

Circular Dichroism of Some Complexes of Cobalt(III) with Ethylenediaminediacetate and Related Ligands¹

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Trimethylenediamine-, diammine-, and dinitro-cobalt(III) complexes with either ethylenediamine-*N,N'*-diacetate (EDDA) or the *N,N'*-dimethyl (DMEDDA) or *N,N'*-diethyl (DEEDDA) derivative coordinated in the *s-cis* geometry have been prepared and resolved. Comparisons of their CD spectra are made to examine the effects of chelate ring size, configuration of chelate rings, and crystal field due to the ligand(s) at the octahedral sites not occupied by the tetradentate ligand, as well as the effect of the EDDA asymmetric nitrogens, on the rotatory strengths. While the differences among the CD spectra of the diammine complexes with EDDA are quite small, significant differences are observed between the CD spectra of the corresponding complexes with DMEDDA or DEEDDA. Assignments of absolute configurations based on the CD spectra are discussed.

Introduction

Circular dichroism (CD) studies^{2,3,4} of Co(III) complexes with the tetradentate ligand ethylenediamine-*N,N'*-diacetate (EDDA) coordinated in the *s-cis* geometry⁵ (oxygen donor atoms trans to one another as shown in Figure 1) have furnished several interesting results. The CD peaks in the first (T_{1g}) absorption band region are quite intense^{2,4} by comparison with those obtained for bis- and tris-bidentate complexes⁸⁻¹⁰ in which the chiral distribution of chelate rings is the same as that found in the *s-cis* EDDA system. In addition it has been shown^{2,4} that the CD spectra of *s-cis* EDDA complexes are much less affected by ligand changes at the remaining two octahedral positions than in the case of *cis*-bis-(bidentates).⁸⁻¹⁰ For example, the complexes $s\text{-}[\text{Co}(\text{EDDA})\text{-L}]^-$, where L = carbonate, oxalate, or malonate, give rise to nearly identical CD spectra⁴ whereas large differences, particularly in intensities, are observed among the CD spectra of the complexes $[\text{Co}(\text{en})_2\text{L}]^+$.¹⁰ Recently, the asymmetric nitrogen atoms of coordinated EDDA were shown to be an important source of rotatory strength in *s-cis* Co^{III}-EDDA complexes.¹¹ The present work is a continuation of efforts to clarify the relationship between rotatory strength and structure in the Co^{III}-EDDA system.

Experimental Section

The following compounds were prepared by the methods of Legg

- (1) This work was supported by a research grant (GM-10829) from the Division of General Medical Studies, U. S. Public Health Service. Presented, in part, at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.
- (2) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, **6**, 700 (1967).
- (3) J. I. Legg and B. E. Douglas, *Inorg. Chem.*, **7**, 1452 (1968).
- (4) A. C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 115 (1969).
- (5) Three methods of distinguishing geometrical isomers of EDDA complexes have appeared in the literature. The nomenclature used here was suggested by Worrell and Busch⁶ for complexes of dithiamine ligands and has been recommended by Brubaker, *et al.*,⁷ for complexes of all linear tetradentates. *s-cis* is equivalent to *trans(O)* and α -*cis*. In using either the α/β or *s/uns* nomenclature, *cis* and *trans* are included to indicate the relationship of the octahedral sites not occupied by the tetradentate ligand. When a bidentate ligand occupies these sites the relationship is, of necessity, *cis* so that this part of the prefix is redundant.
- (6) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969).
- (7) G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, **7**, 161 (1971).
- (8) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
- (9) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).
- (10) W. T. Jordan, L. R. Froebe, B. J. Brennan, and B. E. Douglas, submitted for publication.
- (11) C. W. Maricondi and B. E. Douglas, *Inorg. Chem.*, **11**, 688 (1972).

and Cooke:¹² barium *N,N'*-dimethylethylenediamine-*N,N'*-diacetate, barium *N,N'*-diethylethylenediamine-*N,N'*-diacetate, and *cis*-diammine-*s*-(ethylenediamine-*N,N'*-diacetato)cobalt(III) chloride. In the formulas which follow (+) and (-) refer to the sign of the dominant CD peak in the ligand field region.

Resolution of *cis*-Diammine-*s*-(ethylenediamine-*N,N'*-diacetato)-cobalt(III) Nitrate, *s-cis*-[Co(EDDA)(NH₃)₂]NO₃. The resolution was carried out by a method analogous to that used by Legg, Cooke, and Douglas² for [Co(EDDA)en]⁺. Eight grams (0.0265 mol) of [Co(EDDA)(NH₃)₂]Cl was dissolved in 100 ml of water at 70° and to this solution was added 2.0 g (0.013 mol) of *d*-tartaric acid and 4.8 g (0.013 mol) of silver *d*-tartrate. The resulting mixture was stirred for 10 min at about 75° before removing the silver salts by filtration. The silver salts were washed with 10 ml of hot water and the combined filtrate and washings were allowed to cool slowly in ice to 20°, yielding red flocculent crystals. After being cooled to 10°, the mixture was filtered and the solid was washed with 40 ml of 75% ethanol, 95% ethanol, and ether and dried by suction. The yield of diastereomer was 5.0 g ($[\Delta\epsilon]_{530} + 0.743$).¹³ The diastereomer was recrystallized from a minimum of water at 50° by cooling to 15°. After one recrystallization of this material the value increased to $[\Delta\epsilon]_{530} + 0.836$. Further recrystallization did not result in improvement of this value. Upon addition of 2.0 ml of concentrated HNO₃ to a mixture of 3.0 g of diastereomer in 40 ml of room-temperature water, all diastereomer dissolved, and, within a few seconds, dark red crystals appeared. These were filtered and washed with 95% ethanol and ether and air-dried. The yield of (+)[Co(EDDA)(NH₃)₂]NO₃ ($\Delta\epsilon_{530} + 4.05$) was 1.8 g.

To the filtrate (100 ml) containing the (-) diastereomer was added gradually 100 ml of 95% ethanol. The solution was stirred in ice to obtain fine dark red crystals which were filtered and washed with 95% ethanol and ether and air-dried. The yield ($[\Delta\epsilon]_{530} - 0.865$) was 3.9 g. This was recrystallized to a maximum value of $[\Delta\epsilon]_{530} - 0.935$. The (-) diastereomer (1.4 g) was stirred with 20 ml of water and treated with 1 ml of concentrated nitric acid as with the (+) diastereomer above. The yield of (-)[Co(EDDA)(NH₃)₂]NO₃ ($\Delta\epsilon_{530} - 4.05$, $\Delta\epsilon_{457} + 2.00$, $\Delta\epsilon_{382} - 0.21$) was 1.0 g. *Anal.* Calcd for [Co(C₆H₁₆N₄O₄)]NO₃: C, 21.89; H, 4.89; N, 21.28. Found: C, 21.99; H, 5.06; N, 21.44.

