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THE ISOLATION AND CHARACTERIZATION OF COBALT(III) COMPLEXES OBTAINED FROM THE REACTIONS OF ETHYLENEDIAMINETETRAACETATO- AND R-PROPYLENEDIAMINETETRAACETATO-COBALTATE(III) WITH ETHYLENEDIAMINE

Myung-Ki DOH, Hiroshi OGINO, Junnosuke FUJITA*, Kazuo SAITO
and Nobuyuki TANAKA
Department of Chemistry, Faculty of Science, Tohoku University,
Sendai, Aoba 980

Five new mixed ligand cobalt(III) complexes containing ethylenediamine(or R-propylenediamine)tetra(or tri)acetate and ethylenediamine have been obtained by the reactions of [Co(edta)]$^-$ and [Co(R-pdta)]$^-$ with ethylenediamine in water. The reactivity of these mixed complexes with ethylenediamine contradicts the mechanism of the reactions of [Co(edta)]$^-$ and [Co(pdta)]$^-$ with ethylenediamine proposed by Busch et.al.

It is known that [Co(edta)]$^-$(edta = ethylenediaminetetraacetate ion) and [Co(pdta)]$^-$(pdta = propylenediaminetetraacetate ion) react easily with ethylenediamine to form [Co(en)$_3$]$^{3+}$(en = ethylenediamine) at room temperature.$^{1)}$ However, so far no report has been published on the isolation of possible reaction intermediates containing both edta(or pdta) and ethylenediamine. This paper deals with the isolation and characterization of such intermediates, mixed ligand complexes formed by the reactions of [Co(edta)]$^-$ and [Co(R-pdta)]$^-$ with ethylenediamine in dilute aqueous solutions.

An aqueous solution (1 ℓ) containing Na[Co(edta)]4H_2O (44.2 g), ethylenediamine (9.0 g) and ethylenediamine-dihydrochloride (6.65 g) was warmed at 50 °C for 1 hr. The solution was cooled, acidified (pH$\sim$2) with hydrochloric acid, diluted to 20 ℓ with water and poured on a column (ϕ 5 x 60 cm) of Dowex 50W-X8 cation exchange resin in H$^+$ form. By eluting the adsorbed band with 0.15M hydrochloric acid, two separate red bands were obtained, a large amount of [Co(en)$_3$]$^{3+}$ remaining on the top of the column. The first and the second band gave trans(O-O)(I)-[Co(en)(H_2edta)]Cl·3H_2O (red)(1) and trans(O-O)(I)-[Co(en)(Hedtra)]Cl·3H_2O(red)(2), respectively, on evaporation of each eluate. (edtra = ethylenediaminetriacetate ion). In a similar way, three complexes, trans(O-O)(I)-[Co(en)(R-H_2pdta)]Cl(red)(3), trans(O-O)(II)-[Co(en)(R-H_2pdta)]Cl(red)(4) and [Co(enH)(R-Hpdta)]Cl·3H_2O(violet)(5) were isolated from the reaction product between K[Co(R-pdta)]3H_2O and ethylenediamine. In these reactions, the formations of trans(O-O)-[Co(en)(edda)]$^+$ (edda = ethylenediaminediacetate ion) and trans(O-O)(I)-[Co(en)(R-Hpdtra)]$^+$ (pdtra = propylenediaminetriacetate ion) were also confirmed by column chromatography and the uv absorption spectra, but the amounts were too little to be isolated.

The compositions of these complexes have been determined by elemental analyses and the structures assigned on the bases of pH titration, optical resolution and ir, uv and pmr spectroscopy. Fig.1 shows the pH titration curves for the complexes (1) and (5). From these curves, it is concluded that the ethylenediamines in the complexes (1) and (5) are in chelate and unidentate coordination, respectively. The coordination modes of the ethylenediamine in the complexes (2), (3) and (4) were determined similarly by pH titrations. The ir spectra of all the complexes exhibit a sharp and medium intensity band which is characteristic of the free -COOH group at around 1730 cm^{-1}. The complex (5) will be the first example of cobalt(III) complex containing unidentate ethylenediamine as far as we know. The complexes (1), (3) and (4) will also be the first examples of cobalt(III) complex containing diaminetetraacetate with two free acetate branches.

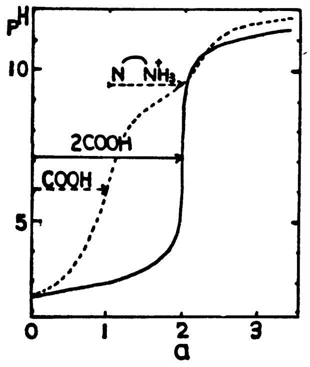


Fig.1
pH Titration curves for the complexes (1) (solid line) and (5) (dashed line) at ionic strength 0.1 ($NaClO_4$) and 25 °C.

The complexes (1) to (4) have four geometric isomers each (Fig.2), while the complex (5) has two isomers.(Fig.3) The pdta complexes have further geometric isomers with respect to the location of the methyl group, but we ignored them in this study.

The complexes (1) and (2) show a typical first absorption band of trans(O-O)-[CoN_4O_2]type.(Fig.4) There are two trans(O-O) isomers, (I) and (II) as shown in Fig.2; the trans(O-O)(I) exists in a pair of enantiomers, while the other trans(O-O) (II) does not. The complexes (1) and (2) were resolved into optical isomers by use

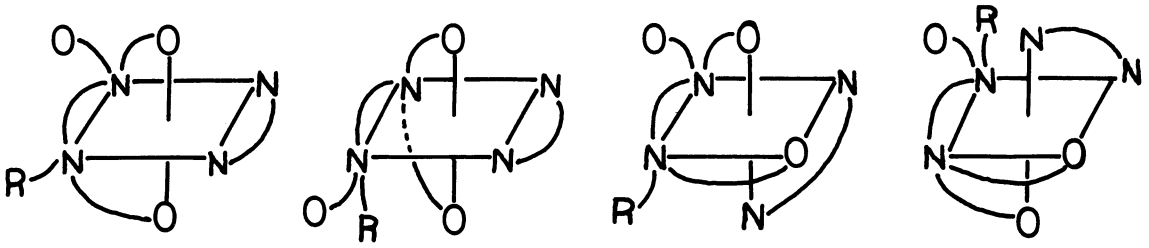
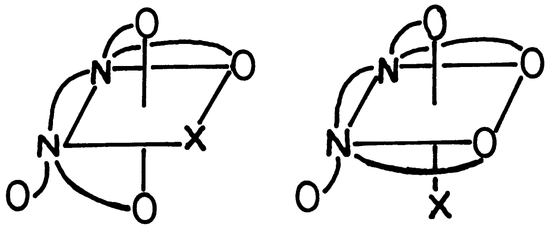


Fig.2 Possible geometric isomers of the complexes (1), (2), (3) and (4).
N⌒N : ethylenediamine, $^{O}_{O}\!>$N——N$<^{O}_{R}$: edta, edtra or pdta



equatorial isomer polar isomer

Fig.3 Possible geometric isomers of the complex (5).
X : $H_2NCH_2CH_2\overset{+}{N}H_3$

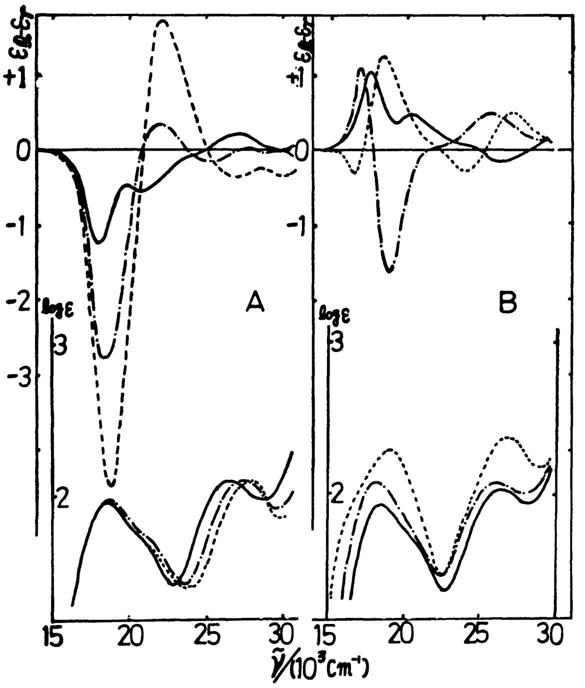


Fig.4 Absorption and CD spectra of the complexes.

A:(———)(-)$_{589}$-isomer of complex(1),
(—·—)(-)$_{589}$-isomer of complex(2),
(-----)(-)$_{589}$-[Co(en)(edda)]$^+$ 2).
B:(———)complex(3), (—·—)complex(4),
(-----)complex(5).

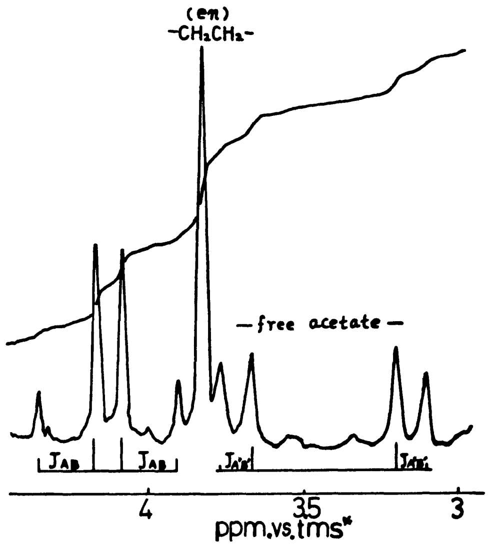


Fig.5 pmr Spectrum(100 MHz) of the complex (1).
The coupling constants for acetate protons, J_{AB} and J'_{AB} are 18.2 and 10.0 Hz, respectively. The symbol, tms* denotes sodium 3-(trimethylsilyl)-1-propane sulfonate.

