Contribution from the Departments of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213, and The Pennsylvania State University, McKeesport, Pennsylvania 15132

Asymmetric Nitrogen Donors. A Critical Factor in Determining Rotational Strengths in Ethylenediaminepolyacetate–Cobalt(III) Complexes

CAROLYN W. MARICONDI* and CHRIS MARICONDI

Received December 16, 1972

The Co(III) complex with ethylenediamine and *N,N'*-dibenzylethylenediamine-*N,N'*-diacetate (DBEDDA) coordinated in the *s* geometry has been prepared and resolved. Its circular dichroism (CD) spectrum is compared with the CD spectrum of the corresponding complexes with ethylenediamine-*N,N'*-diacetate (EDDA) and the *N,N'*-dimethyl derivative (DMEDDA) which have been reported previously. This comparison indicates that the asymmetric nitrogen donor atoms make opposite contributions to the rotatory strength of the complexes when R = H as compared with R = benzyl. The Co(III) complexes with a nitro group and either ethylenediamine-*N,N',N'*-triacetate (ED3A) or its *N*-benzyl derivative (BED3A) have also been resolved. The isomers of $[Co(ED3A)NO_2]^-$ and $[Co(BED3A)NO_2]^-$ with comparable structures give CD curves which have opposite signs over most of the region of the octahedral $A_{1g} \rightarrow T_{1g}$ cobalt(III) absorption. The CD of these complexes is discussed in terms of recent theoretical studies.

Introduction

Circular dichroism (CD) curves of cobalt(III) complexes containing pentadentate N-substituted ethylenediamine-*N,N',N'*-triacetate ligands and a nitro group in the sixth coordination position have been shown[1] to vary significantly as the N substituent is changed (Figure 1). Recent CD studies of ethylenediamine-*N,N'*-diacetate (EDDA) complexes[2] indicate that the substituents on the asymmetric nitrogen donor atoms of coordinated EDDA greatly influence the rotatory strength of the d–d transitions of these complexes. The contribution to the rotatory strength from the asymmetric nitrogen atoms in unsubstituted EDDA was found to be much greater than the contribution from the donor nitrogens in *N*-alkyl-substituted EDDA's. In light of these findings, it was evident that the changes observed in the CD spectra of the ethylenediaminetriacetate complexes were probably due to variations in the asymmetric nitrogen donor atom. An important complex for checking this assumption is one containing unsubstituted ethylenediaminetriacetate (ED3A) prepared previously by Legg, *et al.*[3] The present work reports the resolution and CD of $[Co(ED3A)NO_2]^-$ and of related complexes with *N*-benzyl-substituted ligands.

Experimental Section

Preparation of Ethylenediamine-*N,N',N'*-triacetic Acid (ED3A) and Its Cobalt(III)–Aquo and –Nitro Complexes. The preparations of this ligand and its complexes are very similar to those reported previously by Legg, *et al.*[3] A solution of 65 mmol (11.4 g) of *N,N'*-ethylenediaminediacetic acid, 195 mmol (7.80 g) of NaOH, and 70 mmol (8.2 g) of sodium chloroacetate (Eastman, practical) in 180 ml of water was stirred at 40–45° for 45 min. The solution was then acidified to pH 6, and 65 mmol (18.9 g) of cobaltous nitrate hexahydrate, 5 ml of 30% H_2O_2, and 3 g of activated charcoal were added. Air was bubbled through the mixture for 2 days. The charcoal was then removed and the deep purple-red filtrate diluted to 1 l. This solution was passed through cation- and anion-exchange columns as described by Legg, *et al.*[3] The resulting solution was evaporated to a small volume and white inorganic salts were removed. The filtrate which contained $[Co(ED3A)(H_2O)]$ was used directly to prepare the nitro complex. The solution was cooled in ice and a solution of 70 mmol (5 g) of sodium nitrite in 125 ml of water was added. Ten milliliters of glacial acetic acid was also added and the solution was left in ice overnight. Potassium nitro(ethylenediaminetriacetato)cobaltate(III) monohydrate was isolated by the method of Legg, *et al.*[3] The silver salt of the complex was prepared by mixing solutions containing equimolar amounts of the potassium salt and of $AgNO_3$.

Resolution of Silver Nitro(ethylenediaminetriacetato)cobaltate(III), $Ag[Co(ED3A)NO_2]$. To 25 ml of warm water was added 5 mmol each of $Ag[Co(ED3A)NO_2]$ (assumed formula) (2.22 g) and $(+)_{546}$-$[Co(en)_2ox]Br \cdot H_2O$[4] (1.82 g). The mixture was stirred for 10 min; then the AgBr was removed and washed with 15 ml of warm water. The combined filtrate and wash was cooled and 2.6 g of red solid was removed ($\Delta\epsilon_{520} = 2.3$–$2.4$ assuming a 1:1 diastereoisomer, mol wt 603). This substance was a salt containing the resolving agent and both isomers of the nitro complex. The two diastereoisomers were separated by stirring this material with 10 ml of hot water for 5–10 min and filtering off the undissolved material (the less soluble diastereoisomer). The more soluble diastereoisomer quickly separated from the filtrate. This procedure was repeated, if necessary, until the less soluble diastereoisomer gave $\Delta\epsilon_{595} = -0.58$ and $\Delta\epsilon_{510} = +2.4$ and the more soluble diastereoisomer gave $\Delta\epsilon_{530} = +2.5$ and $\Delta\epsilon_{460} = -0.7$. The yield of each diastereoisomer was about 0.5–0.8 g.

