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Studies of Ethylenediamine-*N*,*N'*-diacetatocobalt(III) Complexes. I.
The Preparation and Some Properties of Ethylenediamine-*N*,*N'*-diacetatocobalt(III) Complexes, with Chloride, Water, Ammonia, Ethylenediamine, 1,10-Phenanthroline, and 2,2'-Dipyridyl as the Additional Ligands

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A series of cobalt(III) complexes containing the tetradentate ethylenediamine-*N*,*N'*-diacetate anion (EDDA) and chloride, water, ammonia, ethylenediamine, 1,10-phenanthroline, and 2,2'-dipyridyl as the ligands occupying the residual coordination positions have been prepared, and some of their physical and chemical properties have been examined. Two isomers have been isolated in the cases of the phenanthroline and dipyridyl complexes; they have been inferred to be the α-*cis*(pink) and the β-*cis*(red) isomers* on the basis of their electronic absorption spectra. A new convenient route for the preparation of the series has been presented, a route which passes through the dichloro, chloroaquo, and diaquo complexes.

Although a number of cobalt(III) complexes which contain the tetradentate ethylenediamine-*N*,*N'*-diacetate anion (EDDA) have been reported in the literature,1–6) the number is still small in comparison with those of such other series as the triethylenetetraminecobalt(III) and nitrilotriacetatocobalt(III) series. The main reason for the rather few instances of isolation is undoubtedly the large solubilities or the difficulty in the crystallization of the members of the series. The addition of an organic solvent such as ethanol to a concentrated reaction mixture, a method which is often used in the complex preparations, almost always gives oily materials or highly hygroscopic precipitates in this series. For example, the carbonato-(ethylenediamine-*N*,*N'*-diacetato)cobalt(III) ion reacts with various anions in the acidic solution, but the addition of ethanol to the reaction mixture gives no satisfactory materials. In order to obtain good crystals, we attempted the crystallization or precipitation of a complex from an aqueous solution, keeping the other components in the solution as few in number as possible. Thus, several new complexes as well as the known species have been isolated in the nonhygroscopic state. A new convenient route of preparation will be reported in this communication.

Theoretically, a di(monodentate)-EDDA-Co(III) complex may exist in three different stereoisomers, and a bidentate-EDDA-Co(III) complex in two, as is shown in Fig. 1. Legg and Cooke isolated α-*cis*-[Co(EDDA)(en)]NO$_3$ and β-*cis*-[Co(EDDA)(en)]-ClO$_4$.2) From the very low yield of the β-*cis* isomer and the failure to isolate β-*cis*-[Co(EDDA)(NH$_3$)$_2$]X, it has been considered that EDDA very much prefers the α-*cis* coordination mode.2–5) Recently, Coleman, Legg, and Steele obtained the α-*cis* and β-*cis* isomers of oxalato-EDDA-Co(III) and malonato-EDDA-Co-

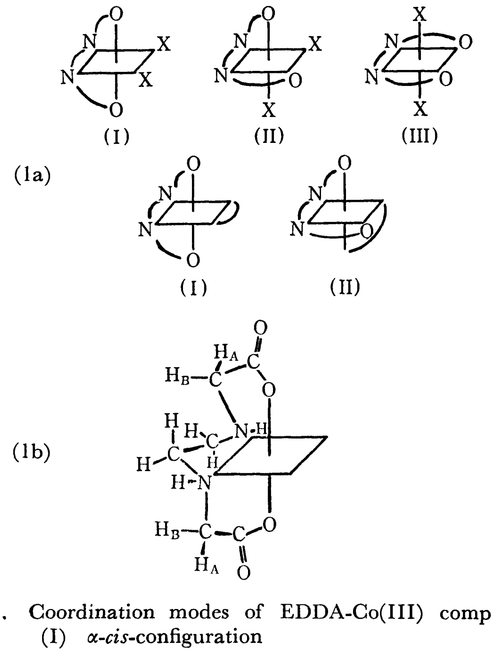

Fig. 1. Coordination modes of EDDA-Co(III) complexes.
(1a) (I) α-*cis*-configuration
(II) β-*cis*-configuration
(III) *trans*-configuration
(1b) conformation of EDDA in the α-*cis*-isomer

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* In this article, the nomenclature proposed by A. M. Sargeson and G. H. Searle (*Inorg. Chem.*, **4**, 45 (1965)) has been adopted in order to distinguish the isomers. The *trans* and *cis* isomer named in several articles are α-*cis* and β-*cis* isomer here, respectively.

1) M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, This Bulletin, **35**, 75 (1962).

