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Stereochemistry of Trimethylenediaminetetraacetatocobaltate(III)*1

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Conformation of trimethylenediaminetetraacetatocobaltate(III) (Cotrdta$^-$) was inferred from the measurement of proton nuclear magnetic resonance spectra. It was found that K[Cotrdta]·$2H_2O$ crystals are mixtures consisting of equimolar amounts of the crystals of K[$(+)_{546}$-Cotrdta]·$2H_2O$ and those of K[$(-)_{546}$Cotrdta]·$2H_2O$; that is, so-called "spontaneous resolution" was found. The absolute configuration of optically active Cotrdta$^-$ was determined by the measurements of optical rotatory dispersion (ORD) and circular dichroism (CD) curves and by the reaction with ethylenediamine to form tris(ethylenediamine)cobalt(III) cation.

The cobalt(III) complexes with ethylenediaminetetraacetate(edta), propylenediaminetetraacetate (pdta) and *trans*-1,2-cyclohexanediaminetetraacetate(cydta) have been extensively investigated. In these complexes, the chelate rings around the central cobalt(III) ions are all five-membered.

Recently, the syntheses of cobalt(III)[1] and chromium(III)[2] complexes with trimethylenediaminetetraacetate(trdta)*2 have been reported, and it was verified that a quadrivalent trdta anion in each metal complex is hexadentate.[1,2] In trdta complex, a six-membered chelate ring involving two nitrogen atoms is formed, in contrast with complexes with edta, pdta and cydta.

As trdta complex occupies an important position in a series of complexes of edta and its homologues, the stereochemical investigations on Cotrdta$^-$ are dealt with in this paper.*3

Experimental

H_4 trdta*4 and K[Cotrdta]·$2H_2O$ were prepared in the same way as has been reported.[1]

H[Cotrdta]·$3H_2O$. K[Cotrdta]·$2H_2O$ (4.4 g) dissolved in 20 m*l* of water was passed through Dowex 50 W X-8 cation exchange resins in hydrogen form. The equivolume of ethanol was then added to the solution. After the solution had been cooled to 0°C, the reddish violet crystals separated were collected and washed with ethanol and ether. The compound was recrystallized from water by the addition of ethanol.

Ag[Cotrdta]·H_2O. To a solution of 2 g of silver nitrate dissolved in 50 m*l* of water was added 1 g of sodium hydroxide dissolved in 50 m*l* of water. Silver oxide thus obtained was washed several times by decantation. After the total volume of the solution was adjusted to be 50 m*l* with water, 4.5 g of H[Cotrdta]·$3H_2O$ was added to the solution. The solution was stirred at 60°C for 20 min and filtered. To the filtrate, 200 m*l* of ethanol was added. The compound deposited was collected and washed with ethanol and ether and then air-dried. The crystals were recrystallized from water by the addition of ethanol.

Ba[Cotrdta]$_2$·$8H_2O$. To 4.2 g of H[Cotrdta]·$3H_2O$ dissolved in 40 m*l* of water 1.6 g of barium hydroxide was added. The solution was stirred at 65°C for 20 min and filtered. To the filtrate was added 40 m*l* of ethanol. The compound deposited was washed and recrystallized in the same way as Ag[Cotrdta]·H_2O.

Resolution of Cotrdta$^-$. The resolution of Cotrdta$^-$ was carried out by a similar method to that for Copdta$^-$ and Cocydta$^-$.[4,5]

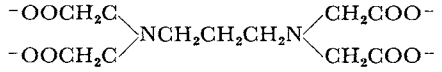
[*d*-Co(NO_2)$_2$en$_2$][$(-)_{546}$Cotrdta]·$3H_2O$.*5 Resolving agent, *cis*-[*d*-Co(NO_2)$_2$en$_2$]Br (en denotes ethylenediamine) was prepared according to the direction by Dwyer and Garvan.[6] *cis*-[*d*-Co(NO_2)$_2$en$_2$]Br (21.1 g)

*1 Presented at the 18th Symposium on Coordination Chemistry, Kyoto, Oct., 1968.

1) N. Tanaka and H. Ogino, This Bulletin, **37**, 877 (1964).

2) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

*2 trdta denotes



*3 After the completion of this work, a study on the circular dichroism of cobalt(III) trdta complex was *reported by Van Saun and Douglas.*[3]

3) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969).

