ml of methanol, the solution was cooled in a refrigerator to obtain the purple complex. Three recrystallizations were carried out from water by addition of methanol. Two recrystallizations were enough to obtain purple plate crystals with a constant $\Delta\varepsilon_{561}(-0.70)$. Yield: 0.63 g. The second and third fractions were combined and treated in the same way as above. Recrystallization of silver salt was carried out four times. Three recrystallizations were enough to reach a constant $\Delta\varepsilon_{561}(+0.70)$. Yield: 0.18 g. *Anal.* Calcd for $Ag[Co(TMDDA)(mal)]\cdot 2H_2O$: C, 24.36; H, 3.68; N, 5.68. Found: C, 24.69; H, 3.61; N, 5.86.

Spectra

The absorption spectra were recorded on a Cary 14 spectrophotometer at room temperature using a tungsten source. For the carbonato complex, the racemate was used for the absorption spectrum, while active forms were used for the oxalato and malonato complexes. The CD spectra were recorded on a Roussel–Jouan Dichrograph using a tungsten source.

Analyses

Elemental analyses were performed by Chemalytics Inc., Tempe, Arizona.

Results and Discussion

The CD and absorption spectra for the complexes *uns-cis*-$[Co(TMDDA)L]^-$ where $L^{2-} = CO_3^{2-}$, ox^{2-} or mal^{2-} are shown in Figure 2. As expected for *cis*-N_2O_4 type complexes, there is little splitting of the ligand field absorption bands.[12–15] The symmetrical absorption bands give no indication of effective symmetry lower than O_h. The maxima of the first absorption bands (T_{1g}) are shifted to lower energy in the order $mal^{2-} \rightarrow ox^{2-} \rightarrow CO_3^{2-}$. The maxima of the second absorption bands (T_{2g}) of ox^{2-} and mal^{2-}, complexes, however, occur at the same energy, but that of CO_3^{2-} is at slightly lower energy. These facts are in accord with the weaker ligand field of CO_3^{2-} in comparison to ox^{2-} or mal^{2-}. The maxima of the first absorption bands of these complexes are located to higher energy than the corresponding *s-cis*-EDDA complexes and to lower energy than the corresponding *uns-cis*-EDDA complexes.[4,11,16] Since TMDDA has a weaker ligand field[10] than EDDA, if the present complexes were *s-cis* isomers, their first absorption maxima would be located at lower energy than those of the *s-cis*-EDDA complexes. Therefore the above facts suggest that the present three complexes are *uns-cis* isomers. This assignment is also confirmed by the great similarity of the CD spectra of *uns-cis*-TMDDA and *uns-cis*-EDDA complexes,[11] as will be discussed later. Absorption spectra of all three *uns-cis*-TMDDA complexes have much lower intensities than the corresponding EDDA complexes in both *d–d* absorption bands.[11] This might be expected because of the less rigid TMDDA framework.[17] Low intensities of absorption bands were also observed for diamine-*uns-cis*-TMDDA cobalt(III) complexes.[10]

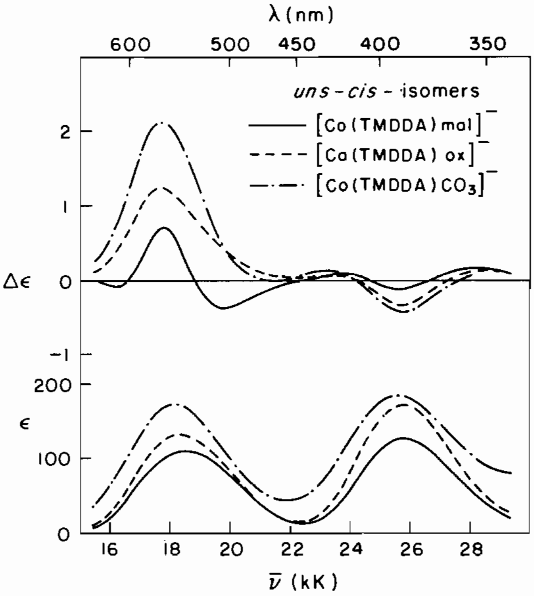

Figure 2. Absorption and CD spectra of *uns-cis*-$[Co(TMDDA)(mal)]^-$, *uns-cis*-$[Co(TMDDA)(ox)]^-$ and *uns-cis*-$[Co(TMDDA)(CO_3)]^-$.