Preparation and Resolution of *cis*-Diammine-*s*-(*N,N'*-dimethylethylenediamine-*N,N'*-diacetato)cobalt(III) Chloride, *s-cis*-[Co(DMEDDA)(NH₃)₂]Cl. A mixture of 10.6 g (0.0313 mol) of Ba(DMEDDA) and 8.7 g (0.031 mol) of CoSO₄·7H₂O in 90 ml of water was stirred at 60° for 15 min and then filtered. To the hot filtrate were added 3.4 g (0.063 mol) of NH₄Cl and then 6 ml of 30% H₂O₂ dropwise. After stirring a few minutes, air was bubbled through the solution for 2 hr. The violet solution was then mixed with 10 ml of concentrated ammonia and 3 g of charcoal and allowed to stand for a few hours before removing the charcoal by filtration. The filtrate was allowed to evaporate in a rotary evaporator at 40° until red crystals appeared. The

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

(13) $[\Delta\epsilon]_{\lambda} = (\Delta\epsilon_{\lambda})(100)/\text{MW}$; see ref 10 for a fuller explanation. This specific $\Delta\epsilon$ (corresponding to specific rotation) permits one to report a CD value for a diastereomer for which the molecular weight (particularly the extent of solvation) is unknown. $[\Delta\epsilon]$ can be followed during a resolution and checked by other workers more conveniently than a CD intensity at some concentration which is not conveniently duplicated.

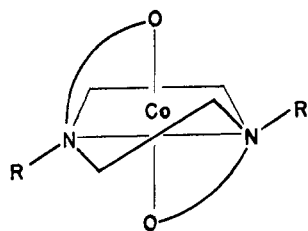


Figure 1. The $\Lambda(C_2)_2$ -SS configuration of an EDDA-type complex with *s*-cis geometry.

mixture was then cooled in ice and filtered. The crystals of $[\text{Co}(\text{DMEDDA})(\text{NH}_3)_2]\text{Cl}$ were washed with 95% ethanol and ether and dried by suction. The yield was 5.5 g. More product was obtained by further evaporation of the filtrate. The $[\text{Co}(\text{DMEDDA})(\text{NH}_3)_2]\text{Cl}$ complex (assumed to be anhydrous) was resolved using *d*-tartaric acid and silver *d*-tartrate as described above. The diastereomer was recrystallized twice from water at 70° by cooling in ice to obtain 1.3 g of compound ($[\Delta\epsilon]_{531} + 0.370$). The CD intensities were unchanged by further recrystallization of the diastereomer.

The other diastereomer was obtained by recrystallization of fractions taken from the filtrate to a maximum value of $[\Delta\epsilon]_{531} - 0.370$. The optical isomers were obtained by adding 3 ml (0.003 mol) of 1 *M* HNO_3 to 1.3 g (0.0030 mol) of diastereomer stirred in 5 ml of water. The red crystals of $(\pm)[\text{Co}(\text{DMEDDA})(\text{NH}_3)_2]\text{NO}_3$ which formed almost immediately were washed with 95% ethanol and ether ($\Delta\epsilon_{531} \pm 1.76$, $\Delta\epsilon_{369} \mp 0.15$). *Anal.* Calcd for $[\text{Co}(\text{C}_8\text{H}_{20}\text{N}_4\text{O}_4)]\text{NO}_3$: C, 26.87; H, 5.64; N, 19.61. Found: C, 26.72; H, 5.45; N, 19.42.

Preparation and Resolution of *cis*-Diammine-*s*-(*N,N'*-diethylethylenediamine-*N,N'*-diacetato)cobalt(III) Chloride, *s-cis*-[Co(DEEDDA)(NH₃)₂Cl]. This complex was prepared as described above for the corresponding DMEDDA complex. The red crystals obtained contained some orange crystals presumed to be $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. After repeated recrystallization, about 2 g of *s-cis*-[Co(DEEDDA)(NH₃)₂Cl] was obtained. The complex was resolved as described above. The yield of diastereomer ($[\Delta\epsilon]_{534} + 0.184$) was 1.8 g. After one recrystallization the value was increased to $[\Delta\epsilon]_{534} + 0.220$. The CD intensities were unchanged by further recrystallization of the diastereomer. The (–) diastereomer was obtained by recrystallizing fractions taken from the filtrate to a maximum value of $[\Delta\epsilon]_{534} - 0.220$. Each diastereomer was converted to the nitrate salt using a few drops of concentrated nitric acid to give small red crystals of *s-cis*-[Co(DEEDDA)(NH₃)₂NO₃]. The crystals were filtered and washed with 95% ethanol and ether ($\Delta\epsilon_{534} \pm 1.20$, $\Delta\epsilon_{366} \mp 0.20$). *Anal.* Calcd for $[\text{Co}(\text{C}_{10}\text{H}_{24}\text{O}_4)(\text{NH}_3)_2]\text{NO}_3$: C, 31.17; H, 6.28; N, 18.18. Found: C, 31.55; H, 6.21; N, 17.71.

Preparation of *s-cis*-(Ethylenediamine-*N,N'*-diacetato)(trimethylenediamine)cobalt(III) Nitrate, *s-cis*-[Co(EDDA)tn]NO₃. A mixture of 4.8 g (0.040 mol) of CoCO_3 and 7.0 g (0.040 mol) of $\text{H}_2(\text{EDDA})$ in 60 ml of water was stirred at 50° until CO_2 evolution was no longer observed. Concentrated HNO_3 (2.5 ml, 0.040 mol), 3.0 g (0.040 mol) of trimethylenediamine, and 3 g of activated charcoal were stirred in and the mixture was air oxidized for 12 hr. The charcoal was removed by filtration and the filtrate was allowed to evaporate in a stream of air until red crystals appeared. These were filtered and washed with 95% ethanol and ether and dried by suction. The yield was 6.6 g.