The sodium salts of the optical isomers of the nitro complex were obtained by treating each diastereoisomer separately as follows. The diastereoisomer was dissolved in about 5 ml of warm water and stirred several minutes with 4 g of Dowex 50W-X8 cation-exchange resin in the Na^+ form. The resin was removed and washed with 2 ml of water. The filtrate was treated with another 2 g of resin. After this resin had been removed, 40 ml of absolute ethanol was added to the filtrate which was cooled in ice. About 0.4 g of each isomer was obtained. The less soluble diastereoisomer with $(+)_{546}$-$[Co(en)_2ox]Br$ gave Na-$(+)_{589}$-$[Co(ED3A)NO_2] \cdot H_2O$ with $\Delta\epsilon_{582} = -0.72$ and $\Delta\epsilon_{475} = +1.22$, $[\alpha]_{589}$ +290° (0.07 g/100 ml of water). *Anal.* Calcd for $Na[Co(ED3A)NO_2] \cdot H_2O$: C, 25.4; H, 3.45; N, 11.1 Found: C, 25.68; H, 3.48; N, 10.74.

Preparation and Resolution of Sodium Nitro(*N*-benzylethylenediaminetriacetato)cobaltate(III) Dihydrate, $Na[Co(BED3A)NO_2] \cdot 2H_2O$. The ligand *N*-benzylethylenediaminetriacetic acid has been prepared previously by a lengthy procedure.[5] The method used here is that of Dwyer and Garvan[6] for the preparation of 1,2-propylenediaminetetraacetic acid. A solution of 0.3 mol (12 g) of NaOH in 100 ml of water was cooled and then mixed with a solution of 0.3 mol (36 g) of sodium chloroacetate in 100 ml of water. One-tenth mole (15 g) of *N*-benzylethylenediamine (Eastman) was added and the resulting solution was stirred for 0.5 hr. During this time slight spontaneous warming of the solution was observed. After standing at room temperature overnight, the reaction mixture was diluted to 500 ml and 0.1 mol (40 g) of sodium cobaltinitrite was added with stirring. The mixture was heated at 50° for 0.5 hr and then at 85° for 10 min. After the solution had cooled in ice, about 400 ml of ethanol was added. After 0.5 hr 20 g of brick red $Na[Co(BED3A)NO_2] \cdot 2H_2O$ was removed and recrystallized from hot water by cooling in ice. The silver salt was prepared by dissolving the sodium salt in a mini-

---

* Address correspondence ot this author at the University of Pittsburgh.

(1) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, 7, 1393 (1968).

(2) C. W. Maricondi and B. E. Douglas, *Inorg. Chem.*, 11, 688 (1972).

(3) G. L. Blackmer, R. E. Hamm, and J. I. Legg, *J. Amer. Chem. Soc.*, 91, 6632 (1969).

(4) F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Amer. Chem. Soc.*, 83, 1285, (1961).

(5) A. J. Bruno, S. Chaberek, and A. E. Martell, *J. Amer. Chem. Soc.*, 78, 2723 (1956).

(6) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 81, 2955 (1959).

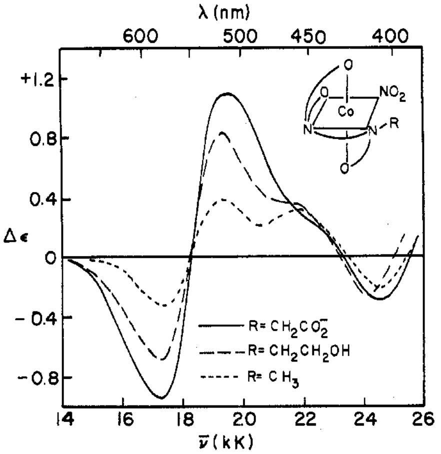


Figure 1. Circular dichroism spectra and absolute configuration of the $(+)_{546}$ isomers of $[Co(EDTA)NO_2]^{2-}$ ($R = CH_2CO_2^-$), $[Co(YOH)NO_2]^-$ ($R = CH_2CH_2OH$), and $[Co(MED3A)NO_2]^-$ ($R = CH_3$).

mum amount of boiling water and adding a solution containing an equimolar amount of $AgNO_3$.

