

(f) The iron to azopyridine charge-transfer band lies at an exceptionally low energy. Other things being equal, the difference in energy between the metal t_{2g} orbitals and the empty ligand orbitals into which they are delocalized (which are higher in energy than the metal t_{2g} orbitals) will be smaller in this case than in the imine ligands previously investigated. This situation will favor extensive delocalization. We might anticipate that the extent of π delocalization will increase with decreasing energy of the iron to ligand charge-transfer band.

All of the items are indicative of a remarkably strong

interaction between the iron atom and azopyridine. The items (b) and (d) seem especially indicative of a π -delocalization mechanism playing an important role in this interaction.⁵⁸ If item (d) is correctly interpreted, we may infer that the iron atom should act as an electron-donating substituent in determining, for example, the substitution pattern of the ligand. Experiments to see if this is so are being undertaken.

Acknowledgment.—D. A. B. is grateful to the Science Research Council (Great Britain) for a research studentship.

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Circular Dichroism of Cobalt(III) Complexes with Ethylenediamine-N,N'-diacetic Acid and a Carbonate, Oxalate, or Malonate Anion¹

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Received July 31, 1968

Preparation and resolution procedures are reported for a series of cobalt(III) complexes with the tetradentate ligand ethylenediamine-N,N'-diacetic acid (EDDA) and a carbonate, oxalate, or malonate anion. Proton magnetic resonance was used to establish the *trans* coordination of the oxygens of EDDA in isomers studied. Absolute configurations of the new complexes are assigned by comparison of their CD curves with that of (+)₈₈₉-*trans*-Co(EDDA)en⁺, for which the absolute configuration is known. Rotational strengths of the d-d transitions were found to be determined largely by the EDDA and to be quite insensitive to the bidentate ligand used.

Introduction

While the relationship between the absolute configuration of cobalt(III) complexes containing chelate rings and the sign of the Cotton effects of their d-d transitions has received considerable attention,² the magnitude of the rotational strengths of these transitions has not been studied systematically. Reasons for variations in intensities of circular dichroism (CD) bands within and between series of related complexes are not known.

With the aim of assessing the influence of ring size on rotational strength, a new series of cobalt(III) complexes has been prepared with each complex containing the tetradentate ligand ethylenediamine-N,N'-diacetate (EDDA) and a carbonate or a dicarboxylate anion. The anions used were carbonate, oxalate (ox), and malonate (mal) giving four-, five-, and six-membered chelate rings, respectively. The geometrical isomers studied were those with the coordinated oxygens of the EDDA *trans* to one another.

For the previously studied complexes containing these bidentate anions, no consistent relationship between ring size and rotational strength has been found.

For the complex ions Co(en)(ox)₂²⁻ and Co(en)(mal)₂²⁻, it was found that the rotational strength in the visible region for the malonato complex was approximately twice that for the oxalato complex.³ On the other hand, for the ions Co(gly)(ox)₂²⁻ and Co(gly)(mal)₂²⁻, the rotational strength in the visible region for the oxalato complex is about twice that for the malonato complex.⁴ For the series Co(en)₂X⁺, where X = CO₃²⁻, ox, or mal, the carbonate complex gave the highest rotational strength and the malonato complex gave the lowest, but it was thought that complete resolution was not achieved for the malonato complex.⁵ More circular dichroism data are needed to determine whether it is ring size or some other property of these anions which is important for determining the rotational strengths of the d-d transitions of these complexes.

Experimental Section

The optically active isomers of the new complexes are characterized by (+) or (-), the sign of the lowest energy CD maximum.

Ethylenediamine-N,N'-diacetic acid was obtained from K & K Laboratories, Inc., or from Pfaltz and Bauer, Inc., and used without further purification.

(1) This work was supported, in part, by a research grant (GM 10829-10) from the Division of General Medical Studies, Public Health Service.

(2) S. Kirchner, *Coord. Chem. Rev.*, **2**, 461 (1967); J. Fujita and Y. Shimura in "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Eds., John Wiley & Sons, Inc., New York, N. Y., 1968, p 156.

(3) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

(4) K. Yamasaki, J. Hidaka, and Y. Shimura, private communication.