Resolution was attempted by means of diastereomer formation with hydrogen *d*-tartrate and antimonyl *d*-tartrate without any observable separation. The use of $[\text{Co}(\text{EDTA})]^-$ was marginally successful but very inconvenient due to the lengthy interval necessary to grow even partially resolved crystals of diastereomer in low yield from a concentrated solution. The following method was far superior. A solution of 6.0 g (0.016 mol) of $[\text{Co}(\text{EDDA})\text{tn}]\text{NO}_3$ in 20 ml of water at 60° was combined with a solution of 5.0 g (0.015 mol) of ammonium *d*- α -bromocamphor- π -sulfonate in 15 ml of water at 60°. After a few minutes of stirring, the solution was allowed to cool in an ice-water bath. After 15 min the sides of the beaker were scratched with a glass rod to induce the precipitation of fine red crystals which were collected after 15 min on a Buchner funnel and washed with 95% ethanol and ether. The yield of diastereomer ($[\Delta\epsilon]_{529} + 0.735$) was 3.5 g. This was recrystallized once from a minimum of water (80°) to obtain 2.0 g of diastereomer ($[\Delta\epsilon]_{529} + 0.750$). The CD intensities were unchanged by further recrystallization of the diastereomer.

A small portion of the diastereomer (0.689 g) was mixed with 25 ml of water and then stirred with 5 g of Dowex 1-X8 anion-exchange resin in the nitrate form. The resin was filtered off and the process was repeated with an additional 5 g of resin. The filtrate was allowed

to evaporate to a volume of 15 ml in a rotary evaporator and then 95% ethanol was added to obtain red crystals of $(+)[\text{Co}(\text{EDDA})\text{tn}]\text{NO}_3$ ($\Delta\epsilon_{529} + 4.58$). The (–) isomer was contained in the filtrate from initial separation of the diastereomer. Addition of 95% ethanol to this solution caused the precipitation of fine red crystals of $(-)[\text{Co}(\text{EDDA})\text{tn}]\text{NO}_3$ ($\Delta\epsilon_{529} - 4.62$, $\Delta\epsilon_{455} + 2.00$, $\Delta\epsilon_{382} - 0.13$, $\Delta\epsilon_{346} + 0.09$). *Anal.* Calcd for $[\text{Co}(\text{C}_9\text{H}_{20}\text{N}_4\text{O}_4)]\text{NO}_3$: C, 29.28; H, 5.46; N, 18.97. Found: C, 29.53; H, 5.54; N, 19.15.

Preparation of *s-cis*-(*N,N'*-Dimethylethylenediamine-*N,N'*-diacetato)(trimethylenediamine)cobalt(III) Iodide, *s-cis*-[Co(DMEDDA)tn]I. A mixture of 13.6 g (0.0400 mol) of Ba(DMEDDA) and 11.2 g (0.0400 mol) of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 160 ml of water was stirred for 15 min at 50° and filtered to remove BaSO_4 which was then washed on the filter with 10 ml of hot water. To the combined filtrate and washings were added 20 ml (0.040 mol) of 2 *M* nitric acid, 3.2 g (0.040 mol) of trimethylenediamine, and 4 g of activated charcoal. This mixture was then stirred at 50° during the dropwise addition of 4.5 g of 30% H_2O_2 and then for an additional 1.5 hr. The charcoal was removed by filtration and the filtrate was reduced in volume, first in a rotary evaporator and later in a stream of compressed air. After removing two fractions of white solid, probably unreacted ligand, fine red needles of the desired product appeared. Several fractions were filtered and washed with 95% ethanol and ether. The combined yield was 6.1 g. This was converted to the iodide by dissolving in a minimum of water and adding an excess of NaI.

Resolution. A mixture of 5.60 g (0.0120 mol) of $[\text{Co}(\text{DMEDDA})\text{tn}]\text{I}$, 0.90 g (0.0060 mol) of *d*-tartaric acid, and 2.20 g (0.00600 mol) of silver *d*-tartrate in 40 ml of water was stirred at 55° for 15 min and then filtered to remove the silver salts. The filtrate was allowed to evaporate in a stream of compressed air to a volume of 20 ml. Some red crystals were filtered and washed with 95% ethanol and ether and dried by suction. The yield ($[\Delta\epsilon]_{536} + 0.503$) was 0.5 g. A second fraction (2.3 g, $[\Delta\epsilon]_{536} + 0.468$) was obtained by adding 20 ml of 95% ethanol and scratching the sides of the beaker with a glass rod to induce crystallization. These two fractions were combined and recrystallized by dissolving in a minimum volume of water and adding 95% ethanol. The yield was 2.0 g ($[\Delta\epsilon]_{536} + 0.566$). The CD intensities were unchanged by further recrystallization of the diastereomer. The other diastereomer was obtained from the filtrate also by addition of 95% ethanol. The yield ($[\Delta\epsilon]_{536} - 0.566$) was 1.3 g. The diastereomer was dissolved in an equimolar amount of 0.5 *M* HNO_3 and cooled in ice to obtain red crystals of optical isomer ($\Delta\epsilon_{603} \mp 0.18$, $\Delta\epsilon_{536} \pm 3.05$, $\Delta\epsilon_{457} \mp 0.16$, $\Delta\epsilon_{375} \mp 0.50$). *Anal.* Calcd for $[\text{Co}(\text{C}_{11}\text{H}_{24}\text{N}_4\text{O}_4)]\text{NO}_3$: C, 33.25; H, 6.09; N, 17.63. Found: C, 33.08; H, 6.25; N, 17.75.

