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Studies of Ethylenediamine-*N*,*N*′-diacetatocobalt(III) Complexes. III.[1] The Preparation and Identification of Ethylenediamine-*N*,*N*′-diacetatocobalt(III) Complexes with Ammonia, Pyridine, or Alkylamines as the Additional Ligand

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A group of cobalt(III) complexes containing the tetradentate ethylenediamine-*N*,*N*′-diacetate anion (EDDA) and ammonia, pyridine, or alkylamines have been derived from ethylenediamine-*N*,*N*′-diacetato(diaquo)cobalt(III) perchlorate. Three different series among the complexes—(1) the aquo(amine) series, $[Co(EDDA)(H_2O)(am)]ClO_4$, (2) the α-*cis*-bis(amine) series, α-*cis*-$[Co(EDDA)(am)_2]ClO_4$, and (3) β-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4$ as well as β-*cis*-$[Co(EDDA)(en)]ClO_4$, have been obtained, depending on the conditions of the reaction between the starting diaquo complex and the amines. Some properties of the complexes have been examined, and the geometrical configuration of each complex has been identified on the basis of the electronic absorption spectra and the proton NMR spectra. The coordination tendency of EDDA and the amines have also been discussed.

In contrast to the great many cobalt(III)-ammine and cobalt(III)-polyamine complexes which have been synthesized, the number of complexes in which monoamines coordinate to the metal ion is extremely small. Only a few types of complexes, such as $[Co(Cl)(amine)(en)_2]^{2+}$ and $[Co(amine)_2(en)_2]^{3+}$, have been prepared,[2] and in such complexes the amine is mostly a primary amine. The weaker tendency of the coordination of monoamines has been attributed to its basic character being larger than ammonia, although the character itself should promote the coordination. That is, in the substitution reaction of a starting complex, *e.g.*, $[Co(Cl)_2(en)_2]^+$, with an amine, a hydroxo-complex, *e.g.*, $[Co(Cl)(OH)(en)_2]^+$, is formed instead of the desired amine-complex (especially in the cases of the secondary and tertiary amines). Furthermore, cobalt(III) complexes in general are relatively unstable in a basic solution and decomposition may occur during the substitution.

In the preceding report of this study,[3] it has been shown that ethylenediamine-*N*,*N*′-diacetato(diaquo)cobalt(III) perchlorate, $[Co(EDDA)(H_2O)_2]ClO_4$, is a suitable starting complex for the preparation of various species of the Co(III)-EDDA series. Since EDDA is a strong chelating agent to the metal, and since the Co(III)-EDDA entity is stable enough in a basic solution, it has been considered to be worth examining the reaction between the diaquo-complex and various amines. Thus, the resulting complexes will be dealt with in this report. It will be shown that aquo(amine)-complexes or α-*cis* isomers of bis(amine)-complexes were obtained, depending on the reaction conditions, and that the β-*cis* isomer of the diammine complex was obtained by the reaction at 100°C. The β-*cis* diammine complex is the first example of a β-*cis* isomer in which two unidentates occupy the residual coordination sites of the Co(III)-EDDA complex.

Experimental

Materials, Analysis, Apparatus, and Measurements. Ethylenediamine-*N*,*N*′-diacetic acid (Dotite Reagents), alkylamines, and pyridine (Nakarai Chemicals), and all the other reagent-grade chemicals were used without further purification. The apparatus used and the procedures for the analysis and the measurements have been described in a preceding report.[3]

Preparations. *(1) Ethylenediamine-*N,N′*-diacetatoaquoamminecobalt(III) Perchlorate,* $[Co(EDDA)(H_2O)(NH_3)]ClO_4$: Into 5 m*l* of water, 0.5 g of ethylenediamine-*N*,*N*′-diacetato(diaquo)cobalt(III) perchlorate[3] was dissolved, and then 1 m*l* of 6N ammonia was added. The mixture was stirred at 45°C until the first-formed blue precipitate disappeared, and then for a further 10 min. After one milliliter of 6N $HClO_4$ had been added,. the mixture was cooled at 0°C. A violet precipitate thus formed was recrystallized from about 3 m*l* of warm water by the addition of a few drops of 6N $HClO_4$. Yield, 0.2 g.

Found: C, 19.22; H, 4.17; N, 11.11%. Calcd for $[Co(EDDA)(H_2O)(NH_3)]ClO_4 = CoC_6H_{15}O_9N_3Cl$ (367.59): C, 19.61; H, 4.11; N, 11.43%.

All the filtrates of the above procedure were combined and mixed with 1 m*l* of 6N ammonia and 0.1 g of active charcoal. Then the mixture was evaporated to dryness at ~45°C with the aid of an air stream. The residue was extracted with cold water and then with hot water. From the latter extract, bright reddish violet crystals appeared upon cooling. A few drops of 6N $HClO_4$ were added for complete precipitation. This is α-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4 \cdot H_2O$. (A different procedure for the preparation of this complex has been described elsewhere.[3,4]) Yield, 0.2 g.

