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# Bis-Type Cobalt(III) and Chromium(III) Complexes with Related Compounds of Iminodiacetic Acid[*1]

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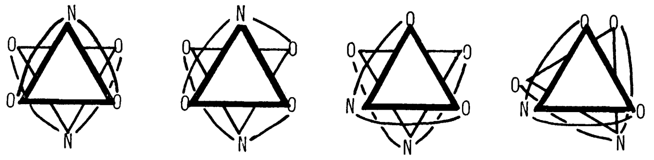
The geometrical structures and some properties of the following complexes were investigated: $K[Co(ida)_2]\cdot H_2O$ (I), $K[Co(ida)_2]\cdot 2H_2O$ (II), $K[Cr(ida)_2]\cdot 3H_2O$ (III), $Ba[Cr(ida)_2]_2\cdot 6H_2O$ (IV), $K[Co(mda)_2]$ (V), $K[Cr(mda)_2]$ (VI), $K[Co(eda)_2]\cdot H_2O$ (VII) and $K[Cr(eda)_2]\cdot H_2O$ (VIII), where ida, mda and eda are the abbreviations of iminodiacetate, methyliminodiacetate and ethyliminodiacetate ions, respectively. IV, VII and VIII are new compounds. On the basis of electronic spectra, it was found that VII and VIII have the *trans* form with respect to nitrogen atoms in the ligands, and IV, the *cis* form. Comparison of the properties and structures of the cobalt(III) complexes with those of the corresponding chromium(III) complexes were also made.

Although the stability constants[1,2] of the metal complexes with iminodiacetic acid(IDA) have been reported, no fundamental discussion on the coordinating structures, especially on geometrical isomerism, has been given, except for a few recent, preliminary works on the analysis of the isomerism of cobalt(III) and chromium(III) complexes with IDA or its derivative as methyliminodiacetic acid (MDA).[3-6]

There are three, geometrically possible isomers in the bis-type complexes with these ligands, their structures being depicted as (A), (B) and (C) in Fig. 1. So far as cobalt(III)-IDA complexes are concerned, the so-called "brown complex" was expected to have either (A) (*trans-fac*) or (B) (*trans-mer*),[4] whereas the "violet complex" was obviously assigned to have (C) structure (*cis-fac*).[3,4] On the other hand, a structural analysis of the complex species such as $[Co(ida)(dien)]^+$ (dien: diethylenetriamine) indicated that IDA prefers the *facial* to the *meridional* configuration.[5] The other works with respect to such configuration also supported the finding that (A) is more stable than (B) because of the more favorable angle ∠C–N–C in (A) than that in (B).[4,6]

Among chromium(III) complexes, $K[Cr(ida)_2]$ has been synthesized,[7,8] and is presumed to have the *cis* configuration (C) on the basis of its spectroscopic results.[9] The bis-type complexes of cobalt(III) and chromium(III) with MDA have also been reported,[5,6,9] where only the *trans-fac* configuration (A in Fig. 1) was assumed. The results that IDA can coordinate either in *cis* or *trans* form, but MDA can not coordinate in *cis* form suggest the presence of some steric hindrance between two methyl groups attached to nitorgen atoms in *cis* isomer.[5,6]

The present work was undertaken (1) to prepare



(A) *trans-fac* (B) *trans-mer* (C) *cis* (D) distorted *cis*

Fig. 1. Possible structures.

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1) G. Schwarzenbach, B. Kamptisch and R. Steiner, *Helv. Chim. Acta*, **28**, 1183 (1945).

2) S. Chaberek, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952).

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

4) J. Hidaka, Y. Shimura and R. Tsuchida, *ibid.*, **35**, 567 (1962).

5) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

6) D. W. Cooke, *ibid.*, **5**, 1141 (1966).

7) H. Mizuochi, S. Shirakata, E. Kyuno and R. Tsuchiya, This Bulletin, **43**, 397 (1970).

8) K. Yamasaki and S. Ito, *Proc. Japan. Acad.*, **42**, 1077 (1966).

9) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

the bis-type complexes of cobalt(III) and chromium (III) with IDA, MDA or the alternative derivative as ethyliminodiacetic acid (EDA), and (2) to investigate systematically the coordinating structures and the properties of the complexes with the above three ligands.

## Experimental

**Preparation of Chelating Agents.** *Methyliminodiacetic Acid.* $CH_3N(CH_2COOH)_2$. 190 g of monochloroacetic acid was dissolved in 300 m*l* of water, and the solution was neutralized by adding slowly 200 g of potassium hydrogen carbonate little by little. To this solution, 75 g of 40% methylamine solution was added, and the resulting solution was heated up to 50°C on a water bath. 200 m*l* of aqueous solution containing 110 g of potassium hydroxide was poured into the warm solution, and a violent reaction took place. Heating was continued for one hour to complete the reaction. After the solution was stood for a while at room temperature, 100 m*l* of concentrated hydrochloric acid was gradually added. At pH 3.5, the wall of the reaction vessel was scrubbed with a glass rod, and white powdered crystals were obtained. Recrystallization was carried out from water. Yield 67 g.

