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Studies of the Mixed Chromium(III) Complexes Containing Ethylenediamine-*N*,*N'*-diacetic Acid*[1]

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Three new mixed chromium(III) complexes containing ethylenediamine-*N*,'*N*-diacetic acid (EDDA) and amino acid, [Cr(edda)(L)] (L=anion of glycine, α-alanine and β-alanine), were prepared from $[Cr_2(OH)_2(edda)_2]\cdot 6H_2O$. On the basis of their chemical analyses and the visible and infrared absorption spectra, the geometrical structure of the three mixed ligand complexes was estimated to be the facial form with respect to the coordinated three nitrogen atoms, where the configuration of the coordinated edda was inferred to take the β-form (*cis* with respect to the coordinated oxygen atoms of edda). The new mixed ligand complex containing the glycine anion, $[Cr(ox)(gly)(en)]\cdot H_2O$, was also prepared from *cis*-$[Cr(ox)(H_2O)_2(en)]Br$, and its geometry was discussed in the connection with its visible absorption spectrum.

In a previous paper1) the preparation of the chromium(III) complexes containing ethylenediamine-*N*,*N'*-diacetic acid (EDDA) was reported. The configuration of the coordinated edda was, however, not established on the basis of their visible absorption spectra, because it was very difficult to distinguish whether the configuration of edda takes the α-form or the β-form on the basis of only their visible absorption spectra in general.

However, if it is possible to prepare the mixed ligand chromium(III) complexes containing edda and the anion of amino acid, their visible absorption spectra will be very useful in identifying the configuration of edda. Thus, if the spectra of the mixed ligand complexes show the pattern of the spectra of a facial-form (N_3O_3)-type complex, the configuration of edda can be determined to be the β-form. Therefore, we tried to prepare the mixed ligand complexes of the [Cr(edda)(L)]*[2] type (L= glycine, α-alanine, and β-alanine), investigating the geometry of these complexes on the basis of their visible absorption spectra.

Since the spectral data of (N_3O_3)-type chromium(III) complexes are scanty, we also tried to prepare a mixed-ligand complex, $[Cr(ox)(gly)(en)]\cdot H_2O$, to provide additional spectral information.

Experimental

Preparation. *1) Ethylenediamine-N,N'-diacetatoglycinatochromium(III) Dihydrate,* $[Cr(edda)(gly)]\cdot 2H_2O$ (I). All three mixed-ligand complexes containing edda were derived from bis-(ethylenediamine-*N*,*N'*-diacetato)-μ-dihydroxodichromium(III) hexahydrate, $[Cr_2(OH)_2(edda)_2]\cdot 6H_2O$ (i).1) A 2.8 g portion (0.005 mol) of the (i) complex as a starting material was suspended in 15 m*l* of water and warmed on the water bath. Then, 4.5 g (0.06 mol) of glycine were added and the mixture was maintained at 90°C for half an hour. When the complex (i) was then gradually dissolved in water, the color of the solution turned from purple to a reddish purple. About 50 m*l* of ethanol were then added, and the glycine thus precipitated was removed by filtration. When the solution was cooled to 0°C, reddish crystals were separated out. They were washed with hot 80% ethanol. Yield, about 2.7 g (81.8%). Found: C, 28.55; H, 5.51; N, 12.18%. Calcd for $[Cr(edda)(gly)]\cdot 2H_2O$: C, 28.57; H, 5.41; N, 12.51%.

2) Ethylenediamine-N,N'-diacetato-α-alaninatochromium(III) Dihydrate, $[Cr(edda)(\alpha\text{-ala})]\cdot 2H_2O$ (II). A 2.8 g portion (0.005 mol) of the complex i was suspended in 15 m*l* of water, and the resulting mixture was warmed on the water bath. 5.3 g (0.06 mol) of α-alanine were then added, and the mixture was heated to about 90°C. When the color of the solution turned from purple to a reddish purple, about 50 m*l* of ethanol were added. On cooling to 0°C, reddish crystals were separated out. The crystals were washed with hot 80% ethanol. Yield, about 2.9 g (82.2%). Found: C, 31.09; H, 5.74; N, 12.29%. Calcd for $[Cr(edda)(\alpha\text{-ala})]\cdot 2H_2O$: C, 30.85; H, 5.77; N, 12.00%.

