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Chromium(III) Complexes with *N,N'*-Ethylenediaminediacetic Acid[*1]

Yuki FUJII,[*2] Eishin KYUNO and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

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The following chromium(III) complexes containing N,N'-ethylenediaminediacetic acid (EDDA) were newly prepared: $[Cr(Hedda)_2]Cl\cdot 3H_2O$ (red) (I), $[Cr_2(OH)_2(edda)_2]\cdot 6H_2O$ (purple) (II), $H[Cr(edda)(ox)]\cdot 2H_2O$ (purple) (III), $[Cr(edda)(dip)]I\cdot 5H_2O$ (orange) (IV), $K[Cr(NCS)_2(edda)]\cdot H_2O$ (reddish purple) (V) and $[Cr(Cl)(edda)(H_2O)]\cdot 3H_2O$ (bluish purple) (VI), where edda, ox and dip are the abbreviations of the N,N'-ethylenediaminediacetate and oxalate anions, and α,α'-dipyridyl respectively. On the basis of the experimental results, it was concluded that EDDA is coordinated as a terdentate ligand in complex I and as a quadridentate in the other complexes prepared in the present work. Furthermore, it was also suggested that complex II has a dimer structure and complex V has *trans* configuration (with respect to the coordinated carboxylate oxygen).

The preparation and properties of the cobalt(III) complexes with N,N'-ethylenediaminediacetic acid (EDDA) have already been reported;[1-3] here EDDA behaves only as a quadridentate ligand, not as a terdentate toward a cobalt(III) ion. In the case of the platinum(II) and platinum(IV) complexes with EDDA, however, it has been pointed out that the ligand behaves as a bidentate or quadridentate toward a platinum(II) ion, whereas it behaves as a terdentate or a quadridentate toward platinum(IV) ion.[4]

The purpose of this study was to find how EDDA could behave toward a chromium(III) ion by attempting to prepare various complexes containing EDDA as a quadridentate or a terdentate ligand and to investigate the structure of these complexes.

Experimental

Preparation of the Complexes. *1) Bis-(hydrogen-N, N'-ethylenediaminediacetato)chromium(III) Chloride Trihydrate,* $[Cr(Hedda)_2]Cl\cdot 3H_2O$ (I). To the aqueous solution of chromium(III) chloride hexahydrate (5g, 0.019 mol), about 10g (0.056 mol) of EDDA were added and the mixture was heated on a water bath. After adjusting the pH of the solution to 2—3, it was cooled to 0°C. Pink crystals were separated out and recrystallized from aqueous solution. Yield, 2.5g (27.1%). Found: Cr, 10.27; C, 29.46; H, 5.41; N, 11.31; Cl, 7.35%. Calcd for $[Cr(Hedda)_2]Cl\cdot 3H_2O$: Cr, 10.57; C, 29.30; H, 5.75; N, 11.39; Cl, 7.24%.

Bromide of the complex I, $[Cr(Hedda)_2]Br\cdot 3H_2O$, was obtained by treating the mixed acetylacetone complex, $[Cr(acac)(edda)]\cdot 2H_2O$,[5] with N-bromosuccinimide in glacial acetic acid. Found: C, 27.14; H, 5.33; N, 10.57%. Calcd for $[Cr(Hedda)_2]Br\cdot 3H_2O$: C, 26.97; H, 4.91; N, 10.49%.

2) Bis-(ethylenediaminediacetato)-μ-dihydroxodichromium(III) Hexahydrate, $[Cr_2(OH)_2(edda)_2]\cdot 6H_2O$ (II). Five

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[*2] Present address: Department of Chemistry, Faculty of Science, Ibaraki University, Mito.

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

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

3) J. I. Legg, D. W. Cooke and B. E. Douglas, *ibid.*, **6**, 700 (1967).

4) C. F. Liu, *ibid.*, **3**, 680 (1964).