*(2) β-*cis*-Ethylenediamine-*N,N′*-diacetato(diammine)cobalt(III) Perchlorate Monohydrate,* β-cis-$[Co(EDDA)(NH_3)_2]ClO_4 \cdot H_2O$:[5] One milliliter of 6N ammonia was added to a solution of the diaquo complex (0.5 g) in 3 m*l* of water. The blue solution, which contained a precipitate, was immersed in boiling water and then concentrated to nearly dryness with stirring. During this process, the precipitate soon disappeared and the solution turned red. After cooling, when the tarry product was stirred with a glass rod, crystals

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[1] Part II of this series, K. Kuroda and K. Watanabe, This Bulletin, **44**, 2550 (1971).

[2] a) J. Meisenheimer and E. Kiderlen, *Ann.*, **438**, 240 (1924); b) J. C. Bailar and L. B. Clapp, *J. Amer. Chem. Soc.*, **67**, 177 (1945); c) S. C. Chan and F. Leh, *J. Chem. Soc.*, *A*, **1966**, 129; d) T. Yasui and Y. Shimura, This Bulletin, **36**, 1286 (1963).

[3] K. Kuroda and K. Watanabe, This Bulletin, **44**, 1034 (1971).

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

[5] This complex has been reported briefly in the following paper: K. Kuroda, *Chem. Lett.*, **1972**, 197.

deposited suddenly and the whole solidified. The product, after washing with methanol, was dissolved in 3 m*l* of warm ($\sim$50°C) water, and then the solution was filtered and cooled. A few drops of 6N $HClO_4$ were added for precipitation. Bright red crystals came out after a while. The product was washed with methanol and ether. Yield, 0.3 g.

Found: C, 18.75; H, 4.60; N, 14.67%. Calcd for $[Co(EDDA)(NH_3)_2]ClO_4 \cdot H_2O = CoC_6H_{18}O_9N_4Cl$ (384.62): C, 18.74; H, 4.72; N, 14.57%.

*(3) Ethylenediamine-*N,N′*-diacetatoaquopyridinecobalt(III) Perchlorate,* $[Co(EDDA)(H_2O)(py)]ClO_4$: In 10 m*l* of water, 0.2 g of the diaquo complex and 0.1 g of pyridine were dissolved, and then the mixture was evaporated at 45°C. During the evaporation red-violet crystals appeared. After the evaporation was complete, the residue was washed with methanol and then recrystallized from 10 m*l* of warm water with the addition of a few drops of 6N $HClO_4$. Yield, 0.2 g.

Found: C, 30.89; H, 3.91; N, 9.96%. Calcd for $[Co(EDDA)(H_2O)(py)]ClO_4 = CoC_{11}H_{17}O_9N_3Cl$ (429.66): C, 30.75; H, 3.99; N, 9.78%.

*(4) α-*cis*-Ethylenediamine-*N,N′*-diacetato(dipyridine)cobalt(III) Perchlorate Hemihydrate, α-*cis*-*$[Co(EDDA)(py)_2]ClO_4 \cdot 0.5H_2O$: In 10 m*l* of water, the diaquo complex (0.3 g), pyridine (0.3 g), and active charcoal (0.1 g) were mixed; the mixture was heated at $\sim$50°C for 1 hr and then evaporated to $\sim$2 m*l* with continuous stirring. The excess of pyridine was removed by mixing the product with ether several times. The resulting product, which contained crystals, was extracted with 15 m*l* of warm water, and a few drops of 6N $HClO_4$ were added to the extract. After standing for 1 hr, the red crystals were collected and washed with ethanol and ether. The product was recrystallized once more. Yield, 0.2 g.

Found: C, 38.30; H, 4.13; N, 11.33%. Calcd for $[Co(EDDA)(py)_2]ClO_4 \cdot 0.5H_2O = CoC_{16}H_{21}O_{8.5}N_4Cl$ (499.75): C, 38.45; H, 4.24; N, 11.21%.

*(5) Ethylenediamine-*N,N′*-diacetatoaquo(methylamine)cobalt(III) Perchlorate Monohydrate,* $[Co(EDDA)(H_2O)(mam)]ClO_4 \cdot H_2O$: To a solution of the diaquo complex (0.3 g) in 10 m*l* of water, 0.2 g of an aqueous solution of monomethylamine (30%) was added. The mixture turned from red-violet to blue, and then it gradually returned to red-violet. After the mixture had evaporated to dryness at 45°C, the residue was recrystallized from a small amount ($\sim$3 m*l*) of water with the addition of a few drops of 6N $HClO_4$. The product was washed with methanol and ether. Yield, 0.3 g.

Found: C, 20.93; H, 4.76; N, 10.80%. Calcd for $[Co(EDDA)(H_2O)(mam)]ClO_4 \cdot H_2O = CoC_7H_{19}O_{10}N_3Cl$ (399.63): C, 21.04; H, 4.79; N, 10.51%.