*4 H_4 trdta was prepared by heating the solution of the mixture of monochloroacetic acid, potassium hydroxide and trimethylenediamine and following acidification of the condensation mixture.[1] In the previous paper,[1] 16.5 g of potassium hydroxide dissolved in 30 m*l* of water should read 33 g of potassium hydroxide dissolved in 60 m*l* of water.

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

5) F. P. Dwyer and F. L. Garvan, *ibid.*, **83**, 2610 (1961).

*5 In this paper, the rotation of *d*- and *l*- refers to the sign of the optical rotation at sodium D line.

6) *F. P. Dwyer and F. L. Garvan, "Inorganic Syntheses,"* Vol. 6, p. 195 (1960).

was suspended in 800 m*l* of water at 60°C. To this suspension, 29.2 g of Ag[Cotrdta]·H_2O dissolved in 200 m*l* of water at 60°C was added and shaken vigorously for 10 min.*6 After filtration of silver bromide, the filtrate was evaporated to 100 m*l* under reduced pressure at a temperature 55°C. The solution was cooled to 0°C, and the brown diastereoisomer [*d*-$Co(NO_2)_2en_2$][$(-)_{546}$Cotrdta]·$3H_2O$ deposited was collected, which was recrystallized from water by the addition of ethanol, washed with ethanol and ether, and then air-dried. An aqueous solution of the diastereoisomer gave $[\alpha]_{546}=-850\pm30°$. The rotation did not change after recrystallization. The filtrate was reserved for the preparation of [*l*-$Co(NO_2)_2en_2$][$(+)_{546}$Cotrdta]·$3H_2O$.

K[$(-)_{546}$Cotrdta]·$2H_2O$. Fifteen grams of [*d*-$Co(NO_2)_2en_2$][$(-)_{546}$Cotrdta]·$3H_2O$, 15 g of potassium iodide and 40 m*l* of water were ground up in a mortar for 5 min and cooled to 0°C for 1 hr. After removal of the [*d*-$Co(NO_2)_2en_2$]I precipitated, equivolume of ethanol was added to the solution. K[$(-)_{546}$Cotrdta]·$2H_2O$ thus obtained was washed with ethanol and ether, and then air-dried. A solution of K[$(-)_{546}$Cotrdta]·$2H_2O$ gave $[\alpha]_{546}=-1560\pm60°$, and the rotation did not change after recrystallization.

[l-$Co(NO_2)_2en_2$][$(+)_{546}$Cotrdta]·$3H_2O$. To the filtrate reserved in the resolution of [*d*-$Co(NO_2)_2en_2$][$(-)_{546}$Cotrdta]·$3H_2O$ mentioned above, 20 g of barium iodide was added and shaken vigorously. After the solution had been cooled to 0°C, [*d*-$Co(NO_2)_2en_2$]I precipitated was removed by filtration. Equivolme of ethanol was added to the solution. The solution was cooled to 0°C and allowed crystallization of Ba[Cotrdta]$_2$·$8H_2O$. The compound collected was recrystallized from water by the addition of ethanol.

Three grams of Ba[Cotrdta]$_2$·$8H_2O$ was dissolved in 20 m*l* of water at 60°C. *cis*-[*l*-$Co(NO_2)_2en_2$]Br (2.1g) and 0.94 g of silver sulfate were mixed in 80 m*l* of water at 60°C and the solution was added to the solution of Ba[Cotrdta]$_2$·$8H_2O$. The solution thus obtained was shaken vigorously for 10 min. The silver bromide and bariumsulfate precipitated were removed. Subsequent procedures were the same as those for preparation of [*d*-$Co(NO_2)_2en_2$][$(-)_{546}$Cotrdta]·$3H_2O$. The diastereoisomer [*l*-$Co(NO_2)_2en_2$][$(+)_{546}$Cotrdta]·$3H_2O$ gave $[\alpha]_{546}=870\pm30°$.

K[$(+)_{546}$Cotrdta]·$2H_2O$. This compound was prepared from [*l*-$Co(NO_2)_2en_2$][$(+)_{546}$Cotrdta]·$3H_2O$ by the same procedure as that for the preparation of K[$(-)_{546}$Cotrdta]·$2H_2O$. The solution of K[$(+)_{546}$Cotrdta]·$2H_2O$ gave $[\alpha]_{546}=1600\pm60°$.

The elementary analyses of the compounds prepared in this work are given in Table 1.

