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Cobalt(II) Complexes of Diethylenetriamine-N,N',N''-triacetic Acid

Toshio Kawato, Hajime Kanatomi, and Ichiro Murase

Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Fukuoka 810

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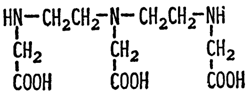
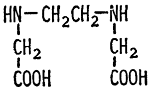
Cobalt(II) complexes of diethylenetriamine-N,N',N''-triacetic acid (DTTA) were prepared. From spectrophotometric and magnetic data, diaquo-DTTA-Co(II) was found to have an octahedral arrangement in which the N,N'-diacetate moiety and two water molecules are in the coordination sphere, and the terminal amino acid residue dangles outside. On heating the diaquo-complex, thermal rearrangement occurred with loss of water and the complex took a tetrahedral configuration. This was confirmed by its electronic spectrum and magnetic moment. The tetrahedral complex turned to another octahedral complex with absorption of water, the configuration of which seemed to differ from the original as judged by spectral difference. Cobalt(II) complexes of ethylenediamine-N,N'-diacetic acid (EDDA) were also prepared and investigated for the sake of comparison.

Diethylenetriaminepentaacetic acid(DTPA) is well-known as a potentially octadentate chelating ligand to form stable complexes with a number of metal ions. Many geometrical isomers are possible for Co(III) complexes of hexacoordination. Recently several Co(III)–DTPA complexes were isolated, the structure of the nitro complex being elucidated by means of PMR spectroscopy.[1] The terminal iminodiacetate group was found to be dangling and free from the coordination sphere. On the other hand, Co(III) complexes of diethylenetriamine-N-acetic acid and diethylenetriamine-N'-acetic acid were isolated as dinitro, dichloro and other derivatives, and their configurations were discussed on the bases of electronic spectra.[2] All the donor groups in these ligands were found to coordinate to the Co(III) ion.



$$\begin{array}{ccccc} HN- & CH_2CH_2- & N- & CH_2CH_2- & NH \\ | & & | & & | \\ CH_2 & & CH_2 & & CH_2 \\ | & & | & & | \\ COOH & & COOH & & COOH \end{array}$$

DTTA



$$\begin{array}{ccc} HN- & CH_2CH_2- & NH \\ | & & | \\ CH_2 & & CH_2 \\ | & & | \\ COOH & & COOH \end{array}$$

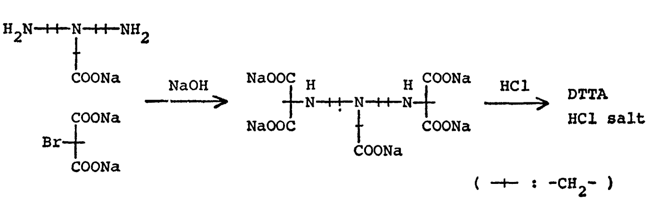
EDDA

It is of interest to study the donor function of hexadentate diethylenetriamine-N,N',N''-triacetic acid (DTTA) with Co(III) ion. We therefore examined the reaction of DTTA with Co(II) ion to obtain a Co(II) complex which might be converted into a Co(III) complex by oxidation. Eventually, it was found that the Co(II) complex was fairly stable against oxidation and isolated as red-pink crystals. It was also found that the red-pink complex shows thermochromism at elevated temperature to blue-violet with loss of water, turning pink at room temperature in moist air. This paper deals with the structure determination of the Co(II) complexes by means of infrared and visible absorption spectra, magnetic moment, differential thermal analysis and thermogravimetric analysis, and the mechanism of thermochromism in terms of structure change. Co(II) and Co(III) complexes of ethylenediamine-N,N'-diacetic acid(EDDA) were also investigated for the sake of comparison.

Experimental

The infrared spectra were determined in potassium bromide disks with a Hitachi EPI-S2 spectrophotometer, while the electronic spectra were measured with a Hitachi EPS-3T spectrophotometer. Measurements of the magnetic moment were carried out at room temperature by the Gouy-method. The DTA curve was recorded under nitrogen stream with a Rigakudenki Thermoflex 8001 with a 5 mg sample on an aluminium cell at a heating rate of 10 °C/min using alumina as a reference.

*Diethylenetriamine-*N,N',N''*-triacetic Acid (DTTA).* The synthetic route of DTTA is shown in scheme. The terminal amino groups of diethylenetriamine-N'-acetic acid[2] were reacted with two equivalent bromomalonic acid in alkaline solution and the product was decarboxylated in dilute hydrochloric acid to give DTTA hydrochloride. It was thus confirmed that an acetic acid group attaches to each nitrogen atom of the diethylenetriamine molecule.



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[1] B. B. Smith and R. H. Betts, *J. Amer. Chem. Soc.*, **91**, 7749 (1969).

[2] P. W. Schneider and J. P. Collman, *Inorg. Chem.*, **7**, 2010 (1968).

A mixture of 25.6 g (0.014 mol) of bromomalonic acid and 19 g (0.071 mol) of diethylenetriamine-*N′*-acetic acid trihydrochloride in 80 ml of water was carefully neutralized with 20% aqueous sodium hydoxide below 15 °C using phenolphthalein as an indicator. The solution was then heated at about 75 °C for an hour, being maintained its pink color by the dropwise addition of sodium hydroxide. After being heated at 85 °C for another hour, the solution was concentrated to 80 ml in a vacuum, the pH being brought to 2 with hydrochloric acid. The acidic solution containing diethylenetriamine-*N′*-acetic-*N,N″*-dimalonic acid was refluxed for 30 min until termination of the evolution of CO_2 and evaporated almost to dryness in a vacuum. The residue was extracted with ethanol containing a small amount of hydrochloric acid, the ethanol solution being evaporated to dryness in a vacuum. The product assumed to be DTTA trihydrochloride was a very hygroscopic glassy material. Since an attempt at crystallization failed, it was used directly for the preparation of the Co(II) complexes.

Diaquo-DTTA-Co(II): Red-pink Complex. To a solution of 5.4 g (0.014 mol) of DTTA trihydrochloride in 20 ml of water was added 3.33 g (0.014 mol) of cobalt(II) chloride hexahydrate in a minimum amount of water. The mixture was carefully neutralized at pH 7 with 20% aqueous sodium hydroxide. After filtration to remove a trace of violet precipitate, the filtrate was concentrated to 15 ml in a vacuum at 60 °C. On standing for a week, a red-pink crystalline powder was obtained, which was collected by filtration and washed with water and dried over calcium chloride at room temperature: yield 2 g. The complex could be recrystallized from boiling water. It was pure enough without further purification.

Found: C, 29.75; H, 5.95; N, 10.51%. Calcd for $[Co(dtta)(H_2O)_2]2H_2O$[3]: C, 29.56; H, 6.20; N, 10.34%.

The reaction conducted under nitrogen gave the same complex indicating that no oxidation took place in the air.

Thermochromisms. On being heated at 150 °C in an open vessel, the red-pink DTTA-Co(II) turned blue-violet, turned pink on cooling to room temperature. When the blue-violet complex was kept in a dry atmosphere, no color change took place even at room temperature.

Blue-violet complex, Found: C, 35.83; H, 5.00; N, 12.64%. Calcd for [Co(dtta)]: C, 35.94; H, 5.13; N, 12.57%.

Pink complex, Found: C, 29.48; H, 6.16; N, 10.44%. Calcd for $[Co(dtta)(H_2O)_2]2H_2O$: C, 29.56; H, 6.20; N, 10.34%.

*Ethylenediamine-*N,N′*-diacetic Acid (EDDA).* Although this compound is well-known, only one method of preparation has been reported with no mention of the yield.[4] We have prepared the hydrochloride in a different way with a fairly good yield.

To a suspension of 26.6 g of ethylenediamine dihydrochloride in 200 ml of ether was added with vigorous stirring 19.6 g of sodium cyanide in 30 ml of water at 2—5 °C. After standing for 10 min, 36 g of formalin (37%) was added dropwise over a period of 30 min at a temperature below 10 °C. The reaction mixture was further stirred for 2 hr at room temperature and 200 ml of methanol was added and chilled to 5 °C. The resulting sodium chloride was filtered and hydrogen chloride was saturated to the filtrate at 10 °C. The resulting precipitate was filtered and washed with methanol. Thus 40 g of ethylenediamine-*N,N′*-diacetonitrile dihydrochloride containing a small amount of sodium chloride was obtained.

To 700 ml of concentrated hydrochloric acid was added portionwise 40 g of freshly prepared dinitrile at 0—5 °C, and the mixture was stirred for 20 hr at room temperature and then diluted with 700 ml of water. The solution was boiled for 2 hr and concentrated in a vacuum until crystals began to deposit. The mixture was diluted with 150 ml of methanol and kept in a refrigerator overnight. The product was filtered and washed with methanol : yield 28 g. Recrystallization was carried out from dilute methanol containing a small amount of hydrochloric acid.

Found: C, 28.86; H, 5.73; N, 11.38%. Calcd for $C_6H_{12}N_2O_4 2HCl$: C, 28.93; H, 5.67; N, 11.25%.

Diaquo-EDDA-Co(II). The procedure was the same as in the preparation of diaquo-DTTA-Co(II) except that 3.5 g (0.014 mol) of EDDA dihydrochloride was reacted in place of DTTA trihydrochloride and the reaction and separation were carried out under nitrogen. The complex was obtained as pink crystals in a yield of 2 g which was then dried over calcium chloride and stored in a nitrogen atmosphere.

Found: C, 25.93; H, 5.35; N, 10.26%. Calcd for $[Co(edda)(H_2O)_2]1/2H_2O$[5]: C, 25.90; H, 5.45; N, 10.07%.

Aquo-hydroxo-EDDA-Co(III). Diaquo-EDDA-Co(II) was dissolved in water and air was bubbled through the solution at room temperature. Oxidation occurred within a few minutes and the solution turned to violet. It was concentrated to a small volume and kept standing in a refrigerator for a week to give violet needles. The sample was dried over calcium chloride in a vacuum.

Found: C, 26.51; H, 5.26; N, 10.19%. Calcd for $[Co(edda)(OH)(H_2O)]$: C, 26.88; H, 4.89; N, 10.45%.

Results and Discussion

DTTA is a tribasic acid and can behave as a hexadentate ligand with N_3O_3 arrangement. The Co(II) complexes obtained were neutral carrying no counter cation. Thus the possibility of hexacoordination with trinegative ligand species can be excluded. The infrared spectrum of red-pink DTTA-Co(II) is shown in Fig. 1. In the carbonyl stretching region, it exhibits two absorptions at 1585 cm^{-1} and 1645 cm^{-1} indicating the presence of two kinds of carboxylic acid groups. Since the stretching vibration of the free carboxylic acid groups is seen at 1740 cm^{-1} in

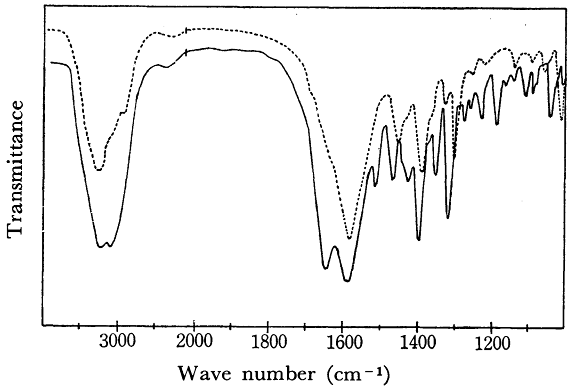

Fig. 1. IR spectra of diaquo-DTTA-Co(II) (——) and diaquo-EDDA-Co(II) (----).

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[3] (dtta) represents a dianion of DTTA.

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

[5] (edda) represents a dianion of EDDA.

DTTA trihydrochloride and EDDA dihydrochloride, no such unionized groups are present in the complex. Thus the two absorptions can be assumed to be due to coordinated and uncoordinated but ionized carboxylate vibrations. The stretching mode of the coordinated carboxylate in a similar ligand can be seen in EDDA-Co(II) in which the two acetate groups undoubtedly coordinate to the metal ion. Diaquo-EDDA-Co(II) was sensitive against air-oxidation, though the infrared spectrum obtained under careful operation showed a single sharp peak at 1585 cm^{-1} which is attributed to COO-Co(II) stretching vibration (Fig. 1). Assuming that EDDA moiety in DTTA molecule coordinates to the Co(II) ion, the absorption at 1585 cm^{-1} in DTTA-Co(II) can be assigned to the coordinated carboxylate as well as that in EDDA-Co(II). The one at 1645 cm^{-1} seems to be due to the remaining carboxylate which exists as a dipolar ion with the α-amino group dangling outside the coordination sphere. This is supported by the fact that the area ratio of the absorption bands in the coordinated and uncoordinated carboxylate is approximately 2 : 1. In other words, DTTA coordinates to the Co(II) ion as a tetradentate ligand of linear O–N–N–O type and the remaining amino acid residue exists as a zwitter ion in crystals.

Since the red-pink complex shows a magnetic moment of $\mu_{\text{effect}}=4.96$ B. M. which is normal for a high-spin octahedral Co(II) complex, the remaining two positions of the coordination sphere are occupied by water molecules, the presence of which was suggested from the elemental and thermal analyses. The charts of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the red-pink complex are given in Fig. 2. The weight loss of 18% up to 150 °C corresponds very closely to four moles of water (calcd: 17.7%), which probably consists of two moles of coordinated and two moles of lattice water. However, no difference is observed between the curves of the two kinds of water. The DTA curve indicates two endothermic peaks at 133 °C and around 155 °C. The large peak at 133 °C is due to the elimination of water as judged from the TGA curve. The other broad peak may be due to some phase transition in the crystalline structure.

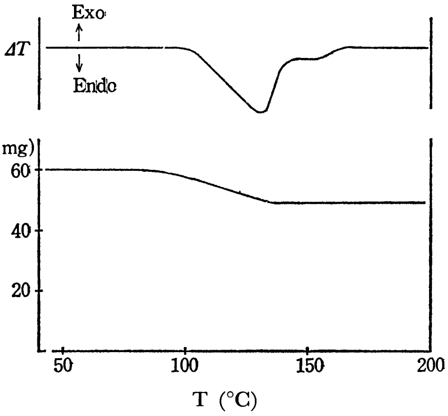

Fig. 2. DTA and TGA curves for diaquo-DTTA-Co(II).

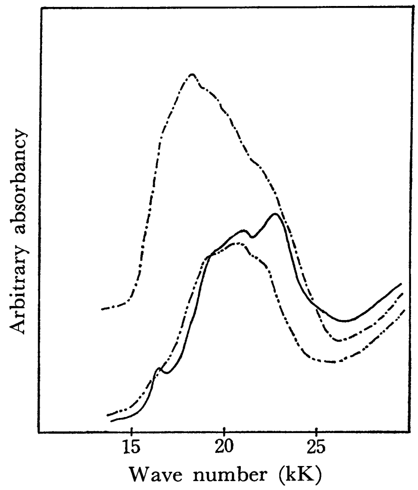

Fig. 3. Reflectance spectra of DTTA-Co(II) complexes: ——: red pink diaquo-DTTA-Co(II); —·—: blue violet anhydrous DTTA-Co(II); —··—: pink diaquo-DTTA-Co(II).

The blue-violet complex obtained by heating the red-pink one at 150 °C carries no water and shows a magnetic moment of $\mu_{\text{effect}}=4.66$ B. M. Because of its high hygroscopicity, no well-defined infrared spectrum could be obtained. The broad absorption around 1590—1650 cm^{-1} suggests the presence of two kinds of carboxylate groups like those in diaquo-DTTA-Co(II). The electronic spectrum in solid exhibits d–d transition as a broad band around 18 kK (Fig. 3). This implies a high spin tetrahedral configuration of low symmetry for the complex, where O–N–N–O coordination occurs around the Co(II) ion and the terminal iminoacetate group dangles like that in diaquo-DTTA-Co(II).

When the blue-violet complex was allowed to come in contact with moist air, the color turned pink with absorption of four moles of water. The pink complex was rather sensitive against air-oxidation. The mag-

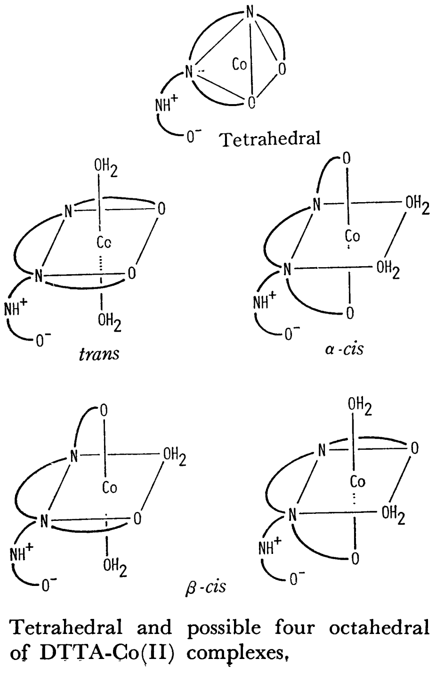

Fig. 4. Tetrahedral and possible four octahedral arrangements of DTTA-Co(II) complexes.

netic moment was slightly lower at $\mu_{\text{effect}}=4.83$ B.M. decreasing gradually on standing in the air. The infrared spectral pattern was superimposable with that of the red-pink complex. An octahedral configuration is therefore reasonable for the pink complex in the same sense as in the red-pink one. On the other hand, the electronic spectrum of the former differs from that of the latter (Fig. 3).

In diaquo-DTTA-Co(II) in which the terminal iminoacetate group dangles, four stereoisomers are possible (Fig. 4). The difference in the electronic spectrum may be due to the fact that the red-pink and pink complexes are stereoisomers of this type. Exact assignment of their configurations, however, is impossible at present.

In diaquo-EDDA-Co(II), the EDDA anion coordinates as a tetradentate ligand. An octahedral configuration is provided, since its spectral pattern is similar to that of diaquo-DTTA-Co(II) (Fig. 5). However, the magnetic moment varied in each sample around an average value of $\mu_{\text{effect}}=4.4$ B.M. which is lower than that for ordinary octahedral Co(II) complexes. This is due to a contamination by a Co(III) complex formed by inevitable air-oxidation during the course of measurements.

The pink coloration of diaquo-EDDA-Co(II) turned violet on heating at 150 °C in the absence of oxygen, returning to pink in a moist atmosphere at room temperature. In contact with air, the latter pink complex turned very quickly to deep violet. The thermochromism from pink to violet was probably due to dehydration. However, an extremely high sensitivity of the violet complex against air-oxidation and moisture made it impossible to confirm it. A tetrahedral configuration is suggested for the violet complex from the electronic spectrum in solid (Fig. 5). It exhibits a d–d transition band having a typical strong absorption at 19.1 kK.

The deep violet one caused by air-oxidation is undoubtedly a Co(III) complex. Elemental analysis indicates formula [Co(edda)(OH)(H_2O)]. This is supported by taking the formation condition into consideration, since no inorganic anion besides a hydroxide ion was present in the solution from which the crystals were obtained. The infrared spectrum shows a carboxylate stretching vibration due to COO–Co(III) at 1650 cm^{-1}. An octahedral configuration is seen in its electronic spectrum in solid which exhibits a typical d–d transition pattern having an absorption maxima at 18.7 kK and 26.3 kK (Fig. 5). Co(III) complexes of EDDA were investigated by several authors[6] and their stereochemistry has already been established. However, the geometry of the hydroxide ion and the water molecule in the octahedral arrangement is not clear in the present complex.

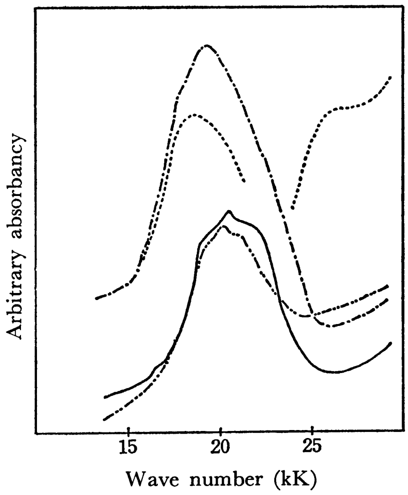

Fig. 5. Reflectance spectra of EDDA-Co(II) and EDDA-Co(III) complexes; ——: pink diaquo-EDDA-Co(II); —·—: violet anhydrous EDDA-Co(II); —··—: pink EDDA-Co(II) from violet one by aquation; ----: violet EDDA-Co(III).

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[6] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965); J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967); J. L. Sudmeier and G. Occupati, *ibid.*, **7**, 2524 (1968); C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969); P. F. Coleman, J. I. Legg, and J. Steele, *ibid.*, **9**, 937 (1970); K. Kuroda and K. Watanabe, This Bulletin, **44**, 1034 (1971); K. Kuroda, *Chem. Lett.*, **1972**, 197, 719.