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

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

4) C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969).

5) P. J. Garnett, D. W. Watts, and J. I. Legg, *ibid.*, **8**, 2537 (1969).

6) P. F. Coleman, J. I. Legg, and J. Steele, *ibid.*, **9**, 937 (1970).

(III) complexes.[6] In these cases, the yields of the two isomers were comparable. It has not yet been clearly established what factors determine the coordination mode of EDDA around the central cobalt ion. In our new preparative procedure, in which the chloroaquo or the diaquo complex was used as the starting material, both *α-cis* and *β-cis* isomers were obtained in the cases of the 1,10-phenanthroline and the 2,2'-dipyridyl complexes. It was possible to control the yield of the isomers by adjusting the reaction temperature.

Experimental

Materials. The ethylenediamine-*N,N'*-diacetic acid (Dotite Reagents), 1,10-phenanthroline, and 2,2'-dipyridyl (Nakarai Chemicals) and all the other reagent-grade chemicals were used without further purification.

Analysis. The cobalt was analysed by a direct EDTA titration, using murexide as an indicator, after the decomposition of a complex with hot concentrated sulfuric and nitric acid. The other elements were analysed at the Institute for Chemical Research in Kyoto University.

Apparatus and Measurements. The visible and ultraviolet absorption spectra were measured with a Hitachi ESP-3 Recording Spectrophotometer. The infrared spectra were recorded with a Hitachi EPI-G Spectrophotometer. The proton nuclear magnetic resonance spectra were recorded with a Japan Electron Optics JNM-4H-100 Spectrometer (100 MHz), using deuterium oxide as the solvent. The temperature of the probe was maintained at 22±1°C. The chemical shifts, referred to TMS as zero, were calculated from the observed shifts of a complex from the resonance of HDO (4.69 ppm downfield from the TMS resonance). The solubility measurements and the reactions with various anionic reagents were carried out by a procedure described elsewhere.[7]

Preparations. *(1) Hydrogen Dichloro(ethylenediamine-*N,N'*-diacetato)cobaltate(III), H[Co(EDDA)(Cl)$_2$]:* In 40 m*l* of water, ethylenediamine-*N,N'*-diacetic acid (1.76 g), sodium hydroxide (0.8 g), and cobalt(II) chloride hexahydrate (2.3 g) were added in this order. We then started to bubble air into the mixture, and 10 m*l* of hydrogen peroxide (30%) were added, drop by drop, through the air inlet. Air bubbling was continued for 5 hr, during which time the color of the solution changed from brown to dark red-violet and finally deep red-violet. Eighty milliliters of concentrated hydrochloric acid were added to the oxidation product, and then the mixture was concentrated on a steam bath, with continuous stirring, to about 60 m*l*. The color changed to a dark bluish green; at the same time a dark green precipitate appeared. After cooling, the precipitate was collected on a filter, and washed with concentrated hydrochloric acid, methanol, and ether. Yield, 2 g.

Found: Co, 19.35; C, 23.43; H, 3.65; N, 9.02%. Calcd for H[Co(EDDA)(Cl)$_2$]=$CoC_6H_{11}O_4N_2Cl_2$ (305.00): Co, 19.32; C, 23.63; H, 3.64; N, 9.18%.

An additional product was obtained by the further evaporation of the filtrate, but the deposit contained colorless crystals (NaCl). This product was useful for the preparation of the following chloroaquo complex.

*(2) Chloroaquo(ethylenediamine-*N,N'*-diacetato)cobalt(III) Monohydrate, [Co(EDDA)(Cl)(H$_2$O)]·H$_2$O:* One gram of hydrogen dichloro(ethylenediamine-*N,N'*-diacetato)cobaltate(III) was dissolved in a minimal amount of water (~30 m*l*); then the solution was kept at room temperature for one day. The blue-violet crystals which deposited were washed with cold water, ethanol, and ether. Yield, 0.5 g. The mother liquid was useful for the preparation of the following diaquo complex.

Found: Co, 19.27; C, 23.71; H, 4.59; N, 8.85%. Calcd for [Co(EDDA)(Cl)(H$_2$O)]·H$_2$O=$CoC_6H_{14}O_6N_2Cl$ (304.58): Co, 19.35; C, 23.66; H, 4.63; N, 9.20%.