Found: N, 9.83; C, 40.63; H, 6.18%. Calcd for $C_5H_9O_4N$: N, 9.52; C, 40.81; H, 6.21%.

*Ethyliminodiacetic Acid.* $C_2H_5N(CH_2COOH)_2$. To 300 m*l* of aqueous solution containing 190 g of monochloroacetic acid, 200 g of potassium hydrogen carbonate was gradually added. 65 g of 70% ethylamine solution was added, and then the solution was heated up to 50°C on a water bath. As 200 m*l* of 50% potassium hydroxide solution was dropped little by little, the reaction gradually proceeded. After the solution was stood at room temperature, 100 m*l* of concentrated hydrochloric acid was added. The solution was gradually concentrated by evaporating on a water bath, and then the deposited potassium chloride was filtered off. The filtrate was concentrated to about 300 m*l*. From the solution stored in a refrigerator, white powdered crystals were obtained. Recrystallization was achieved from water. Yield about 60 g.

Found: N, 8.53; C, 44.36; H, 6.21%. Calcd for $C_6H_{11}O_4N$: N, 8.69; C, 44.63; H, 6.38%.

*Iminodiacetic Acid.* Special grade reagent of Wako Pure Chemical Co. was used.

**Preparation of Complexes.** 1) *trans-Potassium Bis-(iminodiacetato)cobaltate(III) Monohydrate*, *trans*-$K[Co(ida)_2]\cdot H_2O$ (I). The compound was prepared by the method as described in literature.[4)]

2*)* *cis-Potassium Bis-(iminodiacetato)cobaltate(III) Dihydrate*, *cis*-$K[Co(ida)_2]\cdot 2H_2O$ (II). The preparation was carried out following the procedure given in literature.[3,4)]

3*)* *Potassium Bis-(iminodiacetato)chromate(III) Trihydrate*, $K[Cr(ida)_2]\cdot 3H_2O$ (III). This was prepared by a method similar to that outlined in literature.[7,8)]

4*)* *Barium Bis-(iminodiacetato)chromate(III) Hexahydrate*, $Ba[Cr(ida)_2]_2\cdot 6H_2O$ (IV). To 200 ml of aqueous solution containing 5 g of chromium(III) chloride hexahydrate, 5 g of iminodiacetic acid was added, and then 6.8 g of barium hydroxide octahydrate was added little by little under stirring. The mixed solution was evaporated on a water bath for one hour (to approximately 100 m*l*). After cooling, red needle-like crystals were obtained. The products were recrystallized from water.

Found: N, 6.32; C, 21.38; H, 3.49%. Calcd for $Ba[Cr(ida)_2]_2\cdot 6H_2O$: N, 6.41; C, 21.99; H, 3.66%.

5*)* *Potassium Bis-(methyliminodiacetato)cobaltate(III)*, $K[Co(mda)_2]$ (V). The preparation was carried out by the method in literature.[6)]

6*)* *Potassium Bis-(methyliminodiacetato)chromate(III)*, $K[Cr(mda)_2]$ (VI). The crystals were prepared by the method already known.[9)]

7*)* *Potassium Bis-(ethyliminodiacetato)cobaltate(III) Monohydrate*, $K[Co(eda)_2]\cdot H_2O$ (VII). To 200 m*l* of aqueous solution containing 5 g of cobalt(II) chloride hexahydrate, 6 g of EDA was added, and then 3 g of potassium hydrogen carbonate was gradually added. The mixed solution was heated on a water bath for one hour. After the pH of the solution was adjusted to 6—7, a few m*l* of hydrogen peroxide was added, and pink orange crystals were then obtained under cooling. Recrystallization was carried out from water. Yield about 2 g.

Found: N, 6.50; C, 32.98; H, 4.58%. Calcd for $K[Co(eda)_2]\cdot H_2O$: N, 6.45; C, 33.21; H, 4.61%.

8*)* *Potassium Bis-(ethyliminodiacetato)chromate(III) Monohydrate*, $K[Cr(eda)_2]\cdot H_2O$ (VIII). To 250 m*l* of aqueous solution containing 5 g of chromium(III) chloride hexahydrate, 6 g of EDA was added. The solution was heated on a water bath for one hour, and then 3 g of potassium hydrogen carbonate was added little by little to the solution. Heating was continued for one hour. After cooling, orange crystals were separated out. The crystals were recrystallized from water. Yield about 2.5 g.

Found: N, 6.57; C, 33.54; H, 4.52%. Calcd for $K[Cr(eda)_2]\cdot H_2O$: N, 6.55; C, 33.69; H, 4.68%.

**Apparatus.** Electronic and IR spectra, and molar conductivities were measured with a Hitachi EPS Spectrophotometer and a Nippon Bunko DS-301 Infