March, 1987] © 1987 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 60, 1183—1185 (1987) 1183

Preparation and Characterization of the Dicobalt(III) Complexes Containing Bridging Di-μ-hydroxo Ligands

Tomoharu Ama,* Hiroshi Kawaguchi, and Takaji Yasui
Department of Chemistry, Faculty of Science, Kochi University,
Akebono-cho, Kochi 780

(Received September 13, 1986)

Synopsis. Three dicobalt(III) complexes, $[(L)Co(\mu\text{-}OH)_2Co(NH_3)_4]^{2+\text{ or }+}$ (L=edda, (gly)$_2$, or nta), were newly prepared and their structures were assigned on the basis of absorption, ^{1}H NMR, and CD spectral data. Each of them has a structure in which the chromophores of two different types are bridged with two hydroxo ligands and with two hydrogen bonds between carboxyl and amino groups. These three complexes are stable for several days in aqueous solutions.

Although there have been many reports on the preparation and reactivity of dicobalt(III) complexes containing two bridging hydroxo ligands, only a few studies have reported on complexes in which two different cobalt(III) chromophores were bridged with the two hydroxo.[2,3] Complexes of this type are so important for investigations concerning the interaction between two cobalt atoms that a sure method to prepare a number of complexes of this type is required. In previous work,[4] we succeeded in preparing three isomers of $[(en)(gly)Co(\mu\text{-}OH)_2Co(en)(gly)]^{2+}$[1,4] in aqueous solutions. A modification of the method, which is described below, makes it possible to prepare many dicobalt complexes containing two bridging hydroxo. Two of the newly prepared complexes have chiral structures. The CD spectra of the optically resolved isomers will be reported.

Experimental

Preparation of Complexes. $[(edda)Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl_2$ (1): In 20 cm^3 of water, $K[Co(edda)(CO_3)]\cdot H_2O$ (1.7 g)[5] was dissolved and acidified with 60% perchloric acid (2 cm^3). Separately, $[Co(NH_3)_4(CO_3)]ClO_4$ (1.5 g) were suspended in 20 cm^3 of water and acidified with 60% perchloric acid (2 cm^3). The two solutions were mixed with each other. The pH of the mixed solution was adjusted to 8.0 with a 2 mol dm^{-3} NaOH solution and stirred for 40 min in a water bath at 50 °C. The reacted solution was cooled to room temperature and then neutralized using a 2 mol dm^{-3} HCl solution and filtered. The filtrate was chromatographed on an SP-Sephadex column (4.7 cm×50 cm, K$^+$ form) and the adsorbed band was eluted with a 0.2 mol dm^{-3} KCl solution. The eluate from the dark-red band was evaporated to about 10 cm^3 and the KCl deposited was filtered off. To the filtrate, methanol was added in order to eliminate any excess KCl; then, solution was filtered. A crude complex of $[(edda)Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl_2$, obtained by adding ethanol to the filtrate, was optically resolved by the following procedure without further purification.

The crude complex (ca. 100 mg) was dissolved in 20 cm^3 of water and the solution was poured onto an SP-Sephadex column (4.7 cm×50 cm, K$^+$ form). The adsorbed band was developed with a 0.1 mol dm^{-3} $K_2Sb_2(d\text{-tart})_2$ solution. The development was repeated on the same column using a micropump until the adsorbed band completely separated into two dark-red bands. The earlier and later bands denoted (−) and (+) CD signs at 574 nm, respectively. Each band was eluted out with 0.1 mol dm^{-3} $K_2Sb_2(d\text{-tart})_2$; then, each eluate was concentrated to a small volume under reduced pressure. To the concentrated solution, methanol was added to deposit $K_2Sb_2(d\text{-tart})_2$. After the deposited $K_2Sb_2(d\text{-tart})_2$ was filtered off, the filtrate was evaporated almost to dryness in order to exclude methanol. The obtained residue was dissolved in a small amount of water and reloaded on a short QAE-Sephadex column (3 cm×5 cm, Cl$^-$ form). The solution eluted with water was concentrated to a small volume. An optically active isomer was obtained by adding methanol to the concentrated solution, which was recrystallized from water by adding methanol. Found for the $(+)^{CD}_{574}$ isomer: C, 14.84; H, 5.48; N, 17.07%. Calcd for $[(edda)Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl_2\cdot H_2O$=$C_6H_{26}N_6O_7Cl_2Co_2$: C, 14.92; H, 5.43; N, 17.40%.

$[(gly)_2Co(\mu\text{-}OH)_2Co(NH_3)_4]S_2O_6$ (2): This complex was prepared and resolved by a method similar to that employed for **1**, except for the use of $K[Co(gly)_2(CO_3)]$[6] instead of $K[Co(edda)(CO_3)]$. The dithionate of this complex was obtained by adding a saturated solution of $Na_2S_2O_6$ to the aqueous solution (saturated) of the chloride. Found for the $(+)^{CD}_{572}$ isomer: C, 8.28; H, 4.78; N, 14.39%. Calcd for $[(gly)_2Co(\mu\text{-}OH)_2Co(NH_3)_4]S_2O_6\cdot 3H_2O$=$C_4H_{28}N_6O_{15}S_2Co_2$: C, 8.25; H, 4.85; N, 14.43%.

$[(nta)Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl$ (3): In 12 cm^3 of 15% perchloric acid, $[Co(NH_3)_4(CO_3)]ClO_4$ (1.5 g) was dissolved. Separately, $K_2[Co(nta)(CO_3)]$ (2.0 g) was dissolved in 12 cm^3 of perchloric acid. The two solutions were mixed to each other. The pH of the solution was adjusted to 7.5 with a 2 mol dm^{-3} NaOH solution, and heated in a water bath (60 °C) for 30 min. After cooling to room temperature, the solution was diluted to 200 cm^3 with water and poured onto an SP-Sephadex column (4.5 cm×50 cm, K$^+$ form). After the column was swept with 1 dm^3 of water, the adsorbed band was developed with a 0.2 mol dm^{-3} KCl solution. A solution eluted from the dark-violet band (major band) was evaporated to about 10 cm^3. White precipitates, which became deposited upon the addition of methanol (100 cm^3) to the solution, were filtered off. To the filtrate, 100 cm^3 of methanol was added once more and the methanolic solution was allowed to stand overnight in a refrigerator in order to obtain crude **3**, which was recrystallized from water by adding methanol. Found: C, 15.08; H, 4.92; N, 14.49%. Calcd for $[(nta)Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl\cdot 2H_2O$=$C_6H_{24}N_5O_{10}ClCo_2$: C, 15.03; H, 5.04; N, 14.60%.

Results and Discussion

Structural Assignments of the Complexes. On the basis of the following five reasons, **1** was assigned to the structure given in Fig. 1 (A). (1) The column chromatogram gave a single band which was not a mixture of cationic and anionic complexes but was a cationic complex. (2) The elemental analysis data indicates that the NH$_3$/edda ratio is 4. (3) The absorption spectrum shows a characteristic charge-transfer band arising from the Co(μ-OH)$_2$Co moiety at ca. 34000 cm^{-1} (Fig. 2), as [Co$_2$(μ-OH)$_2$(en)$_4$]$^{4+}$ and [Co$_2$(μ-OH)$_2$(NH$_3$)$_8$]$^{4+}$ [8,9] show. (4) The first absorption band is very broad, suggesting that this complex contains chromophores of two different types. (5) In the ^{1}H NMR spectra (Fig. 3), the methylene protons of two glycinate rings (G-rings) in edda appeared as a quartet signal, suggesting that the two G-rings are equivalent in chemical environments; the edda takes an α-cis chelation form[10] (Fig. 3).

The structure illustrated in Fig. 1 (B) is proposed for the **2** on the basis of an arrangement similar to that described above. The possiblity that the Co(gly)$_2$(μ-OH)$_2$ moiety in this complex has a *trans(N)* structure can be ruled out for the following reasons. (1) The absorption spectrum of **2** is quite similar to that of **1**, having a *cis(N)* structure. (2) If the Co(gly)$_2$(μ-OH)$_2$ moiety has a *trans(N)* structure, it is expected that **2** exhibits a band (shoulder) at ca. 16000 cm^{-1}.[11,12] No such shoulder band appears, as shown in Fig. 2. Therefore, this moiety does not have a *trans(N)*-[Co(N)$_2$(O)$_4$] chromophore but has *cis(N)*. (3) Di(μ-hydroxo)dicobalt(III) complexes prefer a structure that is stabilized by two hydrogen bonds (N–H···OCO–) between the two cobalt chromophores (vide post). These hydrogen bonds can be formed in the proposed *cis(N)* structure but not in a *trans(N)* structure.

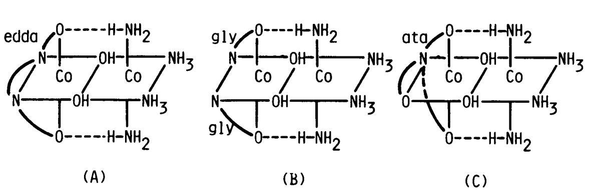

Fig. 1. Structures of the prepared complexes: (A) [(edda)Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ (**1**), (B) [(gly)$_2$Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ (**2**), and (C) [(nta)Co(μ-OH)$_2$Co-(NH$_3$)$_4$]$^+$ (**3**).

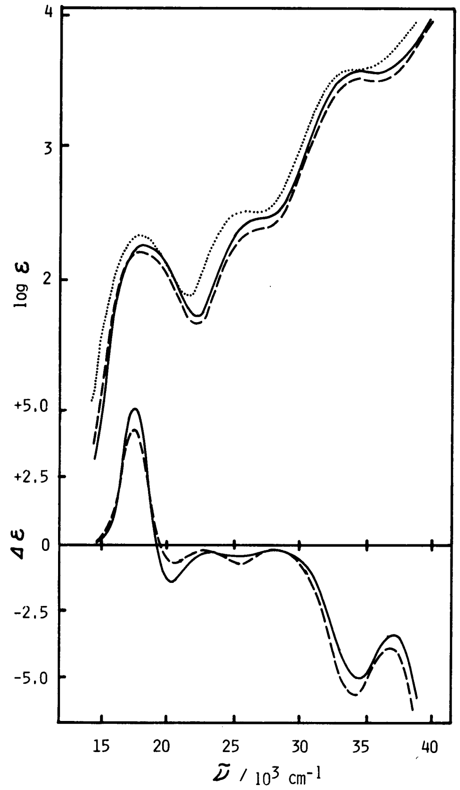

Fig. 2. Absorption and CD curves of the complexes: **1** (——), **2** (– – –), and **3** (······).

The structure illustrated in Fig. 1 (C) is proposed for the **3** on the basis of the following: (1) There are three G-rings in the nta. Two of them appear as a quartet signal in the ^{1}H NMR spectra, showing that their chemical environments are equivalent, and one of them appears as a singlet signal. This result shows that there is a symmetrical plane on one of the G-rings and that the nta coordinates to Co(III) as a quadridentate. (2) The elemental analysis data indicates that the NH$_3$/nta ratio is 4. (3) The absorption spectrum of **3** shows a characteristic charge-transfer band at ca. 33900 cm^{-1} with an intensity similar to those of **1** and **2**, suggesting the di-μ-hydroxo structure. Though some geometrical isomers are possible for [(edda)Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ and [(gly)$_2$Co(μ-OH)$_2$Co(NH$_3$)$_4$)]$^{2+}$, only one geometrical isomer (achiral) is possible for this [(nta)Co-(μ-OH)$_2$Co(NH$_3$)$_4$]$^+$.