*(6) α-*cis*-Ethylenediamine-*N,N′*-diacetatobis(methylamine)cobalt(III) Perchlorate Monohydrate, α-*cis*-*$[Co(EDDA)(mam)_2]ClO_4 \cdot H_2O$: In 10 m*l* of water, 0.3 g of the diaquo complex, 1 g of aqueous methylamine (30%), and 0.1 g of charcoal were mixed, after which the mixture was evaporated to dryness at $\sim$50°C. The residue was extracted with cold water ($\sim$3 m*l*), and then with warm ($\sim$60°C) water amounting about 30 m*l*. Bright violet-pink crystals appeared upon cooling. A few drops of 6N $HClO_4$ were added to complete the precipitation. The crystals were washed with methanol and ether. Yield, 0.3 g.

Found: C, 23.18; H, 5.15; N, 13.22%. Calcd for $[Co(EDDA)(mam)_2]ClO_4 \cdot H_2O = CoC_8H_{22}O_9N_4Cl$ (412.67): C, 23.28; H, 5.37; N, 13.58%.

*(7) Ethylenediamine-*N,N′*-diacetatoaquo(ethylamine)cobalt(III) Perchlorate Monohydrate,* $[Co(EDDA)(H_2O)(eam)]ClO_4 \cdot H_2O$: This complex was prepared in a manner analogous to that used for the aquo(methylamine)-complex (5), using an equivalent amount of ethylamine instead of methylamine. Violet crystals. Yield, 0.3 g.

Found: C, 22.60; H, 4.94; N, 9.91%. Calcd for $[Co(EDDA)(H_2O)(eam)]ClO_4 \cdot H_2O = CoC_8H_{21}O_{10}N_3Cl$ (413.66): C, 23.23; H, 5.11; N, 10.16%.

*(8) α-*cis*-Ethylenediamine-*N,N′*-diacetatobis(ethylamine)cobalt(III) Perchlorate, α-*cis*-*$[Co(EDDA)(eam)_2]ClO_4$: This complex was prepared in a way similar to that used for the bis(methylamine)-complex (6). Bright pink-violet crystals. Yield, 0.3 g.

Found: C, 27.65; H, 5.62; N, 13.25%. Calcd for $[Co(EDDA)(eam)_2]ClO_4 = CoC_{10}H_{24}O_8N_4Cl$ (422.71): C, 28.41; H, 5.72; N, 13.25%.

*(9) Ethylenediamine-*N,N′*-diacetatoaquo(*n*-propylamine)cobalt(III) Perchlorate Monohydrate,* $[Co(EDDA)(H_2O)(n\text{-}pam)]ClO_4 \cdot H_2O$: This complex was prepared in a way similar to that used for the aquo(methylamine)-complex (5). Since methanol dissolved the complex to some extent, ethanol was used for washing. Reddish-violet crystals. Yield, 0.3 g.

Found: C, 25.26; H, 5.39; N, 9.91%. Calcd for $[Co(EDDA)(H_2O)(n\text{-}pam)]ClO_4 \cdot H_2O = CoC_9H_{23}O_{10}N_3Cl$ (427.68): C, 25.28; H, 5.42; N, 9.83%.

*(10) α-*cis*-Ethylenediamine-*N,N′*-diacetatobis(*n*-propylamine)cobalt(III) Perchlorate, α-*cis*-*$[Co(EDDA)(n\text{-}pam)_2]ClO_4$: This complex was prepared in a way analogous to that used for the bis(methylamine)-complex (6). Pink-violet crystals. Yield, 0.3 g.

Found: C, 31.70; H, 6.15; N, 12.38%. Calcd for $[Co(EDDA)(n\text{-}pam)_2]ClO_4 = CoC_{12}H_{28}O_8N_4Cl$ (450.76): C, 31.98; H, 6.26; N, 12.43%.

*(11) Ethylenediamine-*N,N′*-diacetatoaquo(isopropylamine)cobalt(III) Perchlorate,* $[Co(EDDA)(H_2O)(i\text{-}pam)]ClO_4$: This complex was prepared from 0.5 g of the diaquo complex and 0.2 g of isopropylamine by a procedure similar to that used for the aquo(methylamine)-complex (5). The use of an exess of the amine made an unknown insoluble product, while in the preparations of the other aquo(amine)-complexes the quantity of amines was not so decisive as this case. Violet crystals. Yield, 0.2 g.

Found: C, 25.92; H, 5.06; N, 10.25%. Calcd for $[Co(EDDA)(H_2O)(i\text{-}pam)]ClO_4 = CoC_9H_{21}O_9N_3Cl$ (409.67): C, 26.39; H, 5.15; N, 10.26%.