Preparation and Resolution of *s-cis*-(*N,N'*-Diethylethylenediamine-*N,N'*-diacetato)(trimethylenediamine)cobalt(III) Iodide, *s-cis*-[Co(DEEDDA)tn]I. A mixture of 22.0 g (0.0600 mol) of Ba(DEEDDA) and 16.8 g (0.0600 mol) of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 200 ml of water was stirred at 60° for 15 min and then filtered. To the filtrate were added 8.0 ml (0.060 mol) of concentrated HCl, 2.5 g (0.068 mol) of trimethylenediamine, and 4 g of activated charcoal. A stream of air was then passed through the mixture for about 20 hr. The charcoal was removed by filtration and the solution was allowed to evaporate to about 30 ml. Fine red crystals appeared upon addition of 9.0 g of NaI. These were washed with 95% ethanol and ether. The yield was 15.2 g. The complex was resolved as described for the corresponding DMEDDA complex. The filtrate from the AgI separation was allowed to evaporate in a rotary evaporator at 40° to 25 ml. Red crystals deposited as the solution stood at room temperature. The first three fractions, removed by filtration, had $[\Delta\epsilon]_{532} + 0.417$, $+0.457$, and $+0.423$, respectively. The first and third were combined and recrystallized, $[\Delta\epsilon]_{532} + 0.452$, and this was combined with fraction 2 and recrystallized, $[\Delta\epsilon]_{532} + 0.477$. Resolution was not improved by further recrystallization. The diastereomer (0.9 g) was dissolved in 20 ml of water and stirred with 4 g of Dowex 1-X8 anion-exchange resin in the nitrate form and then filtered. This process was repeated twice on the filtrate. Evaporation of the filtrate to near dryness yielded red crystals which were washed with 70% ethanol, 95% ethanol, and ether. The (–) diastereomer was obtained by combining and recrystallizing fractions 4 and 5. Conversion to the nitrate was identical with the method used for the (+) isomer ($\Delta\epsilon_{532} \pm 2.52$, $\Delta\epsilon_{376} \mp 0.44$). *Anal.* Calcd for $[\text{Co}(\text{C}_{13}\text{H}_{28}\text{N}_4\text{O}_4)]\text{NO}_3 \cdot 2\text{H}_2\text{O}$: C, 33.83; H, 6.99; N, 15.18. Found: C, 34.22; H, 6.77; N, 15.18.

Preparation of Potassium *cis*-Dinitro-*s*-(ethylenediamine-*N,N'*-diacetato)cobaltate(III), $\text{K}[s-cis-[\text{Co}(\text{EDDA})(\text{NO}_2)_2]]$. The preparation of this complex as the cesium salt was reported previously.¹⁴

The following procedure is more direct although the yield is somewhat smaller.

Cobalt(II) carbonate (4.8 g, 0.040 mol) and $H_2(EDDA)$ (7.0 g, 0.040 mol) were combined in 60 ml of water and stirred at 50° until evolution of gas was no longer observed (about 20 min). To this solution were added 7.1 g (0.080 mol) of KNO_2 and 3.0 g of activated charcoal, and air was bubbled through the resulting mixture for 12 hr. After the air-oxidized mixture was stirred for a few minutes at 60° to dissolve any crystalline product, the charcoal was removed by filtration. The filtrate was allowed to evaporate in a stream of air until crystals had accumulated in the beaker. The dark red-brown crystals were filtered and washed with 95% ethanol and ether. By allowing the filtrate to evaporate further, a second batch of crystalline product was obtained. The combined yield was 6 g. Recrystallization from a minimum volume of water by cooling to 20° yielded 5 g of product.

Resolution. Silver acetate (1.4 g, 0.0085 mol) and $(-)_D[Co(en)_2-ox]Br \cdot H_2O$ (3.1 g, 0.0085 mol) were mixed well with a stirring rod before adding 35 ml of water. The mixture was stirred at 55° for 10 min before filtering the silver salts. The filtrate and washings (10 ml of hot H_2O) were added to a stirred solution of 6.2 g (0.017 mol) of $K[Co(EDDA)(NO_2)_2]$ in 50 ml of water. After being stirred a few minutes, this solution was allowed to cool in an ice-water bath to 9° . Red crystals appeared when the sides of the beaker were scratched with a glass rod. The crystals were collected on a filter and washed with 95% ethanol and ether and dried by suction. The yield ($[\Delta\epsilon]_{max} -0.635$) was 3.4 g. The CD intensities were unchanged by further recrystallization of the diastereomer. This was dissolved in 75 ml of water and stirred with 10 g of Dowex 50WX-8 cation-exchange resin in the K^+ form for 15 min and then filtered. The filtrate was stirred with an additional 3 g of resin to ensure complete removal of $(-)_D[Co(en)_2ox]^+$. The resin was again removed by filtration and the filtrate was allowed to evaporate to a volume of 20 ml in a stream of compressed air. The large dark-red crystals which formed were filtered and washed with 95% ethanol and ether. The yield ($\Delta\epsilon_{599} +0.17$, $\Delta\epsilon_{496} -2.50$, $\Delta\epsilon_{413} +0.73$) was 1.6 g. The other isomer was obtained by the same method only using $(+)_D[Co(en)_2ox]I$. *Anal.* Calcd for $K[Co(C_6H_{10}N_4O_8)]$: C, 19.76; H, 2.77; N, 15.38. Found: C, 19.65; H, 3.12; N, 15.28.

Preparation of Potassium *cis*-Dinitro-*s*-(*N,N'*-diethylethylenediamine-*N,N'*-diacetato)cobaltate(III), $K[s-cis-[Co(DEEDDA)(NO_2)_2]]$. A mixture of 10.0 g (0.0270 mol) of $Ba(DEEDDA)$ and 7.6 g (0.027 mol) of $CoSO_4 \cdot 7H_2O$ in 100 ml of water was stirred for about 15 min at 50° and then filtered. To the stirred filtrate was added 4.6 g (0.054 mol) of KNO_2 and 3.0 g of activated charcoal. This mixture was air-oxidized for 12 hr before removing the charcoal by filtration. The filtrate was evaporated in a stream of compressed air until dark red crystals appeared. These were filtered and washed with 95% ethanol and ether. More product was obtained by allowing the filtrate to evaporate further.

Resolution. The resolution procedure was very similar to that used for $[Co(EDDA)(NO_2)_2]^-$. The volume of the solution of the diastereomers was decreased in a rotary evaporator until fine orange crystals appeared. These were filtered and washed with 95% ethanol and ether. The yield ($[\Delta\epsilon]_{526} -0.470$) was 1.5 g. The CD intensities were unchanged by further recrystallization of the diastereomer. A solution of 0.8 g of the diastereomer was converted to the K^+ salt using two portions of Dowex 50W-X8 cation-exchange resin in the K^+ form as before. The filtrate was allowed to evaporate in a stream of compressed air until dark red crystals were obtained. These were filtered and washed with 95% ethanol and ether. The yield ($\Delta\epsilon_{540} -1.09$ and $\Delta\epsilon_{445} +2.50$) of $(+)_K[Co(DEEDDA)(NO_2)_2]$ was 0.2 g. *Anal.* Calcd for $K[Co(C_{10}H_{18}N_4O_8)]$: C, 28.57; H, 4.32; N, 13.33. Found: C, 28.43; H, 4.20; N, 13.14.