(5) R. A. Haines, Ph.D. Thesis, University of Pittsburgh, 1964. Resolution being checked.

Preparation of Potassium *trans*-Ethylenediamine-*N,N'*-diacetato(carbonato)cobaltate(III) Tetrahydrate, $K[trans-Co(EDDA)CO_3] \cdot 4H_2O$.—A solution of $CoCl_2 \cdot 6H_2O$ (11.9 g, 0.05 mol) in water (10 ml) and 30% H_2O_2 (10 ml) was added dropwise to a cold slurry of $KHCO_3$ (25 g, 0.25 mol) in water (20 ml). The mixture was cooled in ice and stirred well during the addition. The resulting green solution was quickly filtered. Solid ethylenediamine-*N,N'*-diacetic acid (8.89 g, 0.05 mol) was added to the filtrate. The solution was heated at 50° for 5 min. The resulting purple solution was cooled in ice and three volumes of 95% ethanol was gradually added. A purple oil separated. The supernatant liquid was decanted, the oil was redissolved in a minimum amount of water, and about one volume of 95% ethanol was slowly added. Purple crystals usually separated at this point. If an oil formed, the above procedure was repeated until crystals were obtained; yield, 5.5 g. The air-dried crystals lost 3 mol of water per mole when dried in a vacuum oven at 40° for 36 hr. The addition of strong acid to the complex caused evolution of CO_2 .

Resolution.— $(-)_546-[Co(en)_2ox]Br \cdot H_2O$ (7.3 g, 0.02 mol) and silver acetate (3.3 g, 0.02 mol) were combined and stirred for several minutes in 25 ml of water at 60°. The $AgBr$ which had formed was removed and washed with warm water (5 ml). Solid $K[trans-Co(EDDA)CO_3] \cdot H_2O$ (4 g, 0.012 mol) was added to the filtrate with good stirring. After the solid had dissolved, the solution was cooled in ice for 1–2 hr. The red diastereoisomer (2.6 g) was removed. This material was recrystallized twice from warm water by cooling in ice; yield, 1.5 g, with $\Delta\epsilon_{565} = -5.7$. *Anal.* Calcd for $[Co(en)_2ox][Co(EDDA)CO_3] \cdot 3H_2O$: C, 25.7; H, 5.26; N, 13.8. Found: C, 25.69; H, 5.48; N, 13.87.

Since optically active $trans-Co(EDDA)CO_3^-$ could not be isolated from the diastereoisomer, its CD spectrum was obtained by subtracting the CD curve of $(-)_546-Co(en)_2ox^+$ from the curve of the diastereoisomer. The validity of this procedure was checked by the comparison of the CD curve of $K[trans-(+)-Co(EDDA)ox]$ with the curve obtained by the same procedure for $[(+)_546-Co(en)_2ox][(-)-Co(EDDA)ox]$ studied over a sixfold concentration range. The curves obtained directly and by subtraction of the contribution for the resolving agent agreed within 5% of $\Delta\epsilon$ or better. The differences between the total areas of peaks were insignificant. Optical activity due to the $trans-Co(EDDA)CO_3^-$ was found to decrease rapidly for aqueous solutions of the diastereoisomer. Reproducible CD values were obtained by making measurements on cold solutions of the diastereoisomer immediately after mixing. A solution was replaced by a fresh one when it no longer gave reproducible data (2–3 min after mixing in ice water). Seven solutions were required to obtain a complete CD curve for the 650–380- $m\mu$ region of the spectrum. If $(+)_546-Co(en)_2ox^+$ was substituted for the $(-)_546$ isomer in the resolution procedure, the diastereoisomer containing the (+) isomer of $trans-Co(EDDA)CO_3^-$ was obtained.