For the resolution 10 mmol (5.36 g) of $Ag[Co(BED3A)NO_2]$ (assumed formula) and 10 mmol (3.64 g) of $(-)_{546}$-$[Co(en)_2ox]Br\cdot H_2O$[4] were stirred for several minutes in 35 ml of warm water. The AgBr was removed and washed with a few milliliters of water. The filtrate was evaporated under a stream of air at room temperature until solid started to separate and was then cooled in ice for several hours. This procedure was repeated until nine fractions had been collected. Fractions 1, 4, 5, and 7 (total 1.7 g) had $\Delta\epsilon_{520} = -3.2$ (assuming a 1:1 diastereoisomer, mol wt 710) and were recrystallized to give $\Delta\epsilon_{520} = -3.3$. Fraction 2 (1.86 g) gave $\Delta\epsilon_{520} = -1.8$ recrystallized to $\Delta\epsilon_{520} = -1.7$. The other fractions had $\Delta\epsilon_{520} \simeq -2.0$ and were combined and recrystallized from water to give more material with $\Delta\epsilon_{520} = -3.3$ or -1.7. The two diastereoisomers were treated with cation-exchange resin as described above for $[Co(ED3A)NO_2]^-$. The diastereoisomer with $\Delta\epsilon_{520} = -3.3$ gave Na-$(-)_{589}$-$[Co(BED3A)NO_2]\cdot 2H_2O$ with $\Delta\epsilon_{580} = +0.66$, $\Delta\epsilon_{515} = -1.1$, and $[\alpha]_{589}$ −120° (0.06 g/100 ml of water). *Anal.* Calcd for $Na[Co(BED3A)NO_2]\cdot 2H_2O$: C, 37.2; H, 4.33; N, 8.76. Found: C, 37.2; H, 3.79; N, 8.56.

Preparation of ***N,N'*****-Dibenzylethylenediaminediacetic Acid (DBEDDA).** The preparation of this ligand reported before[7] is similar to that given here but the previous yield was much lower. Two-tenths mole (48 g) of *N,N'*-dibenzylethylenediamine (Aldrich) was dissolved in 300 ml of 95% ethanol. To this solution were added solutions of 0.6 mol (70 g) of sodium chloroacetate in 150 ml of water and 0.4 mol (16 g) of NaOH in 100 ml of water. More ethanol was added, if needed, to give a clear solution. The solution was stirred then left standing at room temperature for 5 days.

Four hundred milliliters of benzene (to remove unreacted amine) and 600 ml of water were added and the mixture was stirred thoroughly. The aqueous layer was separated and retained. The benzene layer was discarded. Six grams of activated charcoal was added to the aqueous layer which was then stirred for several minutes and filtered. The *N,N'*-dibenzylethylenediaminediacetic acid separated from the aqueous filtrate when it was acidified to pH 4 with concentrated HCl; yield 53.5 g (75%).

Preparation and Resolution of ***s-N,N'*****-Dibenzylethylenediamine-*****N,N'*****-diacetato(ethylenediamine)cobalt(III) Chloride Tetrahydrate,** ***s*****-[Co(DBEDDA)en]Cl·4H₂O.** *N,N'*-Dibenzylethylenediaminediacetic acid (7.2 g, 20 mmol) was dissolved in 50 ml of aqueous NaOH (about 0.2 g). The pH of the resulting solution was adjusted to 6.5 with dilute HCl. A solution of 20 mmol (4.8 g) of $CoCl_2\cdot 6H_2O$ in 50 ml of water was added with stirring, and [Co(DBEDDA)] separated at once and was removed. This Co(II) complex was dissolved in 300 ml of hot methanol and 2 g of activated charcoal was added. Ethylenediamine (1.2 g, 20 mmol) was dissolved in 10–15 ml of methanol and 16.7 ml of 1.2 *N* HCl was added. The resulting solution was added to the [Co(DBEDDA)] mixture. The mixture was kept at 40–60° for 8 hr while air was bubbled through it. The charcoal was then removed and the filtrate was evaporated to dryness. The pink-red solid was recrystallized from a minimum amount of hot water to yield 8 g of *s*-$[Co(DBEDDA)en]Cl\cdot 4H_2O$. The proton magnetic resonance spectrum showed only one AB pattern due to protons on the acetate rings.

Resolution. Hot slurries of Ag-$(-)_{546}$-$[Co(EDTA)]$[2] (4.55 g, 10 mmol) in 25 ml of water and $[Co(DBEDDA)en]Cl\cdot 4H_2O$ (5.8 g, 10 mmol) were combined and the resulting mixture was stirred for several minutes. The AgCl was removed and the filtrate was evaporated to 25–30 ml. An equal volume of 95% EtOH was added and the solution was left at room temperature overnight. About 3 g of solid was removed, $\Delta\epsilon_{595} = +0.7$ (assuming a 1:1 diastereoisomer, mol wt 820). The filtrate was saved for recovery of the other isomer. This solid was redissolved and the $(-)_{546}$-$[Co(EDTA)]^-$ was removed by treatment of the solution with Dowex 1-X8 anion-exchange resin in the Cl^- form. The resin was removed and the filtrate was evaporated to dryness. The resulting red crystals were recrystallized from warm water by cooling in ice, $\Delta\epsilon_{556} = -1.7$. The other isomer was obtained in a similar fashion from the filtrate which had been saved after removal of the less soluble diastereoisomer. About 1.5–1.8 g of each isomer was obtained. The less soluble diastereoisomer with $(-)_{546}$-$[Co(EDTA)]^-$ gave $(+)_{546}$-$[Co(DBEDDA)en]Cl\cdot 4H_2O$ with $\Delta\epsilon_{556} = -1.7$ and $[\alpha]_{546}$ +260° (0.13 g/100 ml of water). *Anal.* Calcd for $[Co(DBEDDA)en]Cl\cdot 4H_2O$: C, 45.4; H, 6.55; N, 9.64; Cl, 6.1. Found: C, 45.31; H, 6.61; N, 9.67; Cl, 6.05.