Preparation of Potassium *cis*-Dinitro-*s*-(*N,N'*-dimethylethylenediamine-*N,N'*-diacetato)cobaltate(III), $K[s-cis-[Co(DMEDDA)(NO_2)_2]]$. The method of preparation was the same as that for $K[Co(DEEDDA)(NO_2)_2]$, except that 9.2 g of $Ba(DMEDDA)$ was substituted for $Ba(DEEDDA)$. As the filtrate from removal of the charcoal evaporated, a fine white solid (probably unreacted DMEDDA) precipitated and was removed by filtration. The very soluble $K[Co(DMEDDA)(NO_2)_2]$ grew out of solution slowly in dark red crystals. These were filtered and washed with 95% ethanol and ether.

Resolution. A mixture of 4.60 g (0.0132 mol) of $(+)_D-cis-[Co(en)_2(NO_2)_2]Br$ and 2.16 g (0.0130 mol) of silver acetate in 35 ml of water was stirred at 55° for 10 min and then filtered. The silver salts were washed on the filter with 5 ml of hot water. The combined filtrate and washings was added to a solution of 5.20 g (0.0132 mol) of $K[Co(DMEDDA)(NO_2)_2]$ in 25 ml of water. After stirring a few minutes, red crystals began to appear. The solution was cooled in ice at 20° and filtered to remove the crystals of diastereomer which were

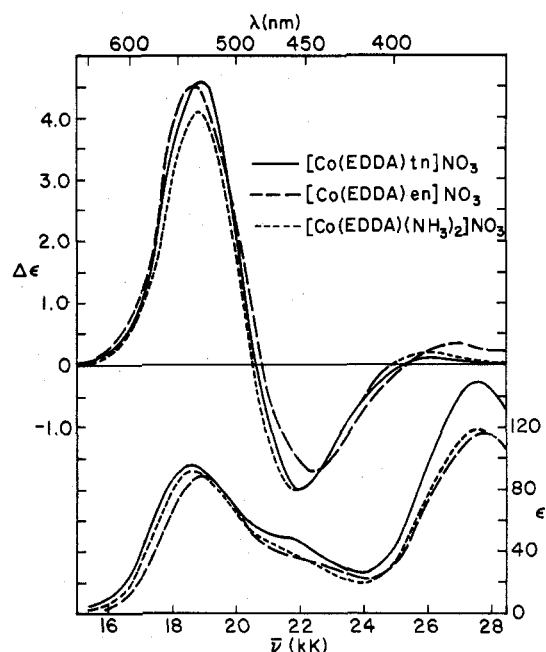


Figure 2. Absorption and circular dichroism spectra of *s-cis*- $[Co(EDDA)tn]NO_3$, *s-cis*- $[Co(EDDA)en]NO_3$, and *s-cis*- $[Co(EDDA)(NH_3)_2]NO_3$.

washed with 95% ethanol and ether and dried on the funnel by suction. The yield ($[\Delta\epsilon]_{540} -0.138$) was 3.0 g. Two recrystallizations yielded pure diastereomer ($[\Delta\epsilon]_{540} -0.148$). The CD intensities were unchanged by further recrystallization of the diastereomer. The other diastereomer was obtained by collecting fractions from the filtrate and recrystallizing to constant CD intensities ($[\Delta\epsilon]_{540} +0.149$). A solution of the optical isomer was prepared by stirring a solution of 1.0 g of the diastereomer in water with 7 g of Dowex 50WX-8 cation-exchange resin in the K^+ form and filtering. The filtrate was stirred with an additional 3 g of resin and again filtered. Dark red crystals of diastereomer ($\Delta\epsilon_{538} \pm 0.90$ and $\Delta\epsilon_{436} \mp 2.41$) were obtained by allowing the filtrate to evaporate to near dryness. *Anal.* Calcd for $K[Co(C_8H_{14}N_4O_8)]$: C, 24.47; H, 3.60; N, 14.28. Found: C, 24.27; H, 3.70; N, 14.14.

Spectra. The absorption spectra were recorded on a Cary 14 spectrophotometer at room temperature using a tungsten source. The CD spectra were recorded on a Roussel-Jouan Dichrograph using a tungsten source.

Analyses. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz.; Galbraith Laboratories, Inc., Knoxville, Tenn.; and Alfred Bernhardt, Elbach, West Germany. The number of waters of hydration was confirmed by determining the weight loss on drying at 100° .

Results and Discussion

The CD and absorption spectra for the complexes *s-cis*- $[Co(EDDA)en]^+$, *s-cis*- $[Co(EDDA)(NH_3)_2]^+$, and *s-cis*- $[Co(EDDA)tn]^+$ are shown in Figure 2. The assignments of the absorption bands and CD peaks in terms of the approximate tetragonal crystal field have been discussed previously for the en complex.^{2,12} The spectra of the tn and diammine complexes can be assigned in the same way. Of the two CD peaks in the region of the first (T_{1g}) absorption band, the dominant peak is assigned to the transition of $E(D_{4h})$ symmetry while the peak of opposite sign at higher energy is due to the $A_2(D_{4h})$ transition.

Substitution of one or more six-membered trimethylenediamine chelate rings for one or more five-membered ethylenediamine rings on a cobalt(III) complex generally produces large changes in the rotatory strengths.^{8,9,15-18} That only

(15) B. J. Brennan, Ph.D. Thesis, University of Pittsburgh, 1971.

(16) J. R. Gollgoly and C. J. Hawkins, *Chem. Commun.*, 689 (1968).

small differences are observed between the CD spectra of *s-cis*-[Co(EDDA)tn]⁺ and *s-cis*-[Co(EDDA)en]⁺ (Figure 2) is consistent with the results obtained for the *s-cis* Co^{III}-EDDA complexes with carbonate, oxalate, and malonate (see above). In fact, complete removal of the chelate ring in question, while maintaining approximately the same crystal field, causes only small changes in the rotatory strengths as evidenced by a comparison of the CD curve for *s-cis*-[Co(EDDA)(NH₃)₂]⁺ on the one hand with the curves for the corresponding en and tn complexes on the other (Figure 2). If, by contrast, two water molecules are substituted for the oxalate of [Co(en)₂ox]⁺, large changes occur in the CD intensities.⁸ It appears, therefore, that a chelate ring due to a bidentate ligand, L, has little effect on the rotatory strengths of complexes of the type *s-cis*-[Co(EDDA)L].