Preparation of Potassium *trans*-Ethylenediamine-*N,N'*-diacetato(oxalato)cobaltate(III) Dihydrate, $K[trans-[Co(EDDA)ox] \cdot 2H_2O$.—Cobalt(II) carbonate (9.0 g, 0.075 mol) and ethylenediamine-*N,N'*-diacetic acid (13.2 g, 0.075 mol) were stirred together in 75 ml of water at 60° for about 20 min. The resulting mixture was added to a solution of $K_2C_2O_4$ (9.2 g, 0.05 mol) and $H_2C_2O_4 \cdot 2H_2O$ (3.2 g, 0.025 mol) in 200 ml of water. Five grams of activated charcoal was added and air was bubbled through the mixture for 17 hr. The charcoal was removed and the red-purple filtrate was evaporated under a stream of air on a steam bath to a volume of 100 ml. The solution was cooled in ice for 2 hr. Purple crystals of $K[trans-Co(EDDA)ox] \cdot 2H_2O$ (3.1 g) were collected. The filtrate was left standing in the refrigerator for several days and a little ethanol was added to obtain 9 g of red solid. Recrystallization of this solid from warm water by cooling in ice gave 1 g of $K[trans-Co(EDDA)ox] \cdot 2H_2O$ as the least soluble fraction. *Anal.* Calcd for $K[Co(EDDA)ox] \cdot 2H_2O$: C, 24.2; H, 3.54; N, 7.08. Found: C, 23.86; H, 3.71; N, 6.93.

Resolution.— $(+)_546-[Co(en)_2ox]I$ (2.3 g, 0.006 mol) and silver

acetate (0.9 g, 0.0055 mol) were stirred together in water (15 ml) at 60°. After several minutes AgI was removed and washed with water (5 ml). The filtrate was warmed to 60° and solid $[trans-Co(EDDA)ox] \cdot 2H_2O$ (2.2 g, 0.006 mol) was added with rapid stirring. The red diastereoisomer began to separate almost at once. The first fraction was removed after about 2 min. This material (1.3 g, $\Delta\epsilon_{556} + 4.6$) was recrystallized once from warm water by cooling in ice. Fractions of diastereoisomer with $\Delta\epsilon_{556} \geq +5.5$ (based on molecular weight assuming 1:1 diastereoisomer of 588) were combined (0.8 g) and stirred for several minutes with KI (1.5 g) in a few milliliters of water. The resolving agent was removed and $K[trans-Co(EDDA)ox] \cdot 2H_2O$ (0.35 g, $\Delta\epsilon_{560} + 5.2$) was recovered from the filtrate by addition of ethanol (several volumes) and cooling in ice. If necessary, the complex can be recrystallized from cold water by adding ethanol and cooling in ice.

The $K(-)-[trans-Co(EDDA)ox] \cdot 2H_2O$ was obtained from the filtrate after removal of the diastereoisomer. This solution was treated with about 2 g of KI and excess resolving agent was removed. Ethanol was then added to precipitate partially resolved $K(-)-[trans-Co(EDDA)ox] \cdot 2H_2O$. This material was fractionally recrystallized from cold water by adding ethanol and cooling in ice. Fractions (0.35 g) were obtained with $\Delta\epsilon_{559} - 5.2$.

Preparation of Potassium *trans*-Ethylenediamine-*N,N'*-diacetato(malonato)cobaltate(III) Trihydrate, $K[trans-Co(EDDA)mal] \cdot 3H_2O$.—Cobalt(II) carbonate (9.6 g, 0.08 mol) and ethylenediamine-*N,N'*-diacetic acid (14.0 g, 0.08 mol) were stirred together in 80 ml of water at 60° for about 20 min. The resulting mixture was added to a solution of malonic acid (10.4 g, 0.1 mol) and KOH (7.6 g, 0.14 mol) in water (80 ml). Three grams of activated charcoal was added and air was bubbled through the mixture overnight (15 hr). The charcoal was removed and the filtrate was evaporated under a stream of air on a steam bath until purple solid began to separate (40–50 ml). The mixture was cooled in ice for 1 hr. Purple $K[trans-Co(EDDA)mal] \cdot 3H_2O$ was removed and washed with ethanol and acetone and air dried; yield, 7.5 g.