5) Y. Fujii, E. Kyuno and R. Tsuchiya, This Bulletin, **42** 1301 (1969).

grams (0.01 mol) of complex I were suspended in 50ml of water and the mixture was heated on a water bath. The complex I was gradually dissolved as a small amount of ammonium carbonate was added and then the color of the solution turned from red to purple. After adjusting the pH of the solution to about 7, it was cooled to 0°C. Reddish purple crystals were separated out and recrystallized from aqueous solution. Yield, 2.5g (84.2 %). Found: Cr. 17.73; H$_2$O, 17.20%. Calcd for [Cr$_2$(OH)$_2$(edda)$_2$]·6H$_2$O: Cr, 17.50; H$_2$O, 18.19%.

The thermal decomposition for this complex was carried out and the complexes which contain various amount of water of crystallization were obtained by successive dehydration. The dehydrated products at several desined temperatures were as follows: [Cr$_2$·(OH)$_2$(edda)$_2$] 4H$_2$O (at 46°C) (Found: C, 26.42; H, 5.32; N, 10.27%. Calcd: C, 25.81; H, 5.09; N, 10.03%), [Cr$_2$(OH)$_2$(edda)$_2$]·2H$_2$O (at 80°C) (Found: C, 27.52; H, 5.09; N, 10.44%. Calcd: C, 27.59; H, 5.04; N, 10.73%), and [Cr$_2$(OH)$_2$(edda)$_2$] (at 110°C) (Found: Cr, 20.80; C, 29.84; H, 4.65; N, 11.12%. Calcd: Cr, 21.38; C, 29.63; H, 4.57; N, 11.52%.).

3) Hydrogen Ethylenediaminediacetatooxalatochromate(III) Dihydrate, H[Cr(edda)(ox)]·2H$_2$O(III). To the aqueous solution of the complex II (2.8g, 0.005 mol), 1.3g (0.01 mol) of oxalic acid dihydrate was added and the solution was heated on a water bath. After adjusting the pH the solution to 1—2 with a small amount of oxalic acid dihydrate, it was cooled to 0°C. Purple crystals were separated out. Yield, about 2.7g (83.6%). Found: Cr, 13.74; C, 27.01; H, 4.45; N, 7.89%. Calcd for H[Cr(edda)(ox)]·2H$_2$O: Cr, 14.81; C, 27.35; H, 4.02; N, 7.98%.

4) Ethylenediaminediacetato- α,α'-dipyridylchromium(III) Iodide Pentahydrate, [Cr(edda)(dipy)]I·5H$_2$O (IV). To the aqueous solution of the complex II (2.8)g, 1.6g (0.01 mol) of α, α'-dipyridyl was added and the mixture was heated on a water bath. After adjusting the pH of the solution to 3—4, about 5 g of sodium iodide, ethanol and ether were added. When it was cooled to 0°C, orange crystals were separated out and recrystallized from the mixed solution of water, ethanol and ether. Yield, about 2.6g (43.3%). Found: C, 32.32; H, 4.35; N, 8.50%. Calcd for [Cr(edda)(dipy)]I·5H$_2$O: C, 32.06; H, 4.72; N, 9.31%.

5) Potassium Diisothiocyanatoethylenediaminediacetatochromate(III) Monohydrate, K[Cr(NCS)$_2$(edda)]·H$_2$O (V). To the aqueous solution of the complex II (2.8g), 4g (0.04 mol) of potassium thiocyanate was added and the solution was heated on a water bath. After adjusting the pH of the solution to 4—5, it was cooled to 0°C. Reddish purple crystals were separated out and recrystallized from aqueous solution. Yield, about 2.4g (60.0%). Found: Cr, 13.19; C, 23.68; H, 3.12; N, 13.71%. Calcd for K[Cr(NCS)$_2$(edda)]·H$_2$O: Cr, 13.02; C, 24.06; H, 3.03; N, 14.03%.

6) Chloroethylenediaminediacetatoaquochromium(III) Trihydrate, [Cr(Cl)(edda)(H$_2$O)]·3H$_2$O (VI). To the aqueous solution of the complex II (2.8g,) 4g (0.03 mol) of ethylenediamine dihydrochloride was added and the solution was heated on a water bath. When it was cooled to 0°C, blusidh purple crystals were separated out. Yield, about 0.5g (15.0%). Found: Cr, 15.09; C, 22.15; H, 4.95; N, 8.48%. Calcd for [Cr(Cl)(edda)(H$_2$O)]·3H$_2$O: Cr, 15.58; C, 21.59; H, 4.84; N, 8.39%.

Apparatus. The absorption spectra, reflecting absorption spectra and infrared absorption spectra were measured with a Hitachi EPS Spectrophotometer, a Hitachi EPU-2A Spectrophotometer equipped with the standard Hitachi Reflection Attachment, and a Nippon Bunko DS-301 Infrared Spectrometer. The quantity of the water of crystallization contained in the complex II was estimated from TGA curves measured with Derivatograph. The magnetic susceptibility was measured with a Gouy balance at room temperature.

Results and Discussion

Electronic Absorption Spectra. The visible absorption spectra for the complexes I, II, IV, V and VI and those by the diffuse-reflectance method for the complexes II and III are shown in Fig. 1, Fig. 2 and Fig. 3, respectively, and the numerical values of the absorption maxima are summarized in Table 1 together with those of the related compounds.

The first absorption peak of the complex I is in good agreement with that of *trans*-K[Cr(ida)$_2$]·3H$_2$O,[*3] differing from that of the complexes II, III, and that of NH$_4$[Cr(edta)]·2H$_2$O[6] and [Cr(acac)(edda)]·2H$_2$O. From these results, it may be presumed that the complex I belongs to N$_2$O$_4$-type complex which has a *trans* structure

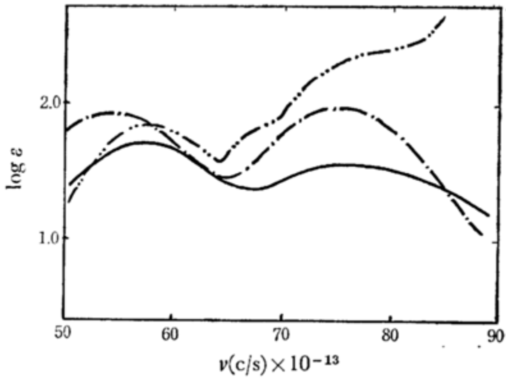

Fig. 1. Electronic spectra: I (——), II (—·—), IV (—··—).

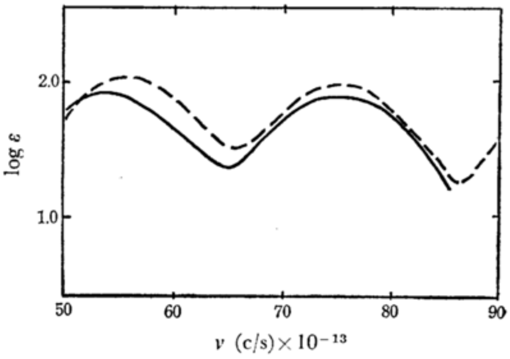

Fig. 2. Electronic spectra: V (----), VI (——).

[*3] It will be published elsewhere.

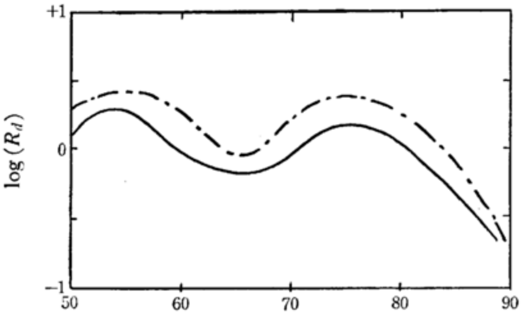

Fig. 3. Absorption spectra by the diffuse-reflectance method: II (—·—), III (——).

with respect to coordinated nitrogen atoms.

Since the spectrum of the complex II in an aqueous solution nearly agrees with the reflecting absorption spectrum of II, it may be suggested that the structure of the complex II in the solid state is also hold in the aqueous solution.

The spectra of the complexes II and III are very close to that of the edta complex, $NH_4[Cr(edta)]\cdot 2H_2O$, and they are also similar to the spectrum of the complex, $[Cr(acac)(edda)]\cdot 2H_2O$. Therefore, it may be suggested that the complexes II and III belong to N_2O_4-type.

The spectrum for the complex IV gives a complicated curve, showing two shoulders at 67.5×10^{13}/sec and at 79.0×10^{13}/sec, probably due to the α,α'-dipyridyl.

The complex V shows a specific absorption band at 100×10^{13} sec ($\log \varepsilon=2.99$) and the presence of this band indicates that the NCS^- coordinates with the chromium(III) ion.[7]

Since the spectrum of the complex VI in an aqueous solution was slowly turned to the spectrum of the complex II, it may suggest that the complex VI gradually undergoes dechlorination to form the dimer structure with respect to chromium(III) ion in an aqueous solution.

Derivatogram and Magnetic Moment. The derivatogram of the complex II is shown in Fig. 4. From the TGA curve, the formula of II may be $[Cr_2(OH)_2(edda)_2]\cdot 6H_2O$ and the composition of the thermal decomposition product between 100 and 180°C must be $[Cr_2(OH)_2(edda)_2]$.

The values of the effective magnetic moment of complex II and of the thermal decomposition products are remarkably lower than that of complex I which corresponds to the spin only value for tervalent chromium, as seen in Table 2. These facts may suggest that complex II and the thermal

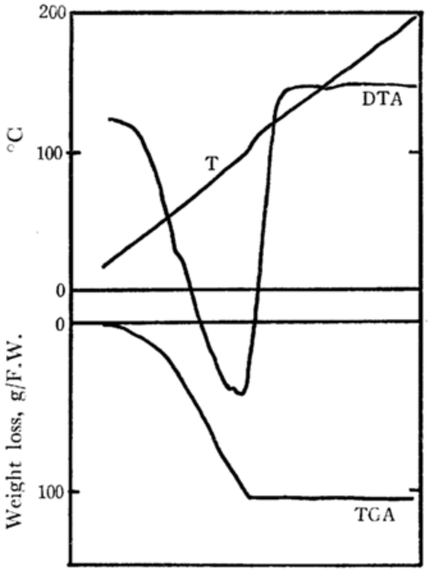

Fig. 4. Derivatogram of the complex II.

TABLE 1. ABSORPTION SPECTRA FOR THE COMPLEXES

Complex	ν_1 ($\log\varepsilon$)	ν_2 ($\log\varepsilon$)	ν_3 ($\log\varepsilon$)
I	57.5 (1.70)	75.0 (1.55)	
II	54.4 (1.93)	75.4 (1.96)	105.5 (sh)
	54.6 (+0.43)*	75.0 (+0.39)*	
III	54.2 (+0.31)*	75.8 (+0.18)*	
IV	57.5 (1.85)	67.5 (sh)	79.0 (sh) 97.1 (4.35)
V	56.3 (2.06)	60.6 (1.99)	100.0 (2.99)
VI	54.1 (1.91)	75.0 (1.87)	
$K[Cr(ida)_2]\cdot 3H_2O$	57.5 (1.85)	77.1 (1.87)	
$NH_4[Cr(edta)]\cdot 2H_2O$	55.2 (2.30)	76.5 (2.06)	
$[Cr(acac)(edda)]\cdot 2H_2O$	55.7 (2.00)	78.7 (2.33)	90.9 (3.80)
cis-$K[Cr(NCS)_2(ox)(en)]$	57.3 (2.07)	76.3 (1.99)	102.4 (3.70)

The frequencies are given in 10^{13} sec^{-1}.
* Data by the diffuse-reflectance method.

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6) E. Kyuno, Read at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

7) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 471 (1938).

Table 2. Magnetic moments

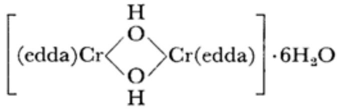
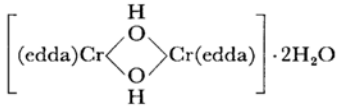
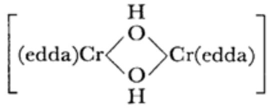
Complex	B. M.
	3.61
	3.52
	3.52
$[Cr(eddaH)_2]Cl \cdot 3H_2O$	3.89
spin only value	3.88

Table 3. IR data (cm^{-1})

Complex	-COO-Cr(III)
$eddaH_2$	1736 (-COOH)
$[Cr(edda\ H)_2]Cl \cdot 3H_2O$	1670, 1635
$[Cr_2(edda)_2(OH)_2] \cdot 6H_2O$	1635
$[Cr(edda)(dipy)]I \cdot 5H_2O$	1656
$H[Cr(edda)(ox)] \cdot 2H_2O$	1655
$K[Cr(NCS)_2(edda)] \cdot H_2O$	1670, 1622
$[Cr(Cl)(edda)(H_2O)] \cdot 3H_2O$	1675(sh), 1640, 1620
$[Cr(edda)(acac))] \cdot 2H_2O$	1675(sh), 1630

decomposition products have a dimer structure bridged by OH^- groups.[8]

IR Spectra. Infrared absorption spectra of the six new complexes were measured to confirm whether carboxylate groups were coordinated or not and to obtain the configurational informations on the coordinated edda. It is well known that the carboxylate group, in general, exhibits the absorption band in the region between 1700 and 1750 cm^{-1} for the free acids.[9]

All the spectra of the complexes studied show bands at 1620 and 1675 cm^{-1}, as seen in Table 3. Therefore, it will be obvious that these bands are due to coordinated carboxylate groups.

The complex V shows the strong $\nu_{C\equiv N}$ band at 2095 cm^{-1}, and *cis*-$K[Cr(NCS)_2(ox)(en)]$[10] shows three strong $\nu_{C\equiv N}$ bands at 2120, 2080 and 2062 cm^{-1}. These suggest that the complex V has a higher symmetry than *cis*-$K[Cr(NCS)_2(ox)(en)]$, and then, α-form may be considered as the configuration of edda in the complex V.

On the other hand, the complex $[Cr(acac)(edda)] \cdot 2H_2O$ shows the splitted bands of ν_{N-H} at 3260 and 3140 cm^{-1} and this suggests that the configuration of the edda in the complex may be β-form (*cis* with respect to coordinated carboxylate oxygens).

Properties of the Complexes. Complex II was prepared from complex I with the appropriate pH adjustment in an aqueous solution, but the conversed attempt to prepare complex I from complex II was successful only in the case when both the pH adjustment and the addition of $eddaH_2$ were achieved. This fact supports that the complex I is 1 : 2 complex, as mentioned in the term of the absorption spectra.

The structure of complex I is very interesting because it has two eight membered-rings in the complex and the edda coordinates to the metal ion as a terdentate ligand, with one nitrogen and two oxygen atoms.

Since it is very easy to expel the water of crystallization from complex II, it is dehydrated to $[Cr_2(OH)_2(edda)_2] \cdot 4H_2O$ not only from hot aqueous solution but also often even at room temperature.

Though complex VI is easily decomposed to complex II in an aqueous solution, it is certain that Cl^- coordinates to Cr(III) ion in the fresh solution of VI, because it is adsorbed by neither Na nor Cl form ion exchangers.

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[8] T. Morishita, K. Hori, E. Kyuno, and R. Tsuchiya, This Bulletin, **38**, 1276 (1965).

[9] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

[10] E. Kyuno, M. Kamada and N. Tanaka, Read at 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.