Even though the absorption spectra do not reveal effective symmetry lower than O_h, the actual symmetry is only C_1. In general, one uses the highest symmetry which is consistent with the spectral data. The major effect in splitting energy levels arises from the fields imposed by the atoms coordinated. It is most convenient to consider *cis*-CoA_4B_2 complexes as having holohedrized tetragonal symmetry[18] (D_{4h}). Under tetragonal symmetry the $T_{1g}(O_h)$ level is split into A_2 and E levels. In the present complexes there is a weaker field along the unique axis (O–O) than in the plane perpendicular to it. Therefore it is predicted that the $A_2(D_{4h})$ level lies higher in energy than the $E(D_{4h})$ level.[19,20] Complexes with D_{4h} symmetry, of course, are not optically active. Here the optical activity arises from the chirality imposed by the chelate rings. The effect of this lowering of symmetry by the chiral chelate rings can be regarded as a pertubation on the microsymmetry (D_{4h}) and transitions can be related to their D_{4h} parentage.[1–7, 10, 11, 21]

The CD spectrum of the mal^{2-} complex shows three peaks in the first absorption band region, while those of the ox^{2-} and CO_3^{2-} complexes show only one peak, as reported for the corresponding *uns-cis*-EDDA complexes.[11] The appearance of three bands has also been observed[22] for $[Co(en)(mal)_2]^-$, but not for $[Co(en)(ox)_2]^-$. For the malonato complex the band at 19.84 kK comes from $A_2(D_{4h})$ and the two bands at lower energy than that come from $E(D_{4h})$, which is split in this case, reflecting the true lower symmetry. On the basis of this assignment (A_2 at 19.84 kK) the corresponding CD peak of [Co(EDDA)(mal)]$^-$ has much lower intensity,[11] comparing these peaks directly or relative to the dominant CD peak. In the diamine-*uns-cis*-EDDA cobalt(III) complexes also the intensity of the A_2 component was reduced from that of the less rigid TMDDA complexes.[10]

The CD intensities, expressed in terms of major peaks or net rotational strengths, decrease in the order of $CO_3^{2-} > ox^{2-} > mal^{2-}$, with increasing size of the dicarboxylato chelate ring. This phenomenon has also been observed in the following systems,[23,24] $[Co(en)_2L]^+$ and $[Co(l\text{-}chxn)_2L]^+$ where $L^{2-} = CO_3^{2-}$, ox^{2-} or mal^{2-}. In the present system, the absorption band intensities change in the same order as the CD intensities, although the changes are smaller for the absorption intensities (Table I).

The absorption and CD intensities for the *uns-cis*-[Co(TMDDA)L] complexes are rather uniformly lower than for the corresponding *uns-cis*-[Co(EDDA)L] complexes.[11] The corresponding *s-cis*-[Co(TMDDA)(O–O)]$^-$ complex ions have not been obtained for comparison, but both *s-cis*- and *uns-cis*-[Co(EDDA)L] complexes have been studied. The absorption intensities are higher for the less symmetrical *uns-cis*-EDDA complexes,[10,11] compared to the corresponding *s-cis*-EDDA complexes, but the CD intensities are *lower* for the *uns-cis*-EDDA complexes. The higher dipole strengths (absorption) and lower rotational strengths (CD) of the *uns-cis* complexes are consistent with the lower net chirality ($\Lambda\Lambda\Lambda\Delta$) compared to the exclusively $\Lambda\Lambda\Lambda$ chirality of the *s-cis* complexes[10,11] (Figure 1). The asymmetric nitrogen atoms for *uns-cis* complexes can adopt the same (*e.g.* RR) or opposite (RS) configurations. The present results do not permit a choice between these possibilities.