Resolution.— $(+)_546-[Co(en)_2ox]I$ (2.8 g, 0.007 mol) and silver acetate (1.1 g, 0.007 mol) were stirred together for several minutes in water (10 ml) at 60°. The AgI which had separated was removed and washed with 10 ml of water. Solid $K[trans-Co(EDDA)mal] \cdot 3H_2O$ (2.5 g, 0.0067 mol) was added to the cooled filtrate with good stirring. An equal volume (20 ml) of 95% ethanol was added to the resulting solution. Red solid separated at once and was quickly removed. This material was recrystallized from a minimum amount of cold water by addition of ethanol to give 1.2 g with $\Delta\epsilon_{575} - 3.65$ (assuming anhydrous 1:1 diastereoisomer). The diastereoisomer was stirred with NaI (3.5 g) in a few milliliters of water for several minutes. After removal of the resolving agent, the malonato complex was precipitated by adding ethanol and cooling in ice. The sodium salt of the complex was isolated because the potassium salt did not crystallize satisfactorily. The fractions obtained were recrystallized from cold water by addition of ethanol to give material with $\Delta\epsilon_{565} - 4.7$. *Anal.* Calcd for $Na[Co(EDDA)mal] \cdot 3H_2O$: C, 26.2; H, 4.36; N, 6.80. Found: C, 26.72; H, 4.39; N, 6.87.

The filtrate from the diastereoisomer was evaporated under a stream of air at room temperature to a volume of 30 ml. NaI (5 g) was added with stirring and after several minutes the resolving agent was removed. The (+) isomer of the malonato complex was obtained by the same procedure as that used for precipitating and purifying the (–) isomer.

Spectra.—The absorption spectra were measured on a Cary Model 14 recording spectrophotometer and the CD curves were recorded with a Roussel-Jouan Dichrograph using a Sylvania Sun Gun light source. The CD spectra were measured in a 2-cm cell at room temperature with the exception of the diastereoisomers with $Co(EDDA)CO_3^-$ which were measured in ice-cold solutions. Concentrations used were about $10^{-3} M$. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer (60 Mcps). The solvent was D_2O ; DSS (sodium

2,2-dimethyl-2-silapentane-5-sulfonate) was added to serve as an internal standard.

Analyses.—Elemental analyses were performed by Alfred Bernhardt, Elbach, West Germany.

Results and Discussion

Preparation of a complex thought to be $K(trans-Co(EDDA)CO_3) \cdot H_2O$ has been reported.⁶ The preparative procedure was the same as that used in this study, but the isolation procedure and the product obtained were different. Several attempts were made to repeat this previous work, but in no case were the red-violet crystals reported obtained. The complex prepared by Mori and coworkers was characterized by its cobalt analysis and absorption spectrum. Its visible absorption spectrum showed only one maximum (526 $m\mu$) and a shoulder (380 $m\mu$), whereas the visible spectrum of the carbonato complex isolated in the present study shows two maxima (Figure 1). The great similarity of the visible absorption, circular dichroism, and proton magnetic resonance spectra for the latter complex to those of the similar oxalato and malonato complexes tends to indicate that it is the $trans-Co(EDDA)CO_3^-$ complex. Since the complex reported previously could not be prepared in this laboratory, no speculation as to its identity is possible.

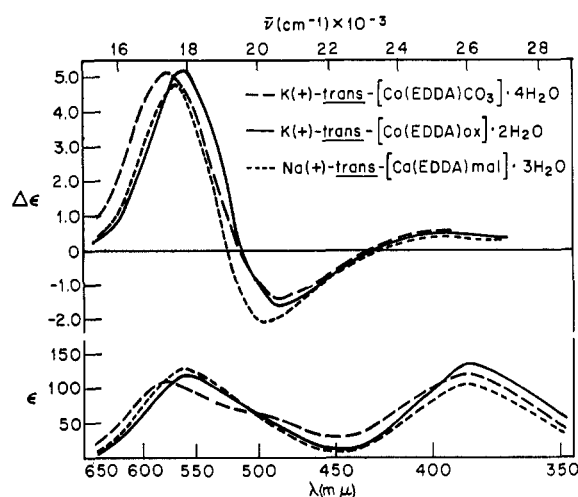


Figure 1.—Circular dichroism and molar absorptivity vs. wave number for the (+)₅₈₉ isomers of $trans-Co(EDDA)CO_3^-$, $trans-Co(EDDA)ox^-$, and $trans-Co(EDDA)mal^-$.