*(3) α-cis-Diaquo(ethylenediamine-*N,N'*-diacetato)cobalt(III) Perchlorate, α-cis-[Co(EDDA)(H$_2$O)$_2$]ClO$_4$:* In 30 m*l* of water, 1 g of the above chloroaquo complex was suspended, and the mixture was heated at 60°C. After the starting complex had dissolved and the color of the solution had changed from blue-violet to red-violet, the solution was concentrated to 5 m*l*, and then 2 m*l* of 6 N HClO$_4$ was added. The mixture was placed in a refrigerator for 1—2 days. The red crystals which formed was washed with methanol and ether. Yield, 1 g. In order to deposit the complex more quickly or to recover the material from the filtrate in this procedure and from the filtrate in the chloroaquo complex preparation, the solution was evaporated in a large, flat dish with an aid of an air stream and gentle heating. When the solution contained a relatively large amount of chloride ions (in the case of the recovery), repeated evaporation was necessary to let chloride ions leave as hydrogen chloride; otherwise, the evaporation residue consisted mainly of the chloroaquo complex.

Found: Co, 15.73; C, 19.70; H, 3.82; N, 7.42%. Calcd for [Co(EDDA)(H$_2$O)$_2$]ClO$_4$=$CoC_6H_{14}O_{10}N_2Cl$ (368.57): Co, 15.99; C, 19.55; H, 3.83; N, 7.60%.

*(4) α-cis-Ethylenediamine-*N,N'*-diacetato(diammine)cobalt (III) Perchlorate Monohydrate, α-cis-[Co(EDDA)(NH$_3$)$_2$]ClO$_4$·H$_2$O:* Though the nitrate of this complex had previously been prepared by Legg and Cooke,[2] the following procedure was found to be simpler. The mixture of cobalt(II) chloride hexahydrate (2.3 g), ethylenediamine-*N,N'*-diacetic acid (1.8 g), active charcoal (0.5 g), and 10 m*l* of 6 N ammonia in 80 m*l* of water was oxidized by vigorous air bubbling for 4 hr. After the removal of the charcoal by filtration, 10 m*l* of 6 N HClO$_4$ were added to the red-purple filtrate. A large amount of crystals appeared after a while. The precipitate was recrystallized from 150 m*l* of warm (~50°C) water with the addition of a few milliliters of 6 N HClO$_4$ for complete precipitation. It was washed with ethanol and ether. Yield, 2.0 g.

Found: Co, 15.35; C, 18.50; H, 4.55; N, 14.42%. Calcd for [Co(EDDA)(NH$_3$)$_2$]ClO$_4$·H$_2$O=$CoC_6H_{18}O_9N_4Cl$ (384.62): Co, 15.32; C, 18.74; H, 4.72; N, 14.57%.

The same product was obtained from [Co(EDDA)(Cl)(H$_2$O)]·H$_2$O. A suspension which contained 0.5 g of the chloroaquo complex in 40 m*l* of water was heated until the complex dissolved completely. The complex aquated during the dissolution, and the color of the solution was red-violet. By the addition of 5 m*l* of 6 N ammonia, the color changed immediately to a more reddish tone. After the solution had been heated till the odor of ammonia vanished, 3 m*l* of 6 N HClO$_4$ were added. The precipitate thus obtained showed properties identical with those of the product prepared by the preceding procedure.

*(5) α-cis-Ethylenediamine-*N,N'*-diacetato(ethylenediamine)-cobalt(III) Perchlorate, α-cis-[Co(EDDA)(en)]ClO$_4$:* Although a procedure for the preparation for the nitrate of this complex had previously been described by Legg and Cooke,[2] the following more simple procedure was found to give a satisfactory yield. A mixture of cobalt(II) chloride hexahydrate (2.3 g), ethylenediamine-*N,N'*-diacetic acid (1.8 g),

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[7] K. Kuroda and P. S. Gentile, This Bulletin, **38**, 1362 (1965).

ethylenediamine (0.8 g), and active charcoal (0.5 g) in 80 m*l* of water was oxidized by vigorous air bubbling for 4 hr. After the removal of the charcoal by filtration, the red solution was concentrated to about 30 m*l* and then cooled. A large amount of a fibrous material thus appeared. (This material, which is probably the chloride of the desired complex, has a curious character; it gets entangled like fine threads in a liquid.) The material was recrystallized from warm water. When it was then mixed with concentrated perchloric acid, the crystalline form changed to powder. The perchlorate thus obtained was washed with ethanol and ether. Yield, 2.2 g.

Found: Co, 14.93; C, 24.52; H, 4.56; N, 14.24%. Calcd for $[Co(EDDA)(en)]ClO_4 = CoC_8H_{18}O_8N_4Cl$ (392.64): Co, 15.01; C, 24.47; H, 4.62; N, 14.27%.