The EDDA asymmetric nitrogens have identical absolute configurations in complexes with the *s-cis* geometry as shown in Figure 1. Maricondi and Douglas¹¹ have shown that when two methyl or ethyl groups are substituted for the amine protons of *s-cis*-[Co(EDDA)L] complexes with L = en or ox, the CD intensities in the first-band region are diminished by a factor of 2 or greater. It is assumed that the vicinal effect induced by the asymmetric nitrogens of the dialkyl-substituted complexes is comparatively small¹¹ since the immediate environment about each nitrogen includes three alkyl groups rather than two alkyl groups and a hydrogen as in EDDA. The difference between the CD curves for related complexes with EDDA and DEEDDA should be primarily due to the difference in vicinal effects.¹¹

Since the rotatory strengths of the dialkyl-EDDA complexes are presumed to be derived primarily from the distribution of chelate rings, it is of interest to see how the CD spectra vary as a function of the nature of the diamine ligand(s) in these complexes. The CD and absorption spectra for the *s-cis* DMEDDA complexes with tn, en,¹¹ and diammine are shown in Figure 3. The spectra for the DEEDDA analogs are found in Figure 4. In each case the dominant peak appears to be related to the dominant peak in the spectrum of the corresponding EDDA complex, though the intensities are substantially diminished. The absolute configurations are, therefore, assigned in the same manner as for the EDDA complexes, a positive dominant peak indicating a Λ configuration.^{2,19,20}

For either set of dialkyl-EDDA complexes there is much greater variation among the CD spectra than for the EDDA complexes, the effect being more pronounced for the DEEDDA series. For all of the EDDA and dialkyl-EDDA complexes with diamine ligands (Figures 2-4) the frequencies of the absorption maxima decrease in the order en > diammine > tn corresponding to decreasing ligand field strength. At the same time, the dominant CD peak frequencies decrease in just the opposite order tn > diammine > en, and the frequency difference between absorption maximum and dominant CD peak frequency increases in the order EDDA < DMEDDA < DEEDDA or with diminishing vicinal effect. The inverted order for the dominant CD peaks suggests significant differences in the degree of splitting of the A₂ and B₂ components of the E transition for the three different diamine ligand systems. For the dialkyl-EDDA-tn complexes,

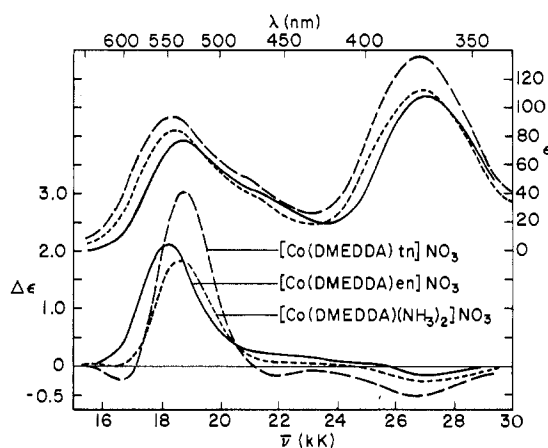


Figure 3. Absorption and circular dichroism spectra of *s-cis*-[Co(DMEDDA)tn]NO₃, *s-cis*-[Co(DMEDDA)en]NO₃, and *s-cis*-[Co(DMEDDA)(NH₃)₂]NO₃.

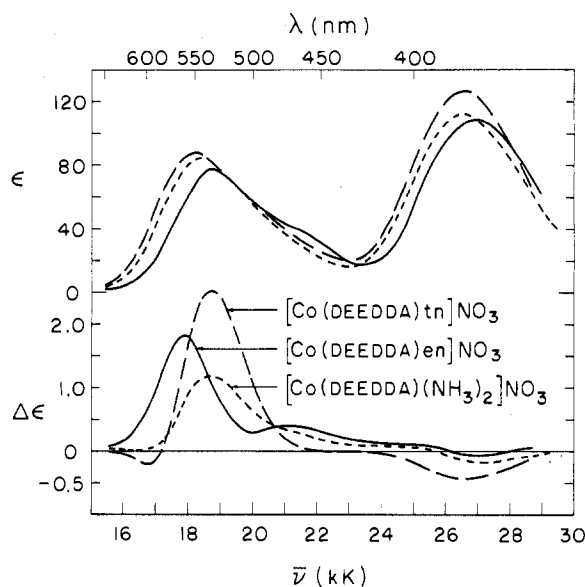


Figure 4. Absorption and circular dichroism spectra of *s-cis*-[Co(DEEDDA)tn]NO₃·2H₂O, *s-cis*-[Co(DEEDDA)en]NO₃, and *s-cis*-[Co(DEEDDA)(NH₃)₂]NO₃.

the splitting is sufficiently large that both E components are observed with three CD peaks in the first absorption band region. Because of the large splitting, the dominant peak occurs at significantly higher energy than the corresponding absorption maximum. The dominant CD peaks in the spectra of the diammine-dialkyl-EDDA complexes also occur at higher energy than the absorption maxima. The lowest energy CD peak disappears completely for the dialkyl-EDDA-en complexes, but the shape of the low-energy tail for the dialkyl-EDDA-(NH₃)₂ complexes suggests the presence of a weak negative component swamped out by the dominant peak. For the dialkyl-EDDA complexes with en, the dominant peaks occur at significantly lower energy than the absorption maxima, and, in the case of the DEEDDA complex, a pronounced minimum is seen on the high-energy side of the dominant peak. This suggests that the components of the E transition change energy order on going from tn and diammine to en. The pertinent variables which might affect the relative energies of the A₂ and B₂ transitions are the field strengths of the diamine ligands and any displacement of the donor atoms from octahedral positions. The latter factor should not apply to unidentate NH₃ ligands.

The smaller differences among the CD spectra of the EDDA

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(18) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc. A*, 1304 (1968).

(19) L. N. Schoenberg, D. W. Cooke, and C. F. Liu, *J. Chem. Soc. A*, 7, 2386 (1968).

(20) The absolute configurations, Δ and Λ , are assigned according to the IUPAC rules as described in *Inorg. Chem.*, **9**, 1 (1970).