of (-)$_{546}$-Ag[Co(edta)]H$_2$O 3) as resolving agent. The CD curves of (-)$_{589}$-[Co(en)(H$_2$edta)]$^+$ and (-)$_{589}$-[Co(en)(Hedtra)]$^+$ are compared with that of the known Δ-trans-(O-O)-[Co(en)(edda)]$^+$ 2) in Fig.4. Furthermore, the pmr spectrum of the complex (1) in D$_2$O exhibits signals due to one kind of coordinated acetate protons, one kind of free acetate protons and the ethylene protons of the chelated ethylenediamine, in the intensity ratio 1:1:1, respectively.(Fig.5) All these data lead to the conclusion that the complexes (1) and (2) have the trans(O-O)(I) structure. The complex (3) shows uv absorption spectrum almost identical with that of the complex (1), but the CD curve is almost enantiomeric with that of its (-)-isomer. The complex (3) should have Λ-configuration owing to the stereospecificity coming from the equatorial orientation of the methyl group, and hence the absolute configuration of the (-)$_{589}$-[Co(en)(H$_2$edta)]$^+$ is assigned to Δ. Thus, the complex (3) is assigned to the trans(O-O)(I) isomer. As shown in Fig.4, the first absorption band of the complex (4) gives a pattern characteristic of trans(O-O)-[CoN$_4$O$_2$]type, but the CD curve is quite different from that of the complex (3). Very recently, C.W.Maricondi and C.Maricondi 4) obtained trans-equatorial isomer of K[Co(NO$_2$)(R-pdtra)]H$_2$O which has a structure analogous to the trans(O-O)(II). Therefore, we have assigned tentatively the complex (4) to the trans(O-O)(II) isomer. The complex (5) will have the equatorial structure, since all complexes with a quinquedentate edta or pdta together with a unidentate ligand are known to exist in the equatorial isomer. 5)

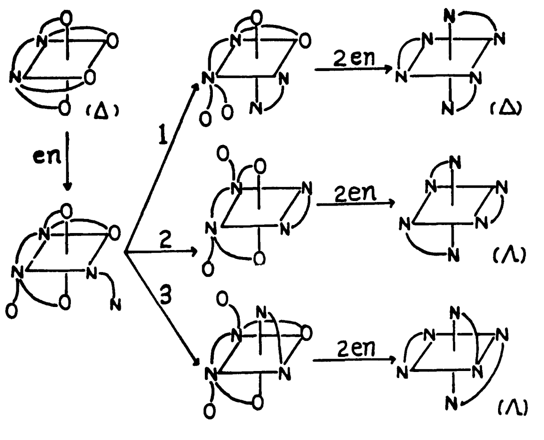


Fig.6 Proposed mechanism for the reactions of [Co(edta)]$^-$ and [Co(pdta)]$^-$ with ethylenediamine.

Busch et. al.6) proposed a mechanism for the replacement of the edta or pdta from the cobalt(III) complex by ethylenediamine, as shown in Fig.6. The proposed mechanism explains reasonably the following observations; in anhydrous ethylenediamine, Δ-[Co(edta)]$^-$ produces Δ- and Λ-[Co(en)$_3$]$^{3+}$ in the 1:2 ratio,6) while Δ-[Co(R-pdta)]$^-$ gives almost 100 % of Δ-[Co(en)$_3$]$^{3+}$ 7), that is, the reaction of the Δ-[Co(edta)]$^-$ proceeds through the paths, 1, 2 and 3 in Fig.6 in an equal probability, while that of the Δ-[Co(R-pdta)]$^-$ does through only the path 1 stereospecifically.

If this mechanism were correct, the complexes (1), (3) and (5) obtained here should react further with ethylenediamine to give [Co(en)$_3$]$^{3+}$ under the same condition as Busch et. al.'s, since these complexes correspond to the intermediates in the proposed reaction paths given in Fig.6. However, the complexes (1) and (3) do not react with ethylenediamine at all under the condition given above. The complex (5) react to give [Co(en)$_3$]$^{3+}$, but the product is almost racemic. These observations are inconsistent with the mechanism proposed by Busch at. al. Further study will be needed.

Finally it is noted that the reaction of Δ-[Co(R-pdta)]$^-$ with anhydrous ethylenediamine produced 67 % of Λ-[Co(en)$_3$]$^{3+}$, the remainder being Δ-[Co(en)$_3$]$^{3+}$. This result is almost the same as the case of Δ-[Co(edta)]$^-$. The observation by Irving and Gillard7) that Δ-[Co(R-pdta)]$^-$ gives only a single enantiomer, Δ-[Co(en)$_3$]$^{3+}$ will not be true.

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* Present address : Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464.

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