The same product was obtained from the chloroaquo complex (2). In 40 m*l* of water, 0.5 g of the chloroaquo complex was aquated by gentle heating. An aqueous solution, which contained the equivalent amount of ethylenediamine (0.11 g), was then added. The color of the solution changed immediately from red-violet to reddish orange. After evaporation to about 10 m*l*, 3 m*l* of concentrated perchloric acid were added. The precipitate thus formed showed properties identical with those of the product prepared by the preceding procedure.

(6) α-cis-Ethylenediamine-N,N'-diacetato(1,10-phenanthroline)cobalt(III) Perchlorate, α-cis-$[Co(EDDA)(phen)]ClO_4$: A mixture of the diaquo complex (0.3 g), 1,10-phenanthroline monohydrate (0.165 g), and active charcoal (0.1 g) in 50 m*l* of a methanol (70%)-water mixture was heated at 40°C for 1 hr with continuous stirring. After the removal of the charcoal by filtration, 2 m*l* of 6 N $HClO_4$ was added to the filtrate. The precipitate thus formed was collected on a filter and then extracted by warm water. The first 10 m*l* extract was disregarded. A few drops of 6 N $HClO_4$ were added to the last main extract (~80 m*l*). The pink precipitate thus formed was washed with ethanol and ether. Yield, 0.3 g.

Found: C, 42.38; H, 3.58; N, 10.85%. Calcd for $[Co(EDDA)(phen)]ClO_4 = CoC_{18}H_{18}O_8N_4Cl$ (512.75): C, 42.16; H, 3.54; N, 10.93%.

(7) β-cis-Ethylenediamine-N,N'-diacetato(1,10-phenanthroline)cobalt(III) Perchlorate, β-cis-$[Co(EDDA)(phen)]ClO_4$: A suspension of 0.3 g of the chloroaquo complex in 20 m*l* of water was gently heated until the complex dissolved completely. The resulting solution was mixed with 0.1 g of active charcoal and a solution which contained 0.217 g of 1,10-phenanthroline in 30 m*l* of methanol, and then the mixture was concentrated to ~10 m*l* with continuous stirring on a steam bath. The reaction temperature was about 90°C. After the removal of the charcoal by filtration, 2 m*l* of 6 N $HClO_4$ were added to the filtrate. The viscous phase which was thus formed became solid after a day. This solid, after crushing, was collected on a filter and then extracted by warm water. The first extract (10 m*l*) was disregarded. To the main extract (~70 m*l*), a few milliliters of 6 N $HClO_4$ were added. The red precipitate thus formed was recrystallized once again in the same way. It was washed with methanol and ether. Yield, 0.15 g.

Found: C, 41.71; H, 3.70; N, 10.55%. Calcd for $[Co(EDDA)(phen)]ClO_4 = CoC_{18}H_{18}O_8N_4Cl$ (512.75): C, 42.16; H, 3.54; N, 10.93%.

(8) α-cis-Ethylenediamine-N,N'-diacetato(2,2'-dipyridyl)cobalt(III) Perchlorate Monohydrate, α-cis-$[Co(EDDA)(dipy)]ClO_4 \cdot H_2O$:

(9) β-cis-Ethylenediamine-N,N'-diacetato(2,2'-dipyridyl)cobalt(III) Perchlorate Monohydrate, β-cis-$[Co(EDDA)(dipy)]ClO_4 \cdot H_2O$:

These two isomers were separated from one reaction product. It is also possible to prepare each isomer separately by procedures similar to those for the phenanthroline complexes described above.

A mixture of 0.3 g of the diaquo complex (3), 0.127 g of 2,2'-dipyridyl, and 0.1 g of active charcoal in 50 m*l* of methanol (70%)-water mixture was heated at 55°C for 1 hr with continuous stirring. After the removal of the charcoal, the filtrate was condensed to 20 m*l*. A pink precipitate began to appear by cooling; it grew to a considerable amount by the addition of a few drops of 6 N $HClO_4$. This precipitate was recrystallized twice from warm water. The filtrate which was separated from the above precipitate was concentrated to 10 m*l*, and then 1 m*l* of 6 N $HClO_4$ was added. The red precipitate thus formed was recrystallized twice from warm water. Both products were washed with ethanol and ether. Yield: the pink *α-cis* isomer, 0.15 g; the red *β-cis* isomer, 0.13 g.

Found: C, 37.77; H, 3.45; N, 11.05% for the pink isomer; C, 37.47; H, 3.82; N, 10.99% for the red isomer. Calcd for $[Co(EDDA)(dipy)]ClO_4 \cdot H_2O = CoC_{16}H_{20}O_9N_4Cl$ (506.74): C, 37.92; H, 3.98; N, 11.06%.