3) Ethylenediamine-N,N'-diacetato-β-alaninatochromium(III) Monohydrate, $[Cr(edda)(\beta\text{-ala})]\cdot H_2O$ (III). This

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1) Y. Fujii, E. Kyuno and R. Tsuchiya, This Bulletin, **42**, 1569 (1969).

*[2] The abbreviations in this paper are as follows: edda, the dianion of ethylenediamine-*N*,*N'*-diacetic acid; gly, the anion of glycine; ala, the anion of alanine; ambuty, the anion of aminobutyric acid; leu, the anion of leucine; ox, the dianion of oxalic acid; en, ethylenediamine.

2) E. Kyuno, N. Tanaka and M. Kamata, Read at the 12 th Symposium on Coordination Chemistry of the Chemical Society of Japan, Tokyo, November, 1962.

Table 1. IR spectra for the complexes (cm^{-1})*

Complex	NH$_2$ str.	COO asym. str.	NH$_2$ bend.	COO sym. str.	NH$_2$ wag.	CCN in-phase str.
I	3150 3230 3270	1645	1575	1382	1305	925
II	3160 3270	1650	1588	1360	1288	930
III	3125 3150 3220	1630 1658	1592	1371 1409	1292	918 927
IV	3150 3240	1640	1615	1385	1318	916

* Abbreviations: str.=stretching; asym.=antisymmetric; sym.=symmetric; wag.=wagging; bend.=bending.

substance was prepared from the complex i and β-alanine in the manner described above in 2). Reddish crystals were obtained in an 80.0% yield. Found: C, 32.53; H, 5.47; N, 12.65%. Calcd for [Cr(edda)(β-ala)]·H$_2$O: C, 32.52; H, 5.42; N, 13.21%.

4) Oxalatoglycinatoethylenediaminechromium(III) Monohydrate, [Cr(ox)(gly)(en)]·H$_2$O (IV). To an aqueous solution of 4.0 g (0.013 mol) of *cis*-oxalatodiaquoethylenediaminechromium(III) bromide,[2] *cis*-[Cr(ox)(H$_2$O)$_2$-(en)]Br, 2.0 g (0.073 mol) of glycine were added, the solution was kept at about 60°C for five minutes. The solution was then cooled to 0°C, whereby a small amount of impurity was deposited out. After the impurity had been filtrated off, 1 g of glycine was added to the filtrate heated to 80°C. The pH of the solution was adjusted to 5.5 by dilute aqueous ammonia, and the resulting solution was allowed to stand for 3 days at room temperature. A pink powder was thus separated out and washed with hot water. Yield, about 2.2 g (60.0%). Found: C, 25.10; H, 4.74; N, 14.56%. Calcd for [Cr(ox)(gly)(en)]·H$_2$O: C, 25.49; H, 4.84; N, 14.39%.

Measurements. The visible absorption spectra of the complexes obtained were recorded on a EPS-3 Hitachi recording spectrometer at room temperature. Since the complex I, II and III all decompose to yield the complex i in an aqueous solution at room temperature, the spectra were measured by using dimethylsulfoxide (the complex I and II) or 50% dimethylsulfoxide (the complex III). Water was used as the solvent in the spectral measurement of the complex IV. The IR spectra were taken on potassium bromide disks using a Hitachi EPI-S2 spectrometer.

Results and Discussion

IR Spectra. The infrared absorption spectra were measured to confirm whether the carboxylate groups were coordinated or not. Since all the spectra of the complexes studied showed asym. νCOO–Cr bands in the range from 1630 to 1670 cm^{-1}, as is shown in Table 1, and since there was no band due to the free carboxylate or free carboxylic acid group, it is clear that all the carboxylate groups are coordinated to the chromium(III) ion.[3–5]

In the case of the complex III, two bands assigned to the asym. νCOO–Cr band were observed, these bands can be explained as follows. Since β-alanine may form a six-membered ring with the chromium(III) ion in the complex III and since the steric strain is thought to be larger in the six-membered ring than in the five-membered ring, the band assigned to the νCOO–Cr of β-alanine will shift to lower evergy sites compared with the band assigned to the νCOO–Cr of acetate groups.

Electronic Absorption Spectra. The visible absorption spectra of the complexes are shown in Figs. 1 and 2. The numerical values of the absorption maxima are summarized in Table 2, together with those of related compounds.[5–10]

It is found that the first bands of the complex I, II, and III have the only one peak located at sites of higher energy than that of the fac-(N$_3$O$_3$) type chromium(III) complexes, [Cr(L)$_3$](L=anions of glycine, α-alanine, α-amynobutylic acid and *l*-leucine).