Spectra. Absorption spectra were obtained using a Cary 14 recording spectrophotometer with a tungsten lamp. CD spectra were recorded on a Roussel-Jouan Dichrograph with a tungsten source.

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

Results

The circular dichroism (CD) and absorption spectra of *s*-$[Co(DBEDDA)en]^+$ are shown in Figure 2. The CD curves of the corresponding complexes of EDDA (R = H)[8] and DMEDDA ($R = CH_3$)[2] are included for comparison. The three curves are for the isomers with the structure sketched in Figure 2. Assignment of *s* geometry[9] to the EDDA portion of the complexes,[10] assignment of the CD bands in terms of tetragonal symmetry,[8] and assignment of the indicated absolute configuration[11] have all been discussed previously.

The circular dichroism and absorption spectra of $[Co(ED3A)NO_2]^-$ (R = H) and $[Co(BED3A)NO_2]^-$ ($R = CH_2C_6H_5$) are shown in Figure 3. The CD curve of the corresponding complex with MED3A ($R = CH_3$[1]) is included for comparison. The three curves are for isomers with the structure sketched in Figure 3. These structures were established by preparation of the nitro complexes with the pentadentate ligands, (*R*)-(−)-PD3A and (*R*)-(−)-PDTA containing (*R*)-(−)-propylenediamine, N substituted with three and four acetate groups, respectively. These ligands were prepared from (*R*)-(−)-propylenediamine and sodium chloroacetate by the methods used before for the preparation of 1,2-propylenediaminetetraacetic acid[6] and of ED3A.[3] They react stereospecifically[12] with cobalt to give complexes with the structure shown in Figure 3. Spectral data for the one isomer of the nitro complex obtained with (*R*)-(−)-propylenediaminetriacetate[13] are given in Table I along with data for Na-$(-)_{546}$-$[Co(ED3A)NO_2]$ (R = H, Figure 3). Similarity of the data indicates that both isomers have the same structure. Dwyer and Garvan's work[12] with the nitro complex with (*R*)-(−)-propylenediaminetetraacetate (pentadentate) indicates that $(+)_{546}$-$[Co(EDTA)NO_2]^-$ ($R = CH_2CO_2^-$, Figure 1) has the structure shown in Figure 3. Since the CD curves of the complexes with $R = CH_2CO_2^-$, CH_3, or $CH_2C_6H_5$ are so similar in general shape and sign pattern, it is safe to assume that the $(+)_{546}$ isomers of the methyl and benzyl complexes, for

---

[7] A. E. Frost, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, 72, 3743 (1950).

[8] J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, 6, 700 (1967).

[9] J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 8, 1563 (1969).

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

[11] L. N. Schoenberg, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, 7, 2386 (1968).

[12] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 83, 2610 (1961).

[13] C. Maricondi and C. W. Maricondi, unpublished results.

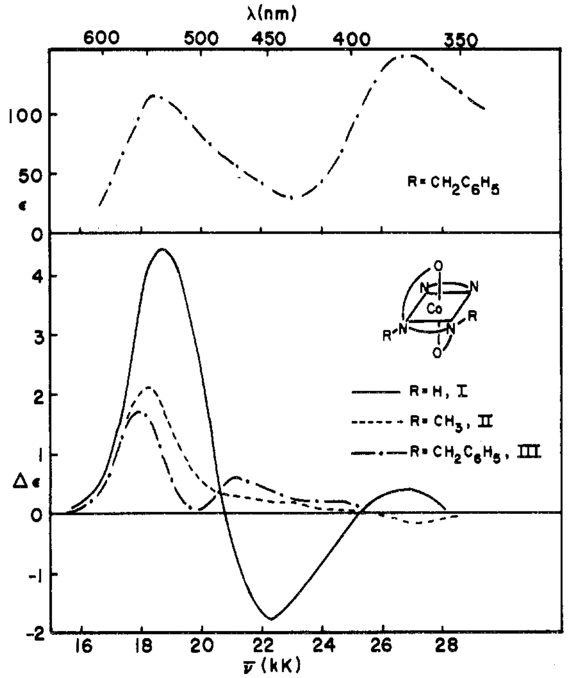


Figure 2. Circular dichroism and absorption spectra of $[Co(DBEDDA)en]^+$ (III); circular dichroism spectra of $[Co(EDDA)en]^+$ (I) and $[Co(DMEDDA)en]^+$ (II). The CD curves are for isomers with the absolute configuration shown.