Results and Discussion

Preparation Procedures. The preparative procedures used in this study are shown schematically

TABLE 1. PREPARATION SCHEME OF EDDA-Co(III) COMPLEXES
(The water of crystallization is omitted.)

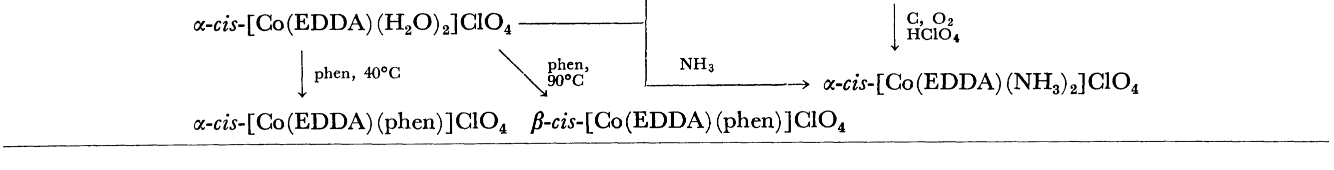

Table 2. Reactions of cationic EDDA-Co(III) complexes with various anionic reagents

		NaBr NaI	Na_2CO_3 $Na_2C_2O_4$	CH_3CO_2Na CCl_3CO_2Na	$NaNO_2$ Na_2SO_3	NaCN NaSCN	Na_2HPO_4	Solubility (ml-H_2O/g)
α-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4$		—	—	—	—	—	—	
(red-violet)		ppt	—	ppt	—	—		240
α-*cis*-$[Co(EDDA)(en)]ClO_4$		ppt	—	—	—	—	—	90
(red)		—	—	ppt	—	—		
	cold	—	violet	—	—	red-brown	violet	
		red	—	—	—	—		
α-*cis*-$[Co(EDDA)(H_2O)_2]ClO_4$		—	brown-violet	violet deeper	orange-red	brown-yellow	violet	very soluble
(pink-violet)	warm	brown-yellow	red-violet	violet deeper	red-brown	red-brown		

—: no observable reaction

ppt: a precipitate occurred

The name of color means the original color changed to the listed color.

No observable reaction occurred by 2 N NH_4Cl, 2 N $NaNO_3$, 2 N $(NH_4)_2SO_4$ with any of the complexes.

Table 3. Absorption maxima of the electronic spectra of Co(III)-EDDA complexes

	Ia		Ib		II	
	$\tilde{\nu}$(kK)	(ε)	$\tilde{\nu}$(kK)	(ε)	$\tilde{\nu}$(kK)	(ε)
α-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4$	18.59	(92.0)	~22	sh	27.55	(118.2)
α-*cis*-$[Co(EDDA)(en)]ClO_4$	18.84	(89.0)	~22	sh	27.70	(113.8)
$H[Co(EDDA)(Cl)_2]$	16.61	(176)	*		23.75	(133)
$[Co(EDDA)(Cl)(H_2O)]$	17.36	(144.5)			24.69	(97.3)
α-*cis*-$[Co(EDDA)(H_2O)_2]ClO_4$	18.21	(136.0)			25.71	(76.2)
α-$[Co(EDDA)(phen)]ClO_4$	18.52	(121.6)	*		~26	sh
β-$[Co(EDDA)(phen)]ClO_4$	*		20.00	(166.8)	~27	sh
α-$[Co(EDDA)(dipy)]ClO_4$	18.57	(129.4)	*		~26	sh
β-$[Co(EDDA)(dipy)]ClO_4$	*		20.04	(182.5)	~27	sh

* A deformation is observable in the region of the first band.

in Table 1. In this new preparative route for the series, the dichloro complex was synthesized first. All of the other species were derived from this complex, although the ethylenediamine and the diammine complexes were synthesized from cobalt(II) chloride and the ligands, too. The preparative procedure for the dichloro complex followed those of *trans*-$[Co(Cl)_2(en)_2]Cl$ and the analogous dichloro complexes. It is satisfactorily simple and gives a good yield.

The solubility of $[Co(EDDA)(Cl)(H_2O)]$, the first aquation product of the dichloro complex, is exceptionally small among the various Co(III)-EDDA complexes. It spontaneously comes out from the concentrated solution of the dichloro complex. It aquates in warm water, resulting in the diaquo complex without any decomposition. The diaquo complex reacts with various anions and neutral ligands almost instantaneously. Therefore, the chloroaquo complex is the most suitable starting substance for the syntheses of the series. This has been illustrated in the present study and will be discussed further in subsequent communications.