Apparatus The proton nuclear magnetic resonance spectra were recorded with a Varian A-60 NMR spectrometer. Sodium trimethylsilylpropanesulfonate (DSS) was used as internal standard.

Polarimetric measurements at sodium D line were done by a JASCO model DIP-SL automatic polarimeter. ORD and CD curves were recorded with a JASCO model ORD/CD-5 polarimeter.

Goniometric measurements of crystals were carried out by a STOE microscope two-circle-polarizing optical goniometer.

Results and Discussion

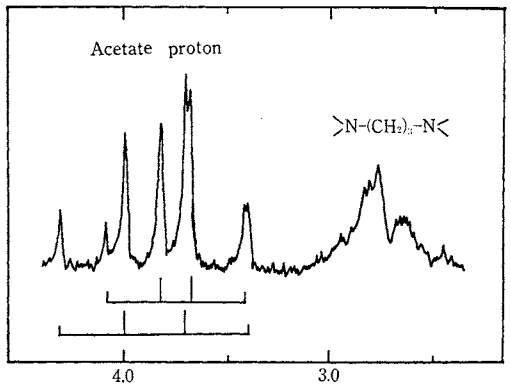
Conformation of Cotrdta$^-$. From the measurement of the infrared spectra of K[Cotrdta]·$2H_2O$, it has been reported that a quadrivalent trdta anion in this complex is hexadentate.[1)]

NMR spectrum of Cotrdta$^-$ in deuterium oxide is shown in Fig. 1. From the intensities and the chemical shifts of signals, signals centered at 2.8 ppm can be assigned to the protons attached to the carbon atoms of trimethylenediamine ring, and eight peaks ranged at 3.3 to 4.3 ppm can be assigned to be acetate protons. The latter eight

Table 1. Elementary analyses (%)

Compound		C	H	N	H_2O
H_4trdta	calcd	43.14	5.92	9.15	
	found	43.00	6.09	9.20	
K[Cotrdta]·$2H_2O$	calcd	30.28	4.16	6.42	8.3
	found	30.27	3.93	6.26	8.1
H[Cotrdta]·$3H_2O$	calcd	31.74	5.09	6.73	13.0
	found	31.97	5.31	6.81	13.7
Ag[Cotrdta]·H_2O	calcd	27.13	3.31	5.75	3.7
	found	26.95	3.60	5.64	4.2
Ba[Cotrdta]$_2$·$8H_2O$	calcd	26.33	4.42	5.58	
	found	26.81	4.54	5.58	
[*l*-$Co(NO_2)_2en_2$]-[$(+)_{546}$Cotrdta]·$3H_2O$	calcd	26.25	5.29	16.33	7.9
	found	26.34	5.46	16.22	7.5
[*d*-$Co(NO_2)_2en_2$]-[$(-)_{546}$Cotrdta]·$3H_2O$	found	26.58	5.87	16.21	
K[$(+)_{546}$Cotrdta]·$2H_2O$	calcd	30.28	4.16	6.42	8.3
	found	30.21	4.11	6.53	8.1
K[$(-)_{546}$Cotrdta]·$2H_2O$	found	30.82	4.29	6.40	

*6 Resolution of Cotrdta$^-$ can be done by using Ba[Cotrdta]$_2$·$8H_2O$. The procedure is the same as that given in the preparation of [*l*-$Co(NO_2)_2en_2$]-[$(+)_{546}$Cotrdta]·$3H_2O$.



Chemical shift, ppm *vs.* DSS

Fig. 1. NMR spectrum of K[Cotrdta]·$2H_2O$ in deuterium oxide.

peaks are attributed to two overlapping AB splitting patterns similar to the eight signals of acetate protons of Coedta$^-$.[7-10] Several parameters of NMR spectra of Cotrdta$^-$ are compared with those of Coedta$^-$ in Table 2.

It is shown in Table 2 that signals of protons attached to the carbon atoms of trimethylenediamine ring are in higher field than those of ethylenediamine ring. This is due to the increasing shielding effect from the applied magnetic field with the increase of methylene group.