Proton nuclear magnetic resonance was used to assign the $trans$ configuration to EDDA in the complexes studied. Since the two acetate rings of $trans$ -coordinated EDDA are in equivalent environments, only one AB pattern is expected for the two sets of acetate ring protons. For the cis isomer, two different AB patterns would be expected, one for the protons of each acetate ring. The nmr spectra of similar complexes have been thoroughly discussed.⁷ Each complex in the present series gave one AB quartet due to acetate ring protons. The resonance fre-

quencies and chemical shifts for these AB patterns are given in Table I. The fact that no cis isomers of these complexes were isolated is consistent with the finding of Legg and Cooke⁷ that the $trans$ configuration of coordinated EDDA is preferred.

TABLE I
PMR FREQUENCIES FOR AB PATTERN DUE
TO ACETATE RING PROTONS

	K[Co-(EDDA)CO ₃]	K[Co-(EDDA)ox]	Na[Co-(EDDA)mal]
Resonance freq from DSS, ppm	4.37	4.42	4.37
	4.07	4.12	4.07
	3.43	3.45	3.38
	3.13	3.15	3.08
Acetate ring proton chem shifts, ^a cps			
H _a	4.14	4.28	4.20
H _b	3.20	3.33	3.25

^a J_{AB} was 18 cps for all three complexes.

The shapes of the CD curves for the complexes investigated (Figure 1) are very similar to those for the related isomers of $trans-Co(EDDA)en^+$ and $trans-Co(EDDA)(S)\text{-ala}$ (Figure 2).⁸ In the following discussion $trans-Co(EDDA)ox^-$ will be used as a representative complex for the three new complexes reported in this paper. Since the three complexes are very similar, the same arguments should apply to all three.

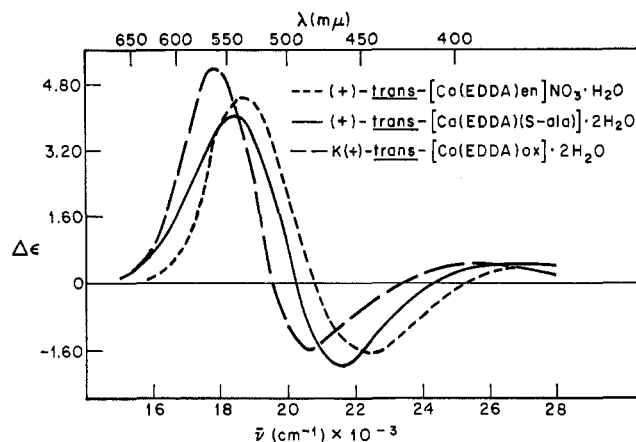


Figure 2.—Circular dichroism vs. wave number for the (+)₅₈₉ isomers $trans-Co(EDDA)en^+$, $trans-Co(EDDA)(S)\text{-ala}$, and $trans-Co(EDDA)ox^-$.

If chelate rings are ignored, the effective crystal field symmetry of $trans-Co(EDDA)ox^-$ is $cis-CoN_2O_4$ while that of $trans-Co(EDDA)en^+$ is $trans-CoO_2N_4$. By the electrostatic model for treating crystal field potentials, both of these complexes (ignoring chelate rings) have tetragonal symmetry.⁹ Under tetragonal symmetry the $T_{1g}(O_h)$ level, which is the first excited state for low-spin Co(III), is split into levels with A_2 and E symmetry. Whether the E state lies lower than the A_2 state or higher depends upon the arrangement of the ligands and their relative crystal field strengths.

(6) M. Mori, M. Shibata, E. Kyumo, and F. Maruyama, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

(7) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(8) J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967).

(9) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 106 f.

When *cis*-CoN₂O₄ and *trans*-CoO₂N₄ complexes are compared, it is predicted that the E level will lie lower than the A₂ level for both complexes. This same order of energy levels for the two types of complexes is predicted because both the arrangement of ligands and their relative crystal field strengths are changed in going from one complex to the other. If only one or the other of these things had been changed, the order of levels would have reversed.

Under the actual C₂ symmetry of the *trans*-EDDA complexes, the E level should split into two nondegenerate levels, one with A and one with B symmetry. For complexes of the type being considered, this latter splitting is apparently small enough so that it does not need to be considered, in general, when using CD curves for relating absolute configurations of the complexes.