The CD spectra of the ox^{2-} and mal^{2-} complexes show three peaks in the second band region, and the CO_3^{2-} complex also seems to have three peaks. Thus the CD spectra of the complexes in the second absorption band region reflect the actual symmetry of the complexes, showing all three possible components. Considering the spread of the three peaks, it is very unlikely that this is the result of the overlap of two peaks of opposite sign.

The absolute configurations of *s-cis*-[Co(EDDA)(O–O)]$^-$ complexes have been assigned by the method of Mason *et al.*,[24] which relates the CD spectra of *cis*-CoA_4B_2 chelates to that of $[Co(en)_3]^+$, for which the absolute configuration is known.[25] The *s-cis*-[Co(EDDA)(O–O)]$^-$ type complexes have a C_2 axis and the chelate ring chirality about this axis can

TABLE I. Absorption and Circular Dichroism Data for Cobalt(III) Complexes Containing TMDDA.

Compound[a]	Absorption		Circular Dichroism	
	kK	ε	kK	$\Delta\varepsilon$
(+)-*uns-cis*-[Co(TMDDA)(CO_3)]$^-$	18.18	170[b]	17.70	+2.11
	25.64	180[b]	23.00	+0.12
			25.97	−0.45
(+)-*uns-cis*-[Co(TMDDA)(ox)]$^-$	18.35	131	17.73	+1.25
	25.81	171	23.59	+0.05
			25.71	−0.34
			28.57	+0.12
(+)-*uns-cis*-[Co(TMDDA)(mal)]$^-$	18.66	108	16.26	−0.09
			17.83	+0.70
			19.84	−0.38
	25.81	125	23.81	+0.09
			25.64	−0.13
			28.17	+0.14

[a] The optically active isomers of the complexes are characterized by (+) or (−), the sign of the main CD bands in T_{1g} region. [b] Values of ε for this complex might be slightly high, see Experimental.

be related directly to the chirality of $[Co(en)_3]^{3+}$. The unique weak field tetragonal axis corresponding to the positions of the two EDDA oxygen donor atoms, is perpendicular to the C_2 axis. In the *uns-cis*-[Co(TMDDA)(diamine)]$^+$ complexes there is a C_2 axis relative to the ligand atoms, but the arrangement of chelate rings does not conform to C_2 symmetry. The unique *strong* field tetragonal axis, corresponding to two coordinated nitrogen atoms, is perpendicular to the pseudo C_2 axis. For the *uns-cis*-[Co(TMDDA)(O–O)]$^-$ complexes there is a C_2 axis defined by the ligand atoms and it is perpendicular to the unique weak field tetragonal axis, as in the *s-cis* complexes. However, the arrangement of the chelate rings does not conform to C_2 symmetry for any *uns-cis*-[Co(TMDDA)L] complexes. The correspondence to the *s-cis* complexes is closer for the *uns-cis*-[Co(TMDDA)(O–O)]$^-$ complexes than for the corresponding diamine complexes, but it is not exact. If we use this correlation, as has been done for the *uns-cis*-EDDA complexes,[11] the complexes corresponding to the spectra in Figure 2, in each of which there is a positive dominant peak, are tentatively assigned the $\Lambda\Lambda\Delta$,[26] or a net Λ configuration.[27] The absolute configurations for the complexes reported here must be the same as those of the corresponding *uns-cis*-EDDA complexes[11] since their CD spectra are so much alike for each compound and they show the same trends. The assignments made for the TMDDA complexes and for the *uns-cis*-EDDA complexes[11] based on CD spectral correlation[24] are supported *independently* by the assignments made of the absolute configurations of complexes of ethylenediamine-N,N′-di-L-α-propionic acid from pmr studies.[3] The TMDDA complexes of the same configuration reported here show the same sign pattern for all three CD peaks in the second absorption band region.

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