The two AB splitting patterns of acetate protons in Cotrdta$^-$ can be attributed to the presence of two acetate rings in N–Co–N plane (in-plane acetates) and of two acetate rings out of N–Co–N plane (out-of-plane acetates), respectively. AB patterns centered at 3.735 ppm were assigned to in-plane acetate and those centered at 3.855 ppm were assigned to out-of-plane acetates, with reference to the data of Coedta$^-$[9,10] and the kinetic study of deuteration reaction of Cotrdta$^-$.*7

The presence of two kinds of AB protons in Cotrdta$^-$ complex means that the magnetic environments of two nitrogen atoms in this complex are equivalent. Unless these magnetic environments are equivalent, it is expected that Cotrdta$^-$ gives four different AB splitting patterns of acetate protons. As an example, it was reported that Copdta$^-$ gives four different AB splitting patterns of acetate protons.[8] In this case, the magnetic environments of two nitrogen atoms are not equivalent by the presence of a methyl group on N–C–C–N chelate ring.

The results of NMR spectra rule out the possibility of the following boat forms as the conformation of trimethylenediamine ring in Cotrdta$^-$:

(A) (B)

In the form (A), the magnetic environments of two nitrogen atoms are apparently non-equivalent. In the form (B), as the protons attached to the central carbon atom of trimethylenediamine approach closely one of out-of-plane acetate rings, the equivalence of two nitrogen atoms does not hold. Furthermore, molecular models show that these forms are strained considerably.

It was revealed that the trimethylenediamine chelate ring in tris(trimethylenediamine)cobalt(III) cation is of a chair form.[11] It was, however, found that such a molecular model of Cotrdta$^-$ in which trimethylenediamine chelate ring is of a chair form and trdta anion in the complex is hexadentate could not be constructed.

Figure 2 shows the most probable conformation which explains the experimental results mentioned above, in which cobalt(III) ion, two nitrogen atoms and one central carbon atom of trimethylenediamine (C_6 in Fig. 2) lie in the same plane,

TABLE 2. NMR SPECTRAL PARAMETERS OF Coedta$^-$ AND Cotrdta$^-$

Complex	δ,* ppm	δ_{AB}^{**}, ppm	J_{AB}^{***}, Hz	Number of protons	Assignment	Ref.
Coedta$^-$	3.746	0.333	16.5	4	in-plane acetate	10
	3.916	0.147	18.5	4	out-of-plane acetate	10
	3.61	—	—	4	$>N\,CH_2CH_2\,N<$	9
Cotrdta$^-$	3.735	0.308	16.1	4	in-plane acetate	This work
	3.855	0.529	18.6	4	out-of-plane acetate	This work
	2.8	—	—	6	$>N\,CH_2CH_2CH_2N<$	This work

* Chemical shift of pattern relative to DSS.
** Relative chemical shift of two AB protons.
*** Coupling constant of AB patterns.

7) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).
8) R. J. Day and C. N. Reilley, *ibid.*, **37**, 1326 (1965).
9) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).
10) J. B. Terrill and C. N. Reilley, *ibid.*, **5**, 1988 (1966).

*7 In acid media, AB protons centered at 3.855 ppm are deuterated faster than those centered at 3.735 ppm. The details will be published elsewhere.

11) Y. Saito, T. Nomura and F. Maruno, This Bulletin, **41**, 530 (1968).

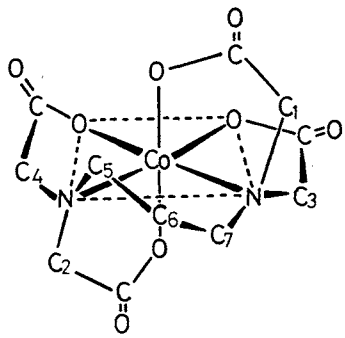


Fig. 2. The most probable conformation of Cotrdta$^-$.
(There is a two-fold axis through Co and C_6.)

and carbon C_5 is above and carbon C_7 below this plane. In this conformation, there is a two-fold axis through a cobalt(III) ion and central carbon atom of trimethylenediamine, C_6. Accordingly, the magnetic environments of two nitrogen atoms in this complex are equivalent. A survey with the use of a molecular model suggested that the in-plane acetate rings in this complex are more strained than the out-of-plane acetate rings.