*(12) Ethylenediamine-*N,N′*-diacetato(ethanolamine)cobalt(III) Perchlorate,* $[Co(EDDA)(elam)]ClO_4$: A mixture of the diaquo complex (0.5 g) and ethanolamine (0.2 g) in 10 m*l* of water was evaporated to nearly dryness at 50°C. The mixture turned from blue to a dark reddish-violet during the process. The tarry residue was dissolved in 4 m*l* of water; after filtration, 6N $HClO_4$ was added till the mixture became more reddish. Crystals appeared gradually when the wall of the vessel was rubbed. After about 5 hr, the violet crystals were recrystallized from a small amount of water by the addition of a few drops of 6N $HClO_4$. Yield, 0.4 g.

Found: C, 24.47; H, 4.32; N, 10.71%. Calcd for $[Co(EDDA)(elam)]ClO_4 = CoC_8H_{17}O_9N_3Cl$ (393.63): C, 24.41; H, 4.35; N, 10.68%.

*(13) β-*cis*-Ethylenediamine-*N,N′*-diacetato(ethylenediamine)cobalt(III) Perchlorate, β-*cis*-*$[Co(EDDA)(en)]ClO_4$: This complex was first prepared by Legg and Cooke.[4] They separated this isomer from the *α-cis* isomer by means of ion-exchange chromatography; this took a long time, and the yield was very low. The following procedure, which is similar to that used for the *β-cis* isomer of the diammine complex (2), is very simple and gives a higher yield. A vessel containing a mixture of the diaquo complex (0.5 g) and ethylenediamine hydrate (0.1 g) in 3 m*l* of water was immersed in boiling water, and the solution was concentrated to nearly dryness. The tarry evaporation product was extracted by 5 m*l* of

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

$$\alpha\text{-}cis\text{-}[\mathrm{Co(EDDA)(H_2O)_2}]\mathrm{ClO_4} \xrightarrow[45^\circ\mathrm{C}]{\text{amine}} \alpha\text{-}cis\text{-}[\mathrm{Co(EDDA)(H_2O)(am)}]\mathrm{ClO_4}$$

$$\xrightarrow[50^\circ\mathrm{C}]{\text{amine, C}} \alpha\text{-}cis\text{-}[\mathrm{Co(EDDA)(am)_2}]\mathrm{ClO_4}$$

$$\xrightarrow[50^\circ\mathrm{C}]{\text{elam}} \alpha\text{-}cis\text{-}[\mathrm{Co(EDDA)(elam)}]\mathrm{ClO_4}$$

$$\xrightarrow[100^\circ\mathrm{C}]{\mathrm{NH_3}\text{ or en}} \beta\text{-}cis\text{-}[\mathrm{Co(EDDA)(NH_3)_2}]\mathrm{ClO_4}\text{ or }\beta\text{-}cis\text{-}[\mathrm{Co(EDDA)(en)}]\mathrm{ClO_4}\text{ (the }\alpha\text{-}cis\text{ isomer included.)}$$

water, and the orange extract, after the addition of a few drops of 6N $HClO_4$, was placed in a refrigerator overnight. The deposit thus formed was recrystallized from 3 m*l* of water, and then washed with methanol and ether. Yield, 0.2 g. The less soluble red residue of the extraction consisted of the α-*cis* isomer. Upon recrystallization from 20 m*l* of warm water, it was purified easily. Yield of the α-*cis* isomer, 0.2 g.

Results and Discussion

Preparation Procedures. The general scheme of the preparations in this study is shown in Table 1. The diaquo complex, $[Co(EDDA)(H_2O)_2]ClO_4$, was used as the starting complex, and all of the complexes were derived by the substitution of the coordinated water with various amines under different conditions. The merit of this preparation procedure has been discussed previously.[3]

As has been described in the preceding section and the Table, the aquo(amine) complexes occurred at relatively low temperatures (~45°C) without charcoal, the α-*cis* isomers of the bis(amine) complexes at low temperatures with charcoal, and the β-*cis* isomers, although the only two species were isolated, at high temperatures (~100°C). It was presumed at the beginning of this study that the coordination mode of EDDA depended on the temperature and that the α-*cis* mode was more stable than the β-*cis* and *trans*; therefore, the occurrence of the β-*cis* isomers needed a heat of rearrangement and, hence, a higher temperature.[3] The preparations were attempted on these assumptions; they were verified to some extent by the isolation of the β-*cis* isomers of the diammine and the ethylenediamine complexes.

The preparation of the complexes containing a secondary amine or a tertiary amine was also attempted in a similar way. The red-violet color of the starting diaquo complex changed to blue and then returned to reddish, as in the cases of the preparation of the primary amine complexes. However, no desired complex has been isolated so far. Since the color change suggests the coordination of the amines in solution, attempts at isolation are still being continued.