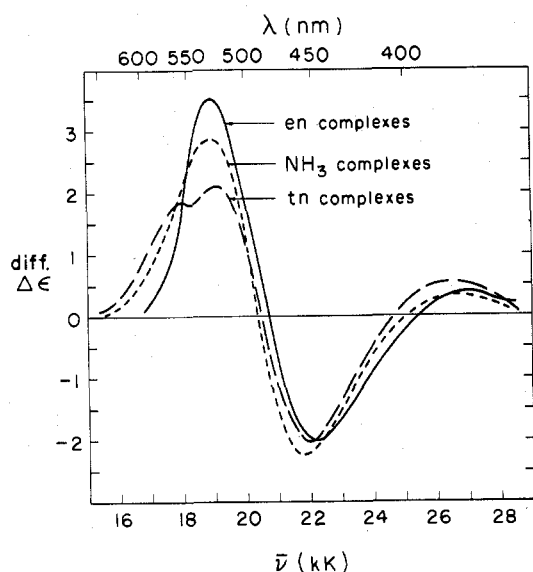


Figure 5. Difference curves, $\Delta\epsilon[\text{Co}(\text{EDDA})\text{L}]^+ - \Delta\epsilon[\text{Co}(\text{DEEDDA})\text{L}]^+$, where L = tn, en, and $(\text{NH}_3)_2$.

complexes with ammonia, en, and tn, in comparison to those of the dialkyl-EDDA complexes, are striking. The variations are greater among the CD spectra of the diethyl- than the dimethyl-EDDA complexes, so perhaps the diminishing differences with increasing vicinal effects is a coincidental result of the way in which the configurational and vicinal contributions to the rotatory strengths add.

The difference CD curves, $\Delta\epsilon[\text{Co}(\text{EDDA})\text{L}] - \Delta\epsilon[\text{Co}(\text{DEEDDA})\text{L}]$, where L = en,¹¹ tn, and diammine, are shown in Figure 5. It is expected that the curves will have the same form since the asymmetric nitrogens are essentially identical in complexes containing the same tetradentate ligand. The difference curves are very nearly identical in the region of the $A_2(D_{4h})$ and $T_{2g}(O_h)$ transitions. In the region of the $E(D_{4h})$ transition the intensities diminish in the order en > diammine > tn with simultaneous curve broadening indicative of increasingly large splittings of the A_2 and B_2 components of the $E(D_{4h})$ transition. The net rotatory strength as measured by the area under a CD curve is about the same in each case.

Tetragonal splitting of the T_{1g} transition is predicted¹² to increase as ligands with a field strength greater than that of the nitrogens of EDDA are substituted at the non-EDDA sites of *s-cis*- $[\text{Co}(\text{EDDA})\text{X}_2]$. The two D_{4h} components of the first absorption band are well-separated in the absorption spectra of $[\text{Co}(\text{EDDA})(\text{NO}_2)_2]^-$ and the dimethyl and diethyl analogs (Figure 6). In these spectra the A_2 transition is observed as a well-defined shoulder at ca. 23 kK on an intense band involving ligand states. The component of E symmetry centered at ca. 19 kK is considerably more intense than the corresponding bands for *s-cis*- $[\text{Co}(\text{EDDA})\text{dicarboxylate}]^-$ or *s-cis*- $[\text{Co}(\text{EDDA})\text{diammine}]^+$ suggesting intensity enhancement due to mixing of ligand and metal electronic states.

The CD spectrum of *s-cis*- $[\text{Co}(\text{EDDA})(\text{NO}_2)_2]^-$ (Figure 6) also exhibits pronounced splitting of the first absorption band. Three CD peaks are observed in this region with the same sign pattern seen in the spectrum of *s-cis*- $[\text{Co}(\text{DMEDDA})\text{tn}]^+$ (Figure 4). The similarity of these curves suggests that the corresponding complexes have the same absolute configuration. The CD curves due to *s-cis*- $[\text{Co}(\text{DMEDDA})(\text{NO}_2)_2]^-$ and *s-cis*- $[\text{Co}(\text{DEEDDA})(\text{NO}_2)_2]^-$ (Figure 6), on the other hand, are quite unlike those of the dicarboxylato and diamine analogs. In spite of the large first-band splitting for the dinitro complexes, only two CD peaks are ob-

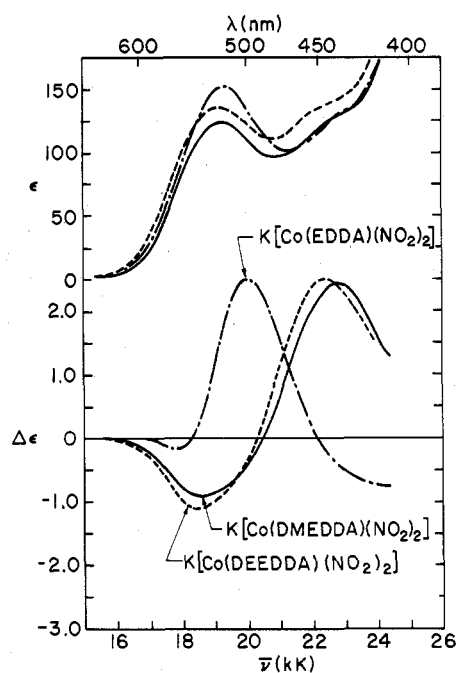


Figure 6. Absorption and circular dichroism spectra of *s-cis*- $[\text{Co}(\text{EDDA})(\text{NO}_2)_2]^-$ and the DMEDDA and DEEDDA analogs.