CD Spectra. The CD spectra of the optically active complexes are illustrated in Fig. 2. $(+)^{\mathrm{CD}}_{574}$ **1** and $(+)^{\mathrm{CD}}_{572}$ **2** show quite similar CD patterns to each other. The absolute configuration around Co(gly)$_2$(μ-OH)$_2$ or Co(edda)(μ-OH)$_2$ moiety is assigned to Λ, because their main CD components in the first absorption band region are (+).[13]

A CD band ($|\Delta\varepsilon|=4-5$) was observed in the charge-transfer band region (ca. 34000 cm^{-1}) in each of the resolved complexes. However, the $|\Delta\varepsilon|$ values are about one half of that observed for the optically active isomer of the [(en)(gly)Co(μ-OH)$_2$Co(en)(gly)]$^{2+}$ complex ($|\Delta\varepsilon|=10.0$).

Stability of the Complexes. Absorption spectral changes with time were measured for aqueous solutions of some di-μ-hydroxo complexes at 20 °C. Solutions of the present complexes showed no spectal change for several days, while that of [Co$_2$(μ-OH)$_2$(NH$_3$)$_8$]Br$_4$ showed an obvious change after one day. This result means that the present complexes are more stable than [Co$_2$(μ-OH)$_2$(NH$_3$)$_8$]$^{4+}$, suggesting that some stabilizing factors exist in the present complexes. Regarding an X-ray study of [Cr$_2$(L-

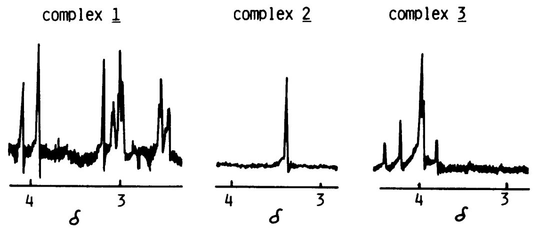

Fig. 3. ^{1}H NMR Spectra of the complexes.

pro)$_4$(μ-OH)$_2$], Oki and Yoneda[14] pointed out that the two intramolecular N-H⋯O hydrogen bonds (bridging two chromophores) stabilize the di-μ-hydroxo structure. Accordingly, it is reasonable to propose two hydrogen bonds as the stabilizing factor of the present complexes. It was not easy to prepare isomers having one or no hydrogen bonds, but it was easy to prepare some having two hydrogen bonds. This result agrees with that obtained for the isomers of [(en)(gly)Co$_2$(μ-OH)$_2$Co(en)(gly)]$^{2+}$,[4] suggesting that the hydrogen bond is important as one of the stabilizing factors.

References

1) The following abbreviations are used in the present paper: H$_2$edda=ethylenediamine-*N,N′*-diacetic acid; Hgly=glycine; H$_3$nta=nitrilotriacetic acid; en=ethylenediamine.

2) K. Nakamoto, J. Fujita, and H. Maruta, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

3) W. Hackbusch, H. H. Rupp, and K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, **1975**, 1015.

4) T. Ama, A. Mukai, K. Miyauchi, H. Kawaguchi, and T. Yasui, *Mem. Fac. Sci. Kochi Univ., Ser C*, **7**, 1 (1986).

5) M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, *Bull. Chem. Soc. Jpn.*, **35**, 75 (1962).

6) M. Shibata, H. Nishikawa, and Y. Nishida, *Inorg. Chem.*, **7**, 9 (1968).

7) M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, *Bull. Chem. Soc. Jpn.*, **31**, 940 (1958).

8) H. Kuroya and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **15**, 427 (1940).

9) J. Springborg and C. E. Schäffer, *Inorg. Synth.*, **18**, 75 (1978).

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

11) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

12) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **40**, 1868 (1968).

13) Y. Shimura, Kagaku Sosetsu, No. 13, 83 (1976).

14) H. Oki and H. Yoneda, *Inorg. Chem.*, **20**, 3875 (1981).