Electronic Absorption Spectra. Table 2 and Figs. 1—4 show the electronic absorption spectra of the complexes studied. In the case of the bis(amine) complexes, the α-*cis* isomers are of the *trans*(*O*)-$[CoN_4O_2]$-type, whereas the β-*cis* and *trans* isomers belong to the *cis*(*O*)-$[CoN_4O_2]$-type. It has been well-established, both experimentally and theoretically, that the *trans*(*O*) isomers exhibit a largely split first band, while the *cis*(*O*) isomers show a more intense, nearly symmetrical first band.[6] As may be seen in Figs. 1 and 2, all the

TABLE 2. ABSORPTION MAXIMA OF THE ELECTRONIC SPECTRA OF Co(III)-EDDA-AMINE COMPLEXES

	I $\bar{\nu}$ (kK) (ε) Ia	Ib	II $\bar{\nu}$ (kK) (ε)
$[Co(EDDA)(H_2O)(NH_3)]ClO_4$	18.90 (101.6)		26.74 (87.0)
$[Co(EDDA)(H_2O)(mam)]ClO_4$	18.87 (105.1)		26.88 (100.5)
$[Co(EDDA)(H_2O)(eam)]ClO_4$	18.87 (117.1)		26.70 (105.6)
[Co(EDDA)(H_2O)(*n*-pam)]ClO_4	18.90 (125.9)		26.63 (108.4)
[Co(EDDA)(H_2O) (*i*-pam)]ClO_4	18.80 (133.6)		26.45 (111.2)
$[Co(EDDA)(H_2O)(py)]ClO_4$	19.12 (133.4)		26.60 (98.0)
α-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4$	18.59 (92.0)	~22 (sh)	27.55 (118.2)
α-*cis*-$[Co(EDDA)(mam)_2]ClO_4$	18.55 (99.3)	~22 (sh)	27.28 (129.7)
α-*cis*-$[Co(EDDA)(eam)_2]ClO_4$	18.48 (104.4)	~22 (sh)	27.21 (138.8)
α-*cis*-[Co(EDDA)(*n*-pam)$_2$]ClO_4	18.45 (111.0)	~22 (sh)	27.17 (150.0)
α-*cis*-$[Co(EDDA)(py)_2]ClO_4$	19.05 (121.3)	~22	27.32 (130.1)
β-*cis*-$[Co(EDDA)(NH_3)_2]ClO_4$	20.04 (153.2)		27.93 (159.4)
β-*cis*-$[Co(EDDA)(en)]ClO_4$	20.24 (150.4)		27.93 (150.6)
$[Co(EDDA)(elam)]ClO_4$	18.69 (90.3)		26.50 (85.1)

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[6] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951) and many other literatures.

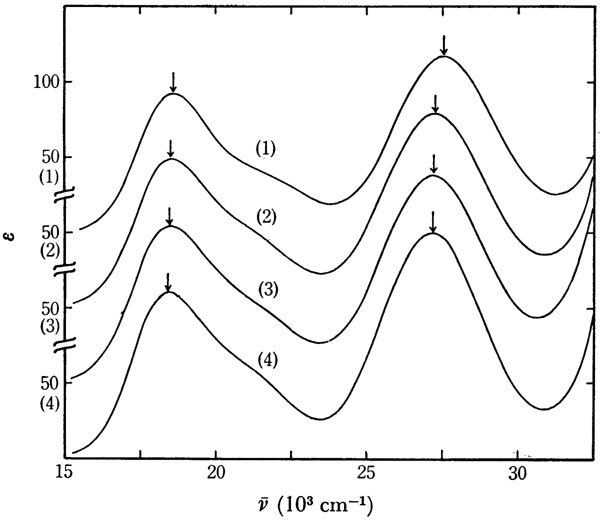

Fig. 1. Absorption Spectra of α-*cis*-[Co(EDDA)(amine)$_2$]ClO$_4$.
(1): α-*cis*-[Co(EDDA)(NH$_3$)$_2$]ClO$_4$,
(2): α-*cis*-[Co(EDDA)(mam)$_2$]ClO$_4$,
(3): α-*cis*-[Co(EDDA)(eam)$_2$]ClO$_4$,
(4): α-*cis*-[Co(EDDA)(*n*-pam)$_2$]ClO$_4$

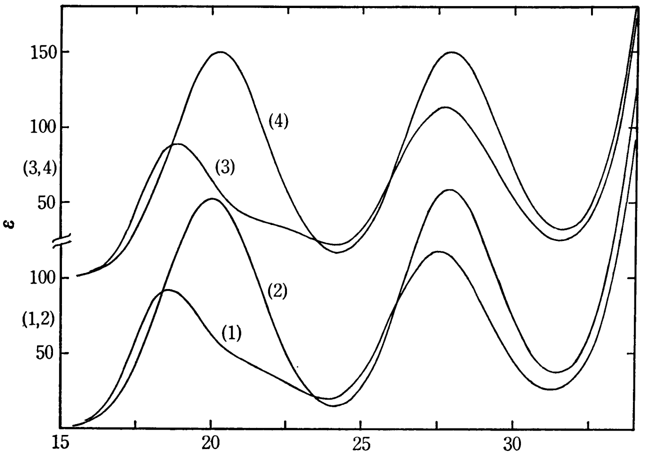

Fig. 2. Absorption Spectra of [Co(EDDA)(NH$_3$)$_2$]ClO$_4$ and [Co(EDDA)(en)]ClO$_4$.
(1): α-*cis*-[Co(EDDA)(NH$_3$)$_2$]ClO$_4$,
(2): β-*cis*-[Co(EDDA)(NH$_3$)$_2$]ClO$_4$,
(3): α-*cis*-[Co(EDDA)(en)]ClO$_4$,
(4): β-*cis*-[Co(EDDA)(en)]ClO$_4$