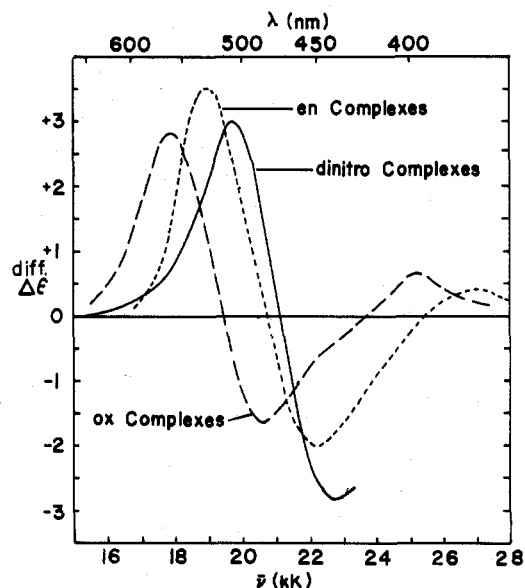


Figure 7. Difference curves, $\Delta\epsilon[\text{Co}(\text{EDDA})\text{L}] - \Delta\epsilon[\text{Co}(\text{DEEDDA})\text{L}]$, for L = oxalate, en, and $(\text{NO}_2)_2$.

served for the dialkyl complexes and the dominant peak, used to assign the configurations of the other *s-cis* EDDA and dialkyl-EDDA complexes, is obscured. We suggest that the Λ configuration can be assigned to the dinitro-dialkyl-EDDA complexes for which the dominant peak at ca. 22.5 kK is positive by comparing the difference curves, $\Delta\epsilon[\text{Co}(\text{EDDA})\text{L}] - \Delta\epsilon[\text{Co}(\text{DEEDDA})\text{L}]$, for the dinitro, ethylenediamine,¹¹ and oxalato¹¹ complexes (Figure 7). Since the configuration about the asymmetric nitrogens is fixed by the arrangement of chelate rings, the complexes with the same absolute configuration give rise to very similar vicinal effect (difference) curves with peaks shifted according to the field strengths of the ligands. It is worth noting that this assignment contradicts that based on the solubility rule.²¹ (+) $[\text{Co}(\text{DEEDDA})$

(21) A. Werner, *Ber.*, 45, 1229 (1912).

$(\text{NO}_2)_2]^-$ and $(-)[\text{Co}(\text{EDDA})(\text{NO}_2)_2]^-$ assigned Λ and Δ , respectively, based on above arguments, both form the less soluble diastereomer with $(-)_D[\text{Co}(\text{en})_2\text{ox}]^+$.

The interpretation of CD spectra of Co(III) chelates is usually complicated by difficulty in identifying the CD peaks and in tracing these peaks through a series of related complexes with different crystal fields. Because of the large vicinal effect associated with *s-cis* EDDA complexes and the fixed chelate ring configurational and conformational contributions of EDDA, these complexes are well suited for the study of

structural origins of optical activity in metal complexes.

Registry No. $(+)[\text{Co}(\text{EDDA})(\text{NH}_3)_2]\text{NO}_3$, 37480-72-1; $(-)[\text{Co}(\text{EDDA})(\text{NH}_3)_2]\text{NO}_3$, 37480-73-2; $(\pm)[\text{Co}(\text{DMEDDA})(\text{NH}_3)_2]\text{NO}_3$, 37480-80-1; *s-cis*- $[\text{Co}(\text{DEEDDA})(\text{NH}_3)_2]\text{NO}_3$, 37480-81-2; $(+)[\text{Co}(\text{EDDA})\text{tn}]\text{NO}_3$, 37480-82-3; $(-)[\text{Co}(\text{EDDA})\text{tn}]\text{NO}_3$, 37480-83-4; $[\text{Co}(\text{C}_{11}\text{H}_{24}\text{N}_4\text{O}_4)]\text{NO}_3$, 37480-84-5; $[\text{Co}(\text{C}_{13}\text{H}_{28}\text{N}_4\text{O}_4)]\text{NO}_3 \cdot 2\text{H}_2\text{O}$, 37475-79-9; $\text{K}[\text{Co}(\text{C}_6\text{H}_{10}\text{N}_4\text{O}_8)]$, 37480-85-6; $(+)\text{K}[\text{Co}(\text{DEEDDA})(\text{NO}_2)_2]$, 37480-86-7; $\text{K}[\text{Co}(\text{C}_8\text{H}_{14}\text{N}_4\text{O}_8)]$, 37480-87-8.

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Four-, Five-, and Six-Coordinate Complexes of Nickel(II) with the Macrocyclic Ligand 2,4,4-Trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene

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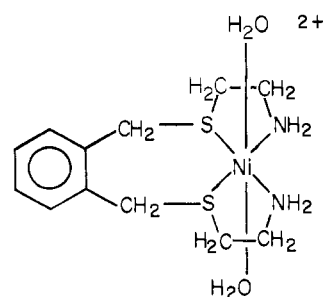
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The reaction of the nickel(II) complex of 1,10-diamino-3,8-dithia-5,6-benzodecene with acetone in methanol solution results in the formation of the nickel(II) complex of the new macrocyclic ligand 2,4,4-trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene. The perchlorate, thiocyanate, chloride, bromide, and iodide derivatives of this new complex ion have been prepared and characterized. In the solid state and in aqueous or methanol solutions the perchlorate derivative possesses a low-spin, square-planar structure as deduced from spectral and magnetic measurements. The solid thiocyanate derivative exhibits properties characteristic of a high-spin, six-coordinate nickel(II) complex. In the solid state and in methanol solution the halide derivatives are shown to be examples of high-spin, five-coordinate nickel(II) complexes by conductance, spectral, and magnetic measurements. In aqueous solutions, the halide derivatives dissociate to yield a low-spin, square-planar complex ion.

Introduction

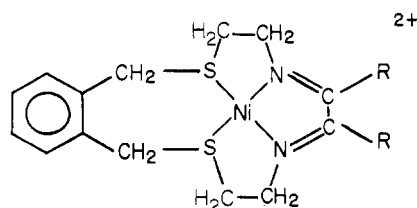
A variety of synthetic routes have been developed leading to the preparation of metal complexes containing macrocyclic ligands.¹ A particularly novel reaction which results in macrocyclic ligand formation has been reported by Curtis.² In this reaction two molecules of acetone condense with two coordinated primary amine functions to yield a six-membered chelate ring. Curtis has applied this reaction to a variety of metal complexes containing aliphatic diamine and tetramine ligands to produce an extensive series of macrocyclic complexes.³ In this laboratory similar amine condensation reactions have been found^{4,5} and the properties of metal complexes arising from these reactions have been extensively studied.⁶ In all cases so far reported, the macrocyclic complexes obtained by these condensation reactions have contained only nitrogen donor atoms.

In order to extend this series of macrocyclic complexes to ligands containing donor atoms other than nitrogen, we have employed the Curtis reaction with a previously known nickel(II) complex (1) of a linear tetradentate ligand con-



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taining as donor atoms two thioether groups and two terminal primary amine functions.⁷ Macrocyclic complexes, 2, containing both imine and thioether donors have been



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prepared previously⁷ via reaction of two coordinated mercaptide groups with a difunctional alkylating agent.

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