On the other hand, the four cobalt(III) complexes with amino acids, fac-[Co(gly)$_3$]·H$_2$O, fac-[Co(α-ala)$_3$], mer-[Co(edda)(gly)]·2H$_2$O and mer-[Co(edda)(α-ala)]·2H$_2$O, have been reported to show the first bands at 57.7×10^{13}/sec, 58.0×10^{13}/sec, 55.3×10^{13}/sec, and 55.3×10^{13}/sec respectively. Since the interpretations of the absorption peaks of cobalt(III) complexes are thought to hold also for the discussions of those of chromium(III)

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3) D. H. Bush and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953); **78**, 716 (1956).

4) A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran and J. V. Quagliqno, *ibid.*, **80**, 5018 (1958).

5) M. Mori, M. Shibata, E. Kyuno and M. Kanaya, This Bulletin, **34**, 1837 (1961).

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7) R. W. Green and K. P. Ang, *J. Am. Chem. Soc.*, **77**, 4582 (1955).

8) M. Mizuochi, E. Kyuno and R. Tsuchiya, Read at the 18 th Symposium on Coordination Chemistry of the Chemical Society of Japan, Kyoto, Oct., 1968, p. 223.

9) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

10) J. I. Legg, D. W. Cooke and B. E. Douglas, *Inorg. Chem.*, **6**, 700 (1967).

Table 2. Absorption spectra fot the complexes*

Complex	ν_1 (log ε)	ν_2 (log ε)	ν_3 (log ε)
I	59.4 (1.95)	81.5 (2.01)	
II	59.4 (1.94)	81.5 (1.96)	
III	60.2 (2.04)	81.1 (1.97)	
IV	57.8 (1.92)	77.3 (1.93)	112.4 (2.38)
fac-[Cr(gly)$_3$]·3H$_2$O6)	55.2 (1.60)	75.0 (1.65)	
fac-[Cr(α-ala)$_3$]·2H$_2$O7)	56.0 (1.85)	75.4 (1.75)	
fac-[Cr(α-ambuty)$_3$]·2H$_2$O8)	55.8 (1.87)	75.0 (1.79)	
fac-[Cr(*l*-leu)$_3$]·2H$_2$O8)	57.7 (1.67)	76.9 (1.79)	
fac-[Co(gly)$_3$]·H$_2$O5),9)	57.7 (2.16)	79.6 (2.08)	140.2 (4.45)
fac-[Co(α-ala)$_3$]5)	58.0 (2.22)	80.4 (2.21)	
mer-[Co(edda)(gly)]·2H$_2$O10)	55.3 (1.95)	63.9 (sh)	
mer-[Co(edda)(α-ala)]·2H$_2$O10)	55.3 (1.98)	64.4 (sh)	

* The frequencies are given in 10^{13}/sec.

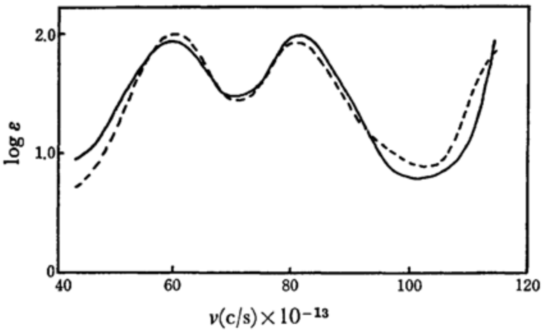


Fig. 1. Electronic absorption spectra.
(——): [Cr(edda)(gly)]·2H$_2$O
(- - -): [Cr(edda)(β-ala)]·H$_2$O

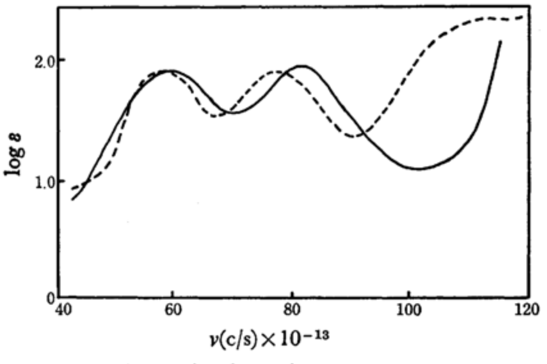
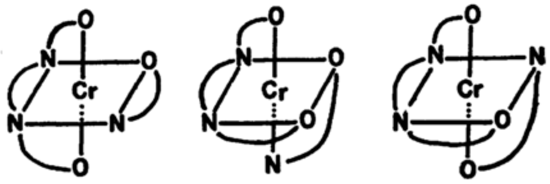


Fig. 2. Electronic absorption spectra.
(——): [Cr(edda)(α-ala)]·2H$_2$O
(- - -): [Cr(ox)(gly)(en)]·H$_2$O

complexes under these circumstances,11) values of 53.0×10^{13}/sec and 53.5×10^{13}/sec may be anticipated as the peaks of the mer-form complexes of [Cr(edda)(L)] (L=glysine and α-alanine) on the basis of the values of the absorption peaks on fac-[Cr(gly)$_3$]·3H$_2$O and fac-[Cr(α-ala)$_3$]·2H$_2$O.



(a) mer(N) (b) fac(N) (c) mer(N)

Fig. 3. Possible structures of [Cr(edda)(amino acid)].

Since the peaks of the I, II, and III complexes appeared at about 59.5×10^{13}/sec and since these values are too high to assign the configuration of the complexes to the mer-form one, it may be suggested that the configuration of the complexes [Cr(edda)(L)](L=anion of glycine, α-alanine and β-alanine) may be fac-form with respect to the coordinated three nitrogen atoms. Though there are three possible geometrical structures for [Cr(edda)(L)], only one structure is possible as a fac-form one. Therefore the structure (b) in Fig. 3 is the most probable as the structure of the complexes I, II, and III. From these observations, it can be concluded that the configuration of edda may take the β-form (*cis* with respect to the coordinated carboxylate oxygen atoms of edda).

Since the complex IV shows the first band at 57.8×10^{13}/sec, and since this band seems to be constructed from only one peak, the configuration of the complex IV probably takes the fac-form with respect to the coordinated three nitrogen atoms.

When plotting the locations of the first band (in sec^{-1}) of the chromium(III) complexes containing oxalic acid and/or ethylenediamine2,12) against the number of the nitrogen atoms participating in the coordination bond formation, we can obtain

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11) H. Yamatera, this Bulletin, **31**, 95 (1956).

12) K. Sone, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **71**, 270 (1950).

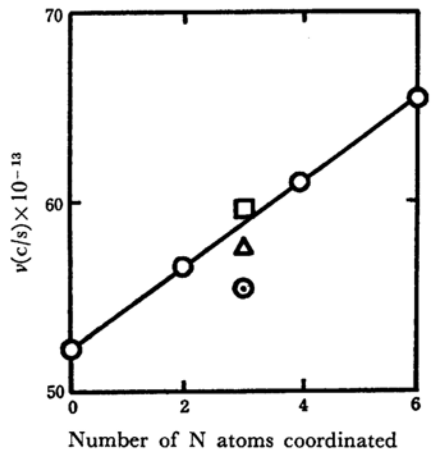

Fig. 4. Frequency positions of the first band of the chromium(III) complexes.

□: $[Cr(edda)(gly))] \cdot 2H_2O$;
△: $[Cr(ox)(gly)(en)] \cdot H_2O$;
⊙: $[Cr(gly)_3] \cdot 3H_2O$;
○: 0, $[Cr(ox)_3]^{3-}$; 2, $[Cr(ox)_2(en)]^-$;
4, $[Cr(ox)(en)_2]^+$; 6, $[Cr(en)_3]^{3+}$.

the linear relation shown in Fig. 4.[13] From this linear relation, a value of *ca.* 59.0×10^{13}/sec is obtained as the maximum of the first band of the (N_3O_3)-type chromium(III) complex. On the other hand, it has been reported that the amino acid complexes with the chromium(III) ion, which have been identified as (N_3O_3)-type complexes,[6-8] show the first band between 55.0 and 58.0×10^{13}/sec. Therefore, it may be reasonable to conclude that the mixed chromium(III) complex containing oxalic acid, glycine, and ethylenediamine, [Cr(ox)(gly)(en)], shows the first band at about 58.0×10^{13}/sec, which is intermediate between the 55.0×10^{13}/sec of the tris-glycine complex and the 59.0×10^{13}/sec of the oxalato-ethylenediamine complex.

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13) M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, **29**, 883 (1956).