bis(amine) complexes show a first band which is apparently composed of two components, and the spectra closely resemble those of such well-known complexes as *trans*-[Co(CH$_3$CO$_2$)$_2$(NH$_3$)$_4$]$^+$,7) *trans*-[Co(CH$_3$CO$_2$)$_2$(en)$_2$]$^+$,7) α-*cis*-[Co(EDDA)(NH$_3$)$_2$]$^+$, and α-*cis*-[Co(EDDA)(en)]$^+$.3,4) Therefore, the configuration of the bis(amine) complexes is α-*cis*, without any question. Some trends are observable in the spectra of the isomers; the maxima of both the first and the second bands shift slightly to a lower wave number, and the intensities of the bands increase with the increase in the methylene number in the amines. It may be estimated that the ligand field strength of amines decreases with the enlargement of the amines, and that the enlargement decreases the symmetry of the complexes and, hence, makes the intensity larger.

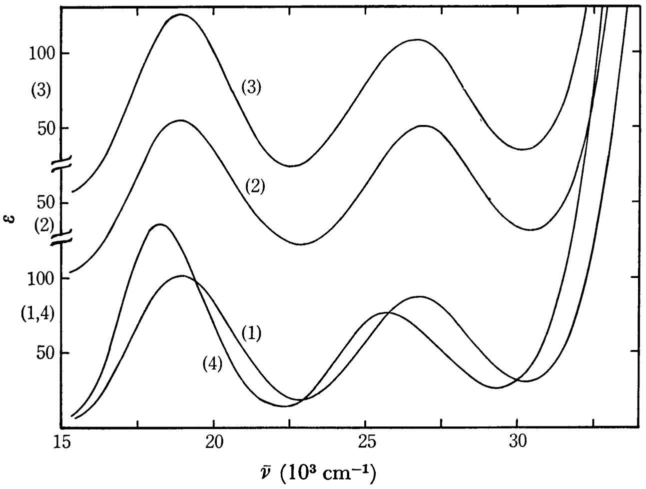

Fig. 3. Absorption Spectra of Some [Co(EDDA)(H$_2$O)(amine)]ClO$_4$.
(1): [Co(EDDA)(H$_2$O)(NH$_3$)]ClO$_4$,
(2): [Co(EDDA)(H$_2$O)(mam)]ClO$_4$,
(3): [Co(EDDA)(H$_2$O)(*n*-pam)]ClO$_4$,
(4): [Co(EDDA)(H$_2$O)$_2$]ClO$_4$

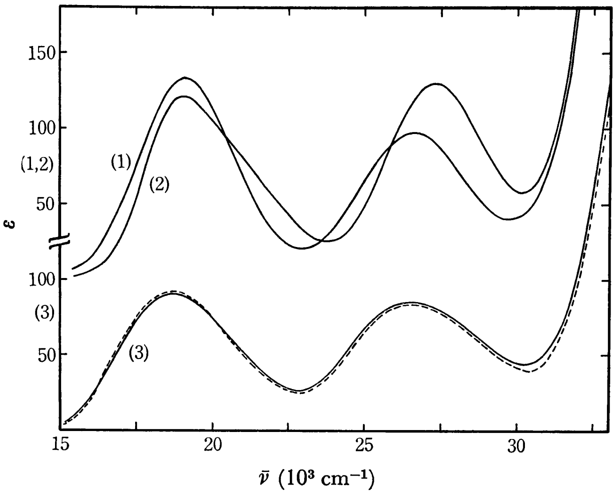

Fig. 4. Absorption Spectra of Pyridine and Ethanolamine Complexes.
(1): [Co(EDDA)(H$_2$O)(py)]ClO$_4$,
(2): α-*cis*-[Co(EDDA)(py)$_2$]ClO$_4$,
(3): [Co(EDDA)(elam)]ClO$_4$
——: in water, - - - -: in dilute HClO$_4$

The spectra of the aquo(amine) complexes are similar to one another. Again, with the increase in methylene in the amines, the maxima of the first and the second bands shift to a lower wave number and the absorption intensity increases, although a few cases of the reverse are included.