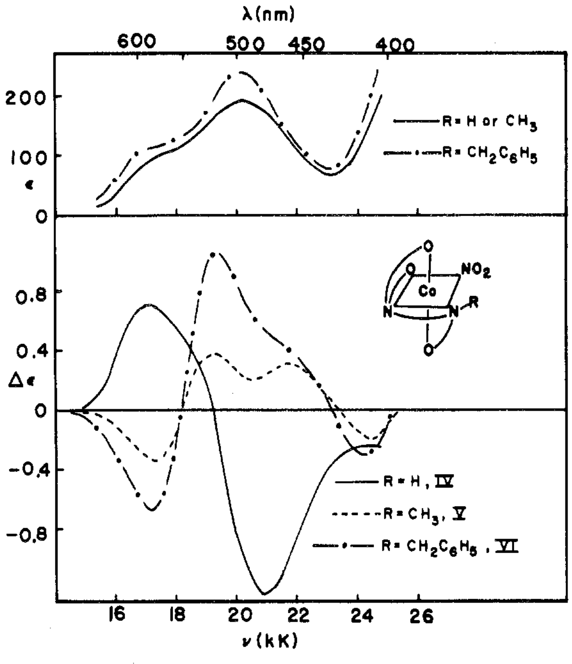


Figure 3. Absorption and circular dichroism spectra and absolute configuration of the $(-)_{546}$ isomer of $[Co(ED3A)NO_2]^-$ (IV) and the $(+)_{546}$ isomers of $[Co(BED3A)NO_2]^-$ (VI) and $[Co(MED3A)NO_2]^-$ (V).

Table I. Absorption and CD Data for Cobalt(III) Pentadentate Complexes

	$(-)_{546}$-[Co((R)-(−)-PD3A)$NO_2]^-$		$(-)_{546}$-$[Co(ED3A)NO_2]^-$	
Complex	λ_{max}, nm	$\Delta\epsilon$	λ_{max}, nm	$\Delta\epsilon$
Circular dichroism	587	+0.77	582	+0.72
	472	−1.04	475	−1.21
Absorption	493	ϵ 191	490	ϵ 193

which CD curves are shown in Figure 3, also have the structure shown (Figure 3).

Discussion

For each of the EDDA complexes (Figure 2) the lowest energy CD band is positive and dominates the spectrum. The net rotational strength for each curve is also positive. This net rotational strength is of about the same magnitude as that observed for C_2 *cis(N)*-$[Co(en)(gly)_2]I$,[14] in which the only source of asymmetry is the configuration of chelate rings. Recent theoretical work by Richardson[15] relates stereochemical features of the ligand environment to the *net* d–d rotatory strength. If his rules are used to find the contribution to the optical activity from the chelate rings only, for the isomer shown in Figure 2, a net positive rotatory strength would be predicted. This result is also compatible with older methods for correlating CD spectra and structure which predict that a Λ (C_3) isomer should have a dominant positive CD band.[16]

The CD spectra for the pentadentate ED3A complexes (Figures 1 and 3) are of interest because the general methods for determining the net helicity due to a given arrangement of chelate rings predict no net helicity for the arrangement of rings present in these complexes (*i.e.*, they contain one Λ and one Δ pair).[17] Similarly, if Richardson's method[18] for determining the sign of the net d–d rotatory strength is applied to these complexes and only the contribution from chelate rings is considered, no net rotatory strength is predicted. In accord with these predictions the *net* rotatory strength (sum of area under CD curve with sign included) in the region of the first absorption band (Figure 3) is small, especially when compared with the net rotatory strength of the EDDA complexes (Figure 2) which have a helicity due to the arrangement of chelate rings. Since the rotatory strength of the ED3A complexes is mainly determined by the nature of the asymmetric donor nitrogen, the differences between the curves for various R groups are particularly striking for this series. For isomers with the structure shown in Figure 3, the net rotatory strength is positive for all the compounds of the series except the one with R = H, for which the net rotatory strength is negative.

The similarity between the CD curves of DMEDDA complexes and similar complexes where the only source of asymmetry is the configuration of chelate rings[2,14,18] indicates that the asymmetric nitrogen donor atoms in coordinated DMEDDA make an insignificant contribution to the rotatory strength of the d–d transitions. An approximation of the contribution of the asymmetric nitrogens to the CD of the EDDA and DBEDDA complexes can thus be obtained by subtracting the curve of the DMEDDA complex from each. The resulting difference curves are shown in Figure 4. For both complexes the first band dominates the difference curve, but it is positive for the unsubstituted EDDA (R = H) and negative for the dibenzyl complex. The intensity of the individual bands is much larger for the EDDA complex than the DBEDDA, but the net rotatory strength is small in both cases.