In the preparation of the phenanthroline and the dipyridyl complexes, the reaction temperature strongly affected the yield of the α-*cis* and the β-*cis* isomers. The α-*cis* isomer occurred at relatively low temperatures (~40°C), whereas the β-*cis* isomer was formed at higher temperatures (>55°C). Because the starting diaquo complex is the α-*cis* isomer and the α-*cis* configuration is probably more stable than the β-*cis* configuration, it is reasonable to consider that the occurrence of the β-*cis* isomer needs the heat of the rearrangement of the ligands and, hence, a higher temperature.

Reactions with Anionic Reagents. The solubility and the reactions with various anionic reagents were examined on several of the cationic complexes prepared. The results are summarized in Table 2. The color change in the diaquo complex with CN^-, NO_2^-, NCS^-, *etc.* are undoubtedly due to the substitution of the coordinated water by the anions. The isolation of these acido-complexes will be reported in subsequent communications.

It has been reported that trichloroacetic acid makes precipitates with *trans*-$[CoN_4O_2]$-type complexes, but not with their *cis*-isomers in general.[8] The diammine and the ethylenediamine complexes in this study, which have the α-*cis* configuration (the *trans* configuration with respect to O), as will be discussed below, make precipitates with trichloroacetate, as is indicated in Table 2; that is to say, the two complexes also have the common property observed previously in the, other *trans*-$[CoN_4O_2]$-type complexes.

Electronic Absorption Spectra. Table 3 and Figs. 2—4 show the visible and ultraviolet absorption spectra

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[8] K. Kuroda and P. S. Gentile, *ibid.*, **38**, 1368 (1965).

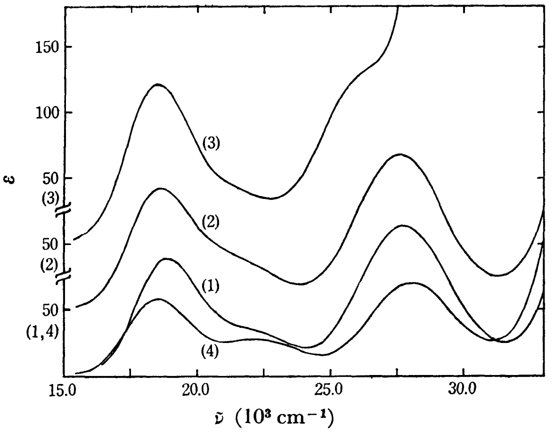

Fig. 2. Absorption spectra of some EDDA-Co(III) complexes, I.
(1) α-*cis*-[Co(EDDA)(en)]ClO_4
(2) α-*cis*-[Co(EDDA)$(NH_3)_2$]ClO_4
(3) α-*cis*-[Co(EDDA)(phen)]ClO_4
(4) *trans*-[Co$(CH_3CO_2)_2$$(en)_2$]$ClO_4$

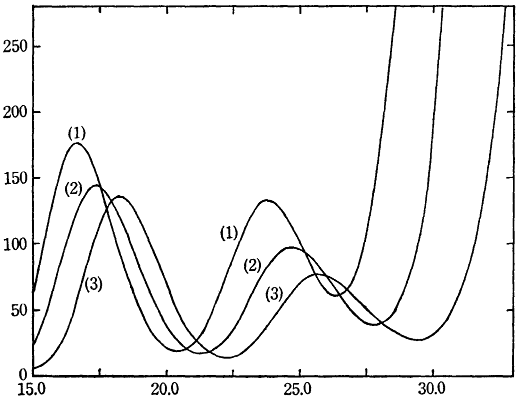

Fig. 3. Absorption spectra of some EDDA-Co(III) complexes, II.
(1) H[Co(EDDA)$(Cl)_2$]
(2) [Co(EDDA)(Cl)(H_2O)]
(3) [Co(EDDA)$(H_2O)_2$]ClO_4