The spectrum of the β-*cis* isomer of the ethylenediamine complex has already been reported by Legg and Cooke.4) The spectrum of the isomer which was prepared by the present procedure agreed with their spectrum except for slight differences in the ε values. The spectrum of the red isomer of the diammine complex closely resembles that of the β-*cis* ethylenediamine

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7) K. Kuroda and P. S. Gentile, This Bulletin, **38**, 1368 (1965).

complex, as may be seen in Fig. 2. The ethylenediamine complex can exist only as the α-*cis* or the β-*cis* isomer; therefore, the similarity indicates that the configuration of the diammine complex is the β-*cis* and not the *trans*.

Infrared Spectra. The infrared spectra were supplementally used to confirm the structure of the complexes prepared. All of the complexes showed a strong fairly broad absorption around 1650 cm^{-1}, the CO-stretching region. The lack of absorption between 1700—1800 cm^{-1} indicates that the carboxyl groups of EDDA certainly coordinate to the central cobalt and are not present as free-acid.[8] Another strong absorption was observed around 1080 cm^{-1}, the absorption of the perchlorate ion. It is, thus, certain that the aquo(amine) complexes are cationic and not the hydroxo(amine) species. (This is natural, since the complexes were precipitated in an acid medium with perchloric acid.)

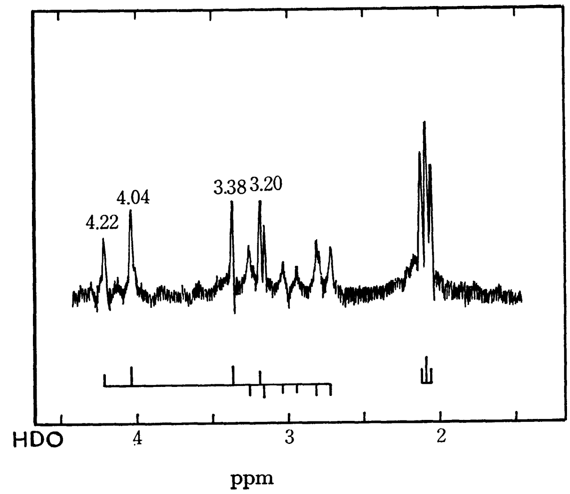

Fig. 5. PMR Spectrum of α-*cis*-$[Co(EDDA)(mam)_2]ClO_4$ in D_2O.

Proton Nuclear Magnetic Resonance Spectra. In the α-*cis* isomer of a bis(amine) complex, the two glycinate rings of EDDA are equivalent and only one AB quartet pattern due to the glycinate ring protons can be expected. In fact, such simple absorptions have been previously observed in several α-*cis* isomers of the Co(III)-EDDA system, *e.g.*, $[Co(EDDA)(NH_3)_2]^+$,[4] $[Co(EDDA)(H_2O)_2]^+$,[3] $[Co(EDDA)(ox)]^-$,[9] and $[Co(EDDA)(N_3)_2]^-$.[1] Figure 5 illustrates the PMR spectrum of α-*cis*-$[Co(EDDA)(mam)_2]ClO_4$ in D_2O as an example. As may be seen in the figure, the absorptions can be divided into three groups—one AB quartet due to the glycinates, a symmetrical absorption from the ethylene backborn protons, and a sharp triplet due to the methyl groups in the coordinated amines. The appearance of the triplet can be attributed to the spin-spin coupling with the amino protons which had not completely exchanged with deuterium at the time of the measurement. Thus, the assignment of the α-*cis* isomers is supported by the PMR spectra.

In the cases of the β-*cis* isomers, the two glycinates are not equivalent and a more complicated absorption pattern can be expected. Legg and Cooke[4] first measured the PMR spectrum of β-*cis*-$[Co(EDDA)(en)]^+$ and observed a single strong absorption due to the protons of glycinate coplanar with the ethylene ring. Legg and his co-workers[10] extended such an observation to the other β-*cis* isomers, such as those of $[Co(EDDA)(ox)]^-$ and $[Co(EDDA)(mal)]^-$; in order to explain the singlet absorption, they indicated that the two protons in the in-plane glycinate are located at magnetically very similar situations. Thus, the appearance of the strong singlet is a remarkable characteristic of the β-*cis* isomers. In Fig. 6, the PMR spectra of the α-*cis* and the β-*cis* isomers of the diammine complex are shown. In contrast to the relatively simple pattern of the α-*cis* isomer, the β-*cis* isomer exhibits an intense absorption as well as the AB quartet of the out-of-plane glycinate protons and the absorptions of the ethylene backborn protons with an unsymmetrical feature.