Spontaneous Resolution of K[Cotrdta]·2H_2O. When hot solutions saturated with K[Cotrdta]·2H_2O were cooled slowly, fairly large crystals appeared.*8 It was found that each crystal deposited is classified to either forms as shown in Fig. 3. The largest crystal obtained up to date is 1 cm along b axis as shown in Fig. 3. Thus, one can distinguish visually the form to which the crystal deposited belongs. Crystal form A in Fig. 3 is the mirror image of form B. It was found that crystals belonging to A form give *levo* rotation at both 546 mμ and sodium D line and crystals belonging to B form give *dextro* rotation at the same wavelengths. In order to know the accurate value of rotation, single crystals deposited from the solution of racemic K[Cotrdta]·2H_2O were dissolved into 5 m*l* water and the optical rotation of the solutions were measured at sodium D line in 1 cm cell. Fig. 4 shows the results thus obtained. The ordinate in Fig. 4 denotes the value of observed rotation in degree and the abscissa the concentration of K[Cotrdta]·2H_2O. The value of rotation of K[(+)$_D$Cotrdta]·2H_2O resolved by using[*l*-Co$(NO_2)_2en_2]^+$ is also plotted in Fig. 4. The plots of crystals belonging to form A lie on a single straight line. The plots of crystals belonging to form B and K[(+)$_D$Cotrdta]·2H_2O resolved with [*l*-Co$(NO_2)_2en_2]^+$ also lie on a straight line. These two straight lines are mirror images of each other within experimental error. This means that each single crystal must contain either *d*- or *l*-isomers. This is a new example of so-called "spontaneous resolution."

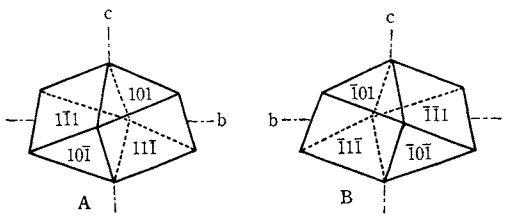


Fig. 3. Two crystal forms of K[Cotrdta]·2H_2O.

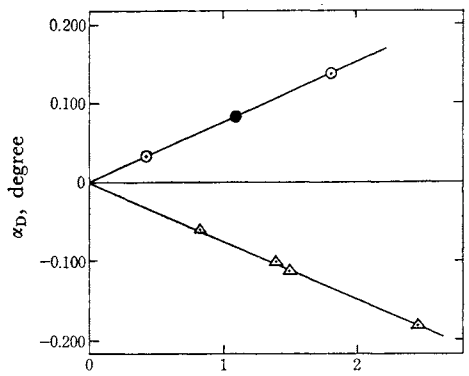


Fig. 4. The relation between optical rotation at sodium D line and the concentration of K[Cotrdta]·2H_2O. △ denotes single crystals belonging to form A in Fig. 3 and ○, single crystal belonging to form B in Fig. 3. ● denotes K[(+)$_D$Cotrdta]·2H_2O resolved with [*l*-Co$(NO_2)_2en_2]^+$. Each single crystal is dissolved into 5 m*l* of water.

In order to know details of the crystal forms, goniometric measurements were carried out. The results of the measurements are given in Table 3.

Table 3. Measured and calculated angle data for K[(−)$_{546}$Cotrdta]·2H_2O crystal obtained by spontaneous resolution

hkl	ρ_{measd}	φ_{measd}	ρ_{calcd}	φ_{calcd}
101	51.0°	89.3°	51.1°	90.0°
$\bar{1}$11	55.1	−59.6	54.8	−61.0
$\bar{1}$01	51.4	−90.3	51.1	−90.0
1$\bar{1}$1	55.1	120.7	54.8	119.0
11$\bar{1}$	125.1	61.9	125.2	61.0
$\bar{1}$0$\bar{1}$	128.8	−89.7	128.9	−90.0
$\bar{1}\bar{1}\bar{1}$	126.0	−117.1	125.2	−119.0
10$\bar{1}$	129.0	90.4	128.9	90.0

ρ represents the polar distance and φ, the azimuth of each crystal face.

It was found that crystals shown in Fig. 3 belong to orthorhombic system. The axial ratios are $a : b : c = 0.5534 : 1 : 0.6858$.

Crystal has a cleavage parallel to (010). Accord-

*8 The solubilities of K[Cotrdta]·2H_2O at 10, 15, 20, 25 and 30°C were 18.1, 22.9, 27.3, 31.8 and 37.4 g/100 m*l*, respectively.

Table 4. The reactions of $(+)_{546}$Coedta$^-$ and $(+)_{546}$Cotrdta$^-$ with 50% aqueous ethylenediamine

Reaction	$(+)_D$Co(en)$_3^{3+}$ resulted, %	$(-)_D$Co(en)$_3^{3+}$ resulted, %	Ref.
$(+)_{546}$Cotrdta$^-$ + 50% aq. en → Co(en)$_3^{3+}$ + trdta^{4-}	56	44	This work
$(+)_{546}$Coedta$^-$ + 50% aq. en → Co(en)$_3^{3+}$ + edta^{4-}	56.6	43.4	14

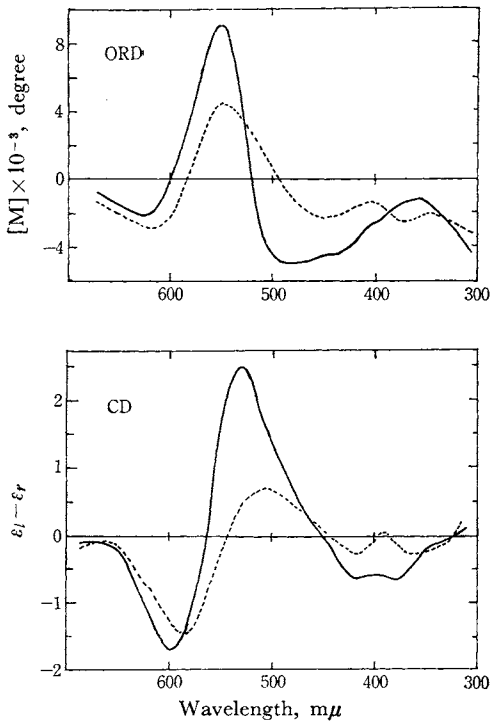
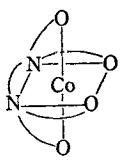


Fig. 5. The ORD and CD curves of $[(+)_{546}$-Cotrdta$]^-$ (——) and $[(+)_{546}$Coedta$]^-$ (----).

ing to this, some modifications of the crystal form shown in Fig. 3 were sometimes found in the crystals of K[Cotrdta]·2H$_2$O.

Absolute Configuration of Optically Active Cotrdta$^-$ Ion. In Fig. 5, the ORD and CD spectra of $[(+)_{546}$ Cotrdta$]^-$ are compared with those of $[(+)_{546}$ Coedta$]^-$. The absolute configuration of $[(+)_{546}$ Coedta$]^-$ has been determined as follows:[12]



The shape and positions of ORD and CD spectra of $[(+)_{546}$ Cotrdta$]^-$ are quite similar to those of $[(+)_{546}$Coedta$]^-$. Therefore, it can be concluded that the absolute configuration of $[(+)_{546}$ Cotrdta$]^-$ is the same as that of $[(+)_{546}$ Coedta$]^-$. This agrees with the result reported by Van Saun and Douglas.[3]

Busch *et al.*[12-14] reported that [Coedta]$^-$ reacts with ethylenediamine (en) to form tris(ethylenediamine)cobalt(III) cation (Co(en)$_3^{3+}$) with partial retention of optical activity. Weakleim and Hoard[15] reported that in-plane acetate rings in Coedta$^-$ are more strained than out-of-plane acetate rings. From this fact, Busch *et al.* clarified the mechanim of the reaction between Coedta$^-$ and ethylenediamine, in which the first group to be displaced in replacing EDTA by ethylenediamine should be one of the in-plane acetate groups.

In this study the reaction between Cotrdta$^-$ and ethylenediamine was investigated and it was found that Cotrdta$^-$ reacts with ethylenediamine to form Co(en)$_3^{3+}$ similar to Coedta$^-$ system. Table 4 shows a comparison of the reactions of Coedta$^-$[14] and Cotrdta$^-$ with ethylenediamine. The degree of retention of optical activity in reaction between $(+)_{546}$Cotrdta$^-$ and ethylenediamine is essentially the same as that in the reaction between $(+)_{546}$-Coedta$^-$ and ethylenediamine. The results shown in Table 4 support the conclusion that absolute configuration of $(+)_{546}$Cotrdta$^-$ is the same as that of $(+)_{546}$Coedta$^-$ and that the in-plane acetate rings in Cotrdta$^-$ are more strained than the out-of-plane acetate rings.

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12) D. H. Busch and D. W. Cooke, *J. Inorg. Nucl. Chem.*, **23**, 145 (1961).

13) D. H. Busch and K. Swaminathan, *J. Inorg. Nucl. Chem.*, **23**, 150 (1961).

14) D. H. Busch, K. Swaminathan and D. W. Cooke, *Inorg. Chem.*, **1**, 260 (1962).

15) H. A. Weakleim and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).