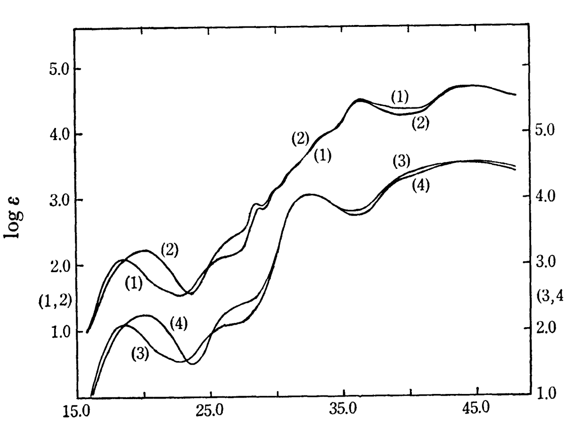

Fig. 4. Absorption spectra of some EDDA-Co(III) complexes, III.
(1) α-*cis*-[Co(EDDA)(phen)]ClO_4
(2) β-*cis*-[Co(EDDA)(phen)]ClO_4
(3) α-*cis*-[Co(EDDA)(dipy)]ClO_4
(4) β-*cis*-[Co(EDDA)(dipy)]ClO_4

of the complexes studied. Two samples of the diammine complex as well as of the ethylenediamine complex, which were obtained by the two different procedures, showed completely identical spectra; those spectra also agreed with those obtained by Legg and Cooke²⁾ within the limits of experimental error. The absorption curves have the characteristic feature of *trans*-isomers, namely, a large split in the first band, and are similar to those of *trans*-[Co$(CH_3CO_2)_2(NH_3)_4$]$^+$ and *trans*-[Co$(CH_3CO_2)_2(en)_2$]$^+$ previously studied.⁸⁾ The spectra show clearly that the complexes have the α-*cis* configuration.

The absorption maxima and their intensities of the dichloro, chloroaquo, and diaquo complexes are on the ordinary line of the spectrochemical and hyperchromic series:

$$\bar{\nu}_{Cl_2} < \bar{\nu}_{ClH_2O} < \bar{\nu}_{(H_2O)_2}$$

$$\varepsilon_{Cl_2} > \varepsilon_{ClH_2O} > \varepsilon_{(H_2O)_2}$$

The spectrum of the dichloro complex is worth examining in relation to its structure. Although the shape of the first band is nearly symmetrical, a small deformation (expansion) in the higher-wave-number region ($\sim 19 \times 10^3$ cm^{-1}) of the band is observable, as may be seen in Fig. 3. If the complex be the *trans*-isomer (III in Fig. 1), a large split in the first band would be expected as the spectrum of *trans*-[Co$(Cl)_2(en)_2$]$^+$, because of the *trans*-coordination of the two chlorine atoms. Therefore, the possibility of the III mode may be eliminated. If the complex be the β-*cis* isomer (II), two atoms of the same kinds (Cl–Cl, N–N, O–O) are at the *cis*-positions. In this configuration, a very intense absorption would be expected, since the ligand field around the central atom is highly unsymmetrical. The α-*cis* configuration (I), though the evidence from the spectrum alone is not conclusive, is the most reasonable assignment for the dichloro complex, and the small deformation mentioned above may be attributed to the *trans(O)*-component of the coordination mode.

Since ethylenediamine, 1,10-phenanthroline, and 2,2′-dipyridyl are near to each other in the spectrochemical series, the spectra of the α-*cis* isomer of the phenanthroline and the dipyridyl complexes are expected to resemble that of α-*cis*-[Co(EDDA)(en)]$^+$, at least in the *d*-*d* transition region. As may be seen in Figs. 2 and 4, one of the two isomers of the phenanthroline and dipyridyl complexes shows an analogous absorption curve between 15×10^3 and 25×10^3 cm^{-1} to that of the ethylenediamine complex, although the Ib absorption is less pronounced. Therefore, the pink isomers have undoubtedly the α-*cis* configuration. It has been observed that the first band of a *cis*-[CoN_4O_2]-type complex has a slight deformation in the lower-wave-number region of the band and has a higher absorption intensity than the corresponding *trans*-isomer.⁹⁾ The red isomers of both the phenanthroline and the dipyridyl complexes showed these characteristics. The facts indicate that the red isomers have the β-*cis* configuration. In the ultraviolet region of

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9) K. Kuroda and P. S. Gentile, *J. Inorg. Nucl. Chem.*, **27**, 155 (1965).

the spectra of these complexes, there are several maxima and shoulders, as may be seen in Fig. 4. These absorptions are sure to be originated from the conjugate π-bond systems of the bidentate ligands. The complete similarity of the curves between the two geometrical isomers means that the ligand specific bands are little influenced by the structure as a whole and that, furthermore, the two substances are certainly a pair of different configurational isomers.