As with EDDA series, an approximation of the vicinal effect in the ED3A and BED3A complexes can be obtained by subtracting the curve of the MED3A complexes from each. These difference curves are shown in Figure 5. Comparison of the difference curves in Figures 4 and 5 shows that they are

---

(14) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, **45**, 2491 (1972).

(15) F. S. Richardson, *Inorg. Chem.*, **11**, 2366 (1972).

(16) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, p 210 ff.

(17) J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2696 (1966); C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 1969 (1965); IUPAC rules, *Inorg. Chem.*, **9**, 1 (1970).

(18) N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **9**, 719 (1970).

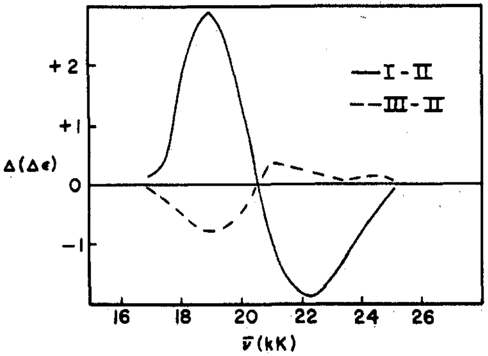


Figure 4. Difference curves: Δε[Co(EDDA)en]$^+$ − Δε[Co(DMEDDA)en]$^+$ (I − II) and Δε[Co(DBEDDA)en]$^+$ − Δε[Co(DMEDDA)en]$^+$ (III − II).

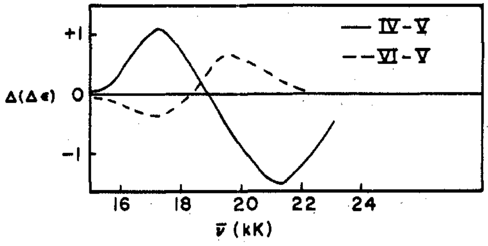


Figure 5. Difference curves: Δε[Co(ED3A)NO$_2$]$^-$ − Δε[Co(MED3A)NO$_2$]$^-$ (IV − V) and Δε[Co(BED3A)NO$_2$]$^-$ − Δε[Co(MED3A)NO$_2$]$^-$ (VI − V).

of the same general shape and sign pattern for complexes with the same R groups. The intensity of the vicinal effect in the EDDA complexes is greater since they contain two asymmetric nitrogens with the same absolute configuration as opposed to only one in the ED3A complexes. Also, for the ED3A complexes the net rotatory strength in the region of the low-energy absorption band is determined by the second or third CD band rather than the first. As with the EDDA complexes the net CD for the hydrogen and benzyl complexes are opposite, but for the ED3A series the complex with R = H gives a negative net rotatory strength whereas that for the benzyl complex is positive. For the corresponding EDDA compounds, the net CD for R = H is positive and that for the benzyl compound is negative. Obvious differences between the EDDA- and ED3A-type complexes which might be responsible for this switch are their different chromophoric symmetries and the presence of the nitro group in the ED3A-type complexes. It is also possible this apparent change in the sign of the net rotatory strength due to the asymmetric nitrogens is an artifact resulting from the crudity of the assumption that these difference curves accurately represent the vicinal effect in these compounds.

The vicinal effect of the EDDA-type complexes can be discussed in terms of a regional rule proposed by Mason[19] for cobalt(III) complexes containing a tetragonal chromophore; he proposed a hexadecadal regional rule for *trans*-bis(diamine)cobalt(III) complexes. If his rule is applied to *s*-[Co(DBEDDA)en]$^+$, the terminal R groups and the chain alkyl groups of the diamine backbone of the EDDA give rise to dissymmetric potentials of opposite sign. If it is assumed (as Mason does) that the R group is the major factor in determining the sign of the rotatory strength, then the isomer shown in Figure 2 should cause the $A_{1g} \rightarrow A_{2g}$ (D_{4h}) component of the octahedral $A_{1g} \rightarrow T_{1g}$ cobalt(III) transition to be positive. The $A_{1g} \rightarrow A_{2g}$ transition is the high-energy component of the $A_{1g} \rightarrow T_{1g}$ transition for *trans*-[CoN$_4$O$_2$] complexes,[20] so this prediction is correct for *s*-[Co(DBEDDA)en]$^+$. When R = H, however, the $A_{1g} \rightarrow A_{2g}$ transition has a negative rotational strength. The change in sign could be explained either by assuming that the chain alkyl groups are now the dominant factor or by assuming that the potential due to the amine hydrogen is opposite to that of the other R groups and thus of the same sign as that due to the backbone atoms. Since the complex with R = H has very intense CD bands, the latter assumption seems the more reasonable. This ambiguity in application of the rule indicates that regional rules derived for a certain type of substituent must be applied with caution to complexes containing substituents which are significantly different. This difficulty with the use of regional rules has been pointed out by Richardson,[15] who warned that use of sector rules requires assumptions about the relative electrostatic and electrodynamic properties of the perturbers.