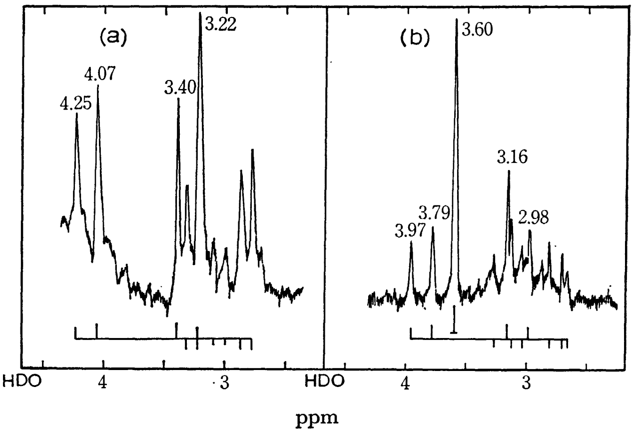

Fig. 6. PMR Spectra of $[Co(EDDA)(NH_3)_2]ClO_4$ in D_2O.
(a) α-*cis* isomer, (b) β-*cis* isomer

The aquo(amine) complexes are considered to have the α-*cis* configuration, since one of the coordinated water molecules of the starting α-*cis* diaquo complex was replaced at a relatively low temperature and since further substitution at that same temperature gave the α-*cis* bis(amine) complexes, as has been discussed above. Even in the α-*cis* configuration, however, the two glycinate rings are not equivalent in these complexes because of the coordination of the two different molecules as the additional ligands. Thus, as may be seen in Fig. 7, two sets of an AB quartet are observable; this is in accordance wih the expected configuration. From a comparison of the spectrum with those of the α-*cis* diammine and diaquo complexes, the quartet of the lower field can be assigned to the glycinate protons near the coordinated ammonia.

In all the AB quartets of the out-of-plane glycinate protons, the differences in the chemical shifts, δ_{AB}, are in the range of 0.80—0.87 ppm and the coupling constants, J_{AB}, are 18 Hz; these values are in good

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

[9] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 115 (1969).

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

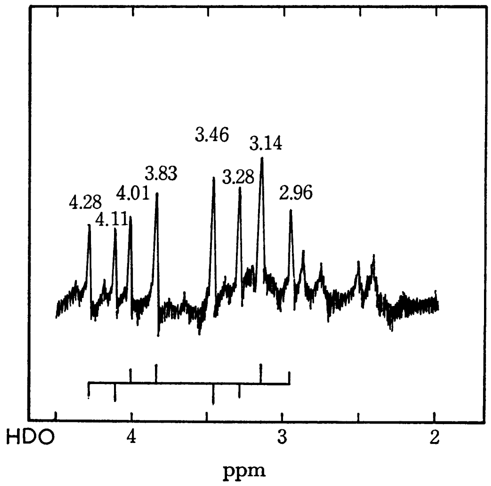

Fig. 7. PMR Spectrum of $[Co(EDDA)(H_2O)(NH_3)]ClO_4$ in D_2O.

accordance with those previously obtained in the other Co(III)-EDDA complexes.

Ethanolamine Complex. Ethanolamine may be a unidentate or a bidentate, and as a bidentate it may be a neutral (as $NH_2-CH_2-CH_2-OH$) or an uninegative (as $NH_2-CH_2-CH_2-O^-$) ligand.[11] Therefore, the coordination of the ligand in the ethanolamine complex (12) is worth considering. Although the complex was prepared by a procedure similar to those used for the aquo(amine) complexes, it is certain that the complex is not the aquo(ethanolamine) complex, because the calculated composition for the aquo(ethanolamine) complex disagrees more than the limits of experimental error with the analytical results. (For example, C is 23.34% for the aquo(ethanolamine) complex against the experimental value of 24.47%.) The coordination of ethanolamine as a bidentate is supported further by its absorption spectrum, which is considerably different from those of the aquo(amine) complexes, as may be seen in Figs. 3 and 4. That is, both the first and the second bands are broad and the intensities are considerably lower than those of the aquo(amine) complexes. These characteristics may indicate that the central cobalt ion is surrounded by a different field from that of the aquo(amine) complexes.

As is indicated in Fig. 4, however, the spectrum of the ethanolamine complex changed slightly upon the addition of perchloric acid, while there was no change in those of the aquo(amine) complexes. In the basic solution, both the aquo(amine) and the ethanolamine complexes, as well as the diaquo complex, exhibited different spectra from those in neutral water. These facts indicate that the hydroxy proton in the ethanolamine complex is more dissociative than that of the coordinated water, and that the complex exists partly in the form of $[Co(EDDA)(NH_2-CH_2-CH_2-O)]$ in water. This conclusion is consistent with the low pH value of the aqueous solution which contains nothing but the complex (3.94 in a 0.0025 molar solution).

Finally, the coordination of EDDA in this complex is considered to be of the α-*cis* mode. The complex was prepared from the α-*cis* diaquo complex at low temperatures (~50°C), as were the α-*cis*-aquo(amine) and α-*cis*-bis(amine) complexes; no sign of the rearrangement of the coordinated EDDA was observed during the reaction. The assignment is supported by the relatively low intensities of its absorption maxima. (The ε_1's of the β-*cis* isomers prepared so far are all over 150, possibly because of the highly unsymmetric structure of the isomers.) The PMR spectrum also showed no characteristic indicating that the complex had the β-*cis* configuration.

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[11] H. Yoneda and S. Kida, *J. Amer. Chem. Soc.*, **82**, 2139 (1960).