Infrared Spectra. The infrared spectra were supplementally used in this study for the estimation of the structure of the complexes prepared. The anhydrous dichloro complex showed only one strong absorption (3165 cm^{-1}) in the NH, OH stretching region, whereas three peaks (3625, 3495, 3170 cm^{-1}) were observed in the chloroaquo complex (monohydrate) and two peaks (3470, 3300 cm^{-1}) in the diaquo complex (anhydrous). Two absorptions, that at 3170 cm^{-1} of the chloroaquo and that at 3300 cm^{-1} of the diaquo complex, may be assigned to the NH-stretching mode. It may be considered that the other two peaks of the former come from the lattice and the coordinated water, and that one peak of the latter originates from the equivalent H_2O ligands of the α-*cis* configuration.

In the complexes which contain ligands with a carboxyl group, another noteworthy region in the infrared spectra is around 1650 cm^{-1}, the CO-stretching region. Each of the complexes studied showed a broad strong absorption in this region, which is considered to be due to the CO-stretching overlapped by the NH_2 and OH_2 deformation modes. The lack of absorption between 1700—1800 cm^{-1} indicates that the two carboxyl groups of EDDA certainly coordinate to the central cobalt and are not present as the free-acid type.[10)]

Proton Nuclear Magnetic Resonance Spectra. Van Saun and Douglas measured the PMR spectra of the M[Co(EDDA)(AA)] they had prepared, where AA= ox, mal; they observed only one AB quartet pattern due to the glycinate ring protons of EDDA.[4)] Because CO_3, of the equivalency of the two glycinate rings in the α-*cis* configuration, they concluded that their complexes were α-*cis* isomers. Recently, Coleman, Legg, and Steele prepared the β-*cis* isomers of $[Co(EDDA)(ox)]^-$ and $[Co(EDDA)(mal)]^-$ and analysed the PMR spectra of the isomers as well as the α-*cis* isomers.[6)] As expected from the configuration of the β-*cis* isomers, the spectra were much more complicated than those of the α-*cis* isomers.

The PMR spectrum of $[Co(EDDA)(H_2O)_2]ClO_4$ is shown in Fig. 5. It can be seen that one AB quartet pattern due to the glycinate protons and a symmetrical A_2B_2 pattern due to the ethylene backbone protons are present, although not all the resonances of the latter protons theoretically expected (12 resonances) can be clearly observed. The chemical shifts of the glycinate protons (H_A and H_B in Fig. 1b) are 4.04 and 3.17 respectively, and the coupling constant, J_{AB}, is 18 Hz. These values are in agreement with those which have been obtained previously with the analogous complexes.[2-6)] These results indicate that the diaquo complex is the α-*cis* isomer.

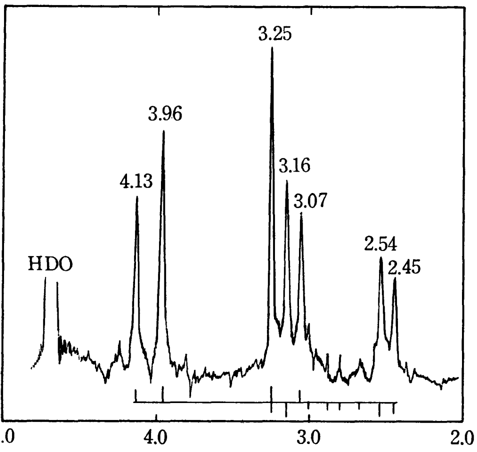

Fig. 5. PMR spectrum of D_2O solution of $[Co(EDDA)(H_2O)_2]ClO_4$.

The spectra of the other complexes are a little more difficult to measure or to analyse because of the low solubility (chloroaquo complex), the rapid aquation (dichloro complex), or the presence of many kinds of protons in a complex ion (phenanthroline and dipyridyl complexes). The research is still in progress.

Conclusion

Seven new complexes, $H[Co(EDDA)(Cl)_2]$, $[Co(EDDA)(Cl)(H_2O)]\cdot H_2O$, α-*cis*-$[Co(EDDA)(H_2O)_2]ClO_4$, α-*cis*- and β-*cis*-$[Co(EDDA)(phen)]ClO_4$, α-*cis*- and β-*cis*-$[Co(EDDA)(dipy)]ClO_4\cdot H_2O$, as well as two known complexes, α-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4\cdot H_2O$ and α-*cis*-$[Co(EDDA)(en)]ClO_4$, have been prepared by new, simple preparation procedures. The α-*cis* and β-*cis* isomers of the phenanthroline and the dipyridyl complexes have been identified by means of their electronic absorption spectra. The α-*cis* configuration of the diaquo complex has been confirmed by a study of the PMR spectrum. The dichloro and the chloroaquo complexes are supposed to be α-*cis* isomers from the electronic absorption spectra, although this is not completely certain.

[10)] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, **75**, 4574 (1953).