Absolute configurations can be assigned to the isomers of the EDDA complexes prepared for this study by comparison of their CD spectra with that for (+)₅₈₉-*trans*-Co(EDDA)en⁺. The absolute configuration of the latter complex (Figure 3) is known from an nmr study of an analogous complex.⁸ Since the new complexes have the same order of energy levels in the region of the T_{1g} (O_h) level (at least in the tetragonal approximation) and the same arrangement of chelate rings, the isomers with the same absolute configuration as (+)₅₈₉-*trans*-Co(EDDA)en⁺ are the ones for which the CD band of lowest energy (related to A₁ → E) is positive (Figures 2 and 3).

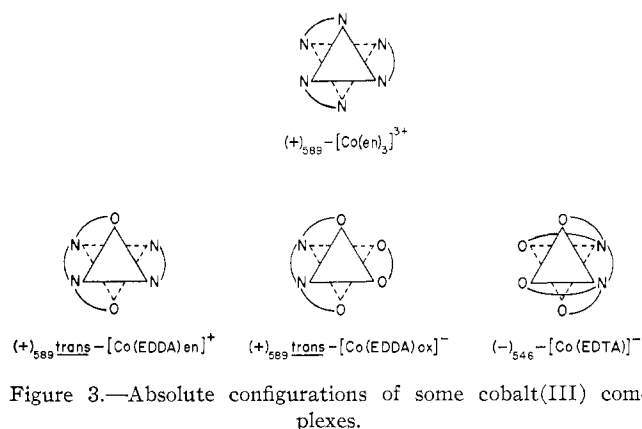


Figure 3.—Absolute configurations of some cobalt(III) complexes.

The complexes *trans*-Co(EDDA)ox⁻ and Co(EDTA)⁻ are both of the type *cis*-CoN₂O₄ and would be expected to have the same order of energy levels in the T_{1g} (O_h)

region. As expected, their CD curves do have the same general shape, although the absolute intensities of the bands differ for the two complexes. Coordinated EDTA contains a backbone structure which can be compared with *trans*-coordinated EDDA. It is interesting to note, however, that (+)₅₄₆-Co(EDTA)⁻, which has the same configuration of this backbone as does (+)-*trans*-Co(EDDA)ox⁻, gives a CD curve for which the corresponding bands have signs opposite those for (+)-*trans*-Co(EDDA)ox⁻.³ It is (-)₅₄₆-Co(EDTA)⁻ which has the same absolute configuration¹⁰ as (+)-*trans*-Co(EDDA)ox⁻ (Figure 3). This relationship is predicted by any one of the several methods¹¹ which can be used for finding the net helicity due to a given arrangement of chelate rings in a complex. The theoretical basis for this observed relationship between the net helicity of a multidentate chelate complex and the sign of the CD band due to the A₁ → E transition (or the related transition in complexes of lower symmetry) is not understood.

The rotational strengths of the d-d transitions of these new complexes are noteworthy for two reasons. The rotational strengths observed are significantly greater than those for most cobalt(III) complexes with similar ligands such as EDTA (hexa- or pentadentate), ethylenediamine, oxalate, etc. Also the rotational strength seems to be largely determined by the EDDA and is quite insensitive to changes in the bidentate ligand used. For this reason no significant change in rotational strength is seen as the size of the bidentate chelate ring is varied in the carbonato, oxalato, malonato series. There is also no significant difference in rotational strengths between these complexes and the comparable complexes with ethylenediamine or (*S*)-alanine. More experimental and theoretical work on the origin of rotational strength in these systems is needed before this dominating influence of the EDDA ligand can be explained.

Acknowledgments.—The authors wish to thank Mr. L. R. Froebe for measurement of the nmr spectra used in this study. Support in the form of a Mellon predoctoral fellowship to C. W. Van Saun is also gratefully acknowledged.

(10) An error in Figure 8 of ref 8 should be noted. The isomer of Co(EDTA)⁻ pictured is (+)₅₄₆-Co(EDTA)⁻ rather than the (-)₅₄₆ isomer as labeled. The isomers are correctly identified in the discussion.

(11) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2696 (1966); C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 1969 (1965); forthcoming tentative IUPAC rule for absolute configurations.