In a recent paper on regional rules Bosnich and Harrowfield[21] specifically mentioned the uncertainty concerning the sign of the potential of hydrogen atoms bonded to donor nitrogens. They indicated that the acidity of the hydrogen atoms in many complexes implies a polar N-H bond and highly deshielded H nucleus which may have a net attractive effect on the d electrons. They assumed that other common ligand substituents give a repulsive interaction. Thus they theorize that regional rules based on repulsive potentials would predict rotatory strengths of opposite signs depending upon whether an amine hydrogen atom or another R group occupied a given position.

Examination of Fisher-Hirschfelder-Taylor models of the ED3A-type complexes shows two structural factors which might influence the shapes of the CD curves of these compounds. First, when R = CH_2CH_2OH, $CH_2CO_2^-$, or $CH_2C_6H_5$, the second carbon atom of the chain is most likely pointed away from the metal ion and the nitro group to minimize crowding. Thus, since the CH_2 group which is common to these R groups is closest to the cobalt(III) and has the same orientation in all three complexes, its position may account for the similarity in the curves for these complexes especially in the region of the third band. Note that when R = H the greatest difference is observed in the region of the third band. The intensities of the first two bands are sensitive to the nature and position of the other atoms in the R chain.

The second structural factor which is noted upon observation of the models is that the CH_2 portion of these R groups interferes with free rotation of the nitro group. In the complex with R = H, rotation of the nitro group is unhindered. It is unlikely, however, that differing orientations of the nitro group are responsible for the switch in the sign of the vicinal effect when R =H is replaced by R = benzyl, since a similar switch is observed in the EDDA series where no nitro groups are present.

The EDDA and ED3A complexes reported here are important to theoretical studies because they show changes in rotatory strength between similar compounds containing asymmetric donor nitrogens with H as a substituent and ones containing asymmetric donor nitrogens with no H substituents. By contrast, previous studies[19,22] of compounds with asymmetric nitrogen donor atoms have compared compounds with an asymmetric donor nitrogen with one H as a substituent with similar compounds with *symmetric* donor nitrogens, usually with two H substituents. Thus the compounds reported

---

(19) S. F. Mason, *J. Chem. Soc. A*, 667 (1971).

(20) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 106 ff.

(21) B. Bosnich and J. Harrowfield, *J. Amer. Chem. Soc.*, 94, 3425 (1972).

(22) See ref 16, pp 196–209.

here give clear evidence for a change in sign of CD bands due to replacement of H by another substituent on an asymmetric nitrogen donor atom. Also although the asymmetric donor nitrogens make significant contributions to the intensity of individual CD bands, their contribution to the net rotatory strength of the compounds reported is quite small. By contrast, the contribution to the net rotatory strength from the configuration of chelate rings is relatively large.

Registry No. Ethylenediamine-*N,N',N'*-triacetic acid, 688-57-3; potassium nitro(ethylenediaminetriacetato)cobaltate(III), 24651-89-6; silver nitro(ethylenediaminetriacetato)cobaltate(III), 39556-12-2; *N,N'*-dibenzylethylenediaminediacetic acid, 39556-13-3; $(+)_{546}$-[Co(en)$_2$ox]Br$\cdot$H$_2$O, 31126-56-4; Na-$(+)_{589}$-[Co(ED3A)NO$_2$]$\cdot$H$_2$O, 39556-15-5; Na[Co(ED3A)NO$_2$]$\cdot$2H$_2$O, 39556-16-6; Ag[Co(BED3A)NO$_2$], 39556-17-7; Na-$(-)_{589}$-[Co(BED3A)NO$_2$]$\cdot$2H$_2$O, 39561-41-6; *s*-[Co(DBEDDA)en]Cl$\cdot$4H$_2$O, 39556-19-9; CoCl$_2$$\cdot$6H$_2$O, 7791-13-1; $(+)_{546}$-[Co(DBEDDA)en]Cl$\cdot$4H$_2$O, 39556-20-2; Na-$(-)_{546}$-[Co(ED3A)NO$_2$]$^-$, 39561-40-5; Na-$(+)_{546}$-[Co(BED3A)NO$_2$]$^-$, 39556-18-8; $(-)_{546}$-[Co(DBEDDA)en]Cl, 39561-39-2.

Acknowledgments. Financial support for this research was provided by the University Science Development Program (GU3184) to C. W. M. and by The Pennsylvania State University to C. M. The authors thank Miss Judy Ferencz for preparation of optically active starting materials.

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Study of the Reaction of Some Cobalt Nitrosyl Complexes with Oxygen[1]

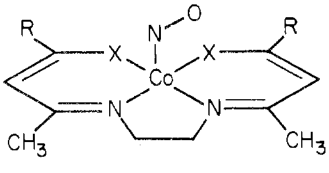
STEVEN G. CLARKSON and FRED BASOLO*

Received January 3, 1973

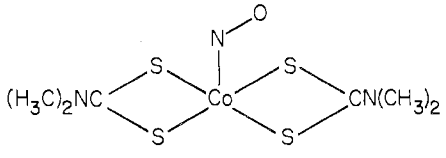
Several cobalt nitrosyl complexes, CoL$_4$NO, reacted with oxygen in the presence of nitrogen and phosphorus bases to yield the corresponding nitro compounds, CoL$_4$(NO$_2$)B, where L$_4$ is the tetradentate dianions *N,N'*-ethylenebis(acetylacetoniminate), *N,N'*-ethylenebis(monothioacetylacetoniminate), *N,N'*-ethylenebis(benzoylacetoniminate), *N,N'*-ethylenebis(salicylideniminate), and two bidentate dimethyldithiocarbamate anions. Exposing an acetonitrile solution of nitrosylbis(ethylenediamine)cobalt diperchlorate to oxygen resulted in the precipitation of [Co(en)$_2$(CH$_3$CN)NO$_2$](ClO$_4$)$_2$. The nitro products, CoL$_4$(NO$_2$)B [where B = pyridine, C$_3$H$_7$NH$_2$, and P(CH$_3$)$_2$(C$_6$H$_5$)] and [Co(en)$_2$(CH$_3$CN)NO$_2$](ClO$_4$)$_2$ were isolated and characterized by elemental analyses and infrared, proton magnetic resonance, and electronic spectra. Kinetic studies revealed that the rates of reaction have a first-order dependence on the concentrations of oxygen and the cobalt nitrosyl complexes. The reaction rates increase with increasing base concentration but reach a limiting rate at high base concentrations. A possible mechanism for the reaction is proposed and discussed.

Introduction

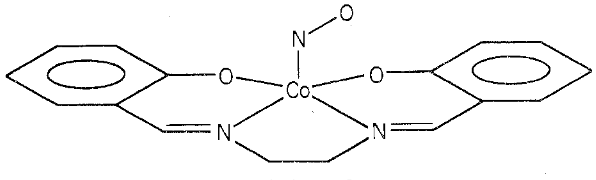
Recently, several authors[2-4] have reported that certain nitrosyl compounds are converted to metal-nitro products in the presence of oxygen. All that was reported was the nature of the products of these reactions. This paper describes in more detail the observations we reported[5] earlier on the reaction of several cobalt nitrosyl complexes with oxygen. The structures and symbols for the complexes are represented as follows.



Co(acacen)NO: R = CH$_3$, X = O
Co(benacen)NO: R = C$_6$H$_5$, X = O
Co(sacsacen)NO: R = CH$_3$, X = S



Co(dtc)$_2$NO



Co(salen)NO

Experimental Section

Solvents. Except for the solvents used in the kinetic studies, the solvents were obtained commercially and used without further purification. Deoxygenated solvents were obtained by bubbling N$_2$ through the solvent for at least 30 min before use. The solvents used in the kinetic studies were ACS reagent grade, and they were distilled prior to use.

Materials. The reagents[6] PPh$_3$, P(C$_6$H$_{11}$)$_3$, P(OPh$_3$)$_3$, 4-NH$_2$py, imidazole, Co(C$_2$H$_3$O$_2$)$_2$$\cdot$4H$_2$O, and Na(dtc) were obtained commercially and used without further purification. The reagents PEt$_3$, PBu$_3$, PEtPh$_2$, PMe$_2$Ph, P(OBu)$_3$, py, 2-Me(py), 3-Me(py), 4-Me(py), 2,4,6-Me$_3$py, C$_3$H$_7$NH$_2$, (*i*-Pr)$_2$NH, Et$_3$N, 1-methylimidazole, and 1,2-dimethylimidazole were obtained commercially and distilled prior to use. The 4-CNpy was obtained commercially and recrystallized from ethanol before use. The nitric oxide (Matheson) was purified by passage through a Dry Ice-acetone bath and a tower of

---

(1) (a) Abstracted from the Ph.D. thesis of S. G. Clarkson, Northwestern University, 1972. (b) Presented in part at the XIVth International Conference on Coordination Chemistry, Toronto, June 1972; see *Proc. Int. Conf. Coord. Chem.*, 14, 193 (1972).

(2) G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 119 (1972).

(3) (a) T. I. Shimyama and T. Matsumura, *Annu. Rep. Radiat. Cent. Osaka Prefect.*, 11, 50 (1970); (b) T. I. Shimyama and T. Matsumura, *Radioisotopes*, 20, 367 (1971).

(4) M. Tamaki, I. Masuda, and K. Shinra, *Bull. Chem. Soc. Jap.*, 45, 171 (1972).

(5) S. G. Clarkson and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 670 (1972).

(6) Symbols used are Ph = C$_6$H$_5$, py = pyridine, Et = C$_2$H$_5$, Bu = *n*-C$_4$H$_9$, Me = CH$_3$, Pr = *n*-C$_3$H$_7$, and *i*-Pr = *i*-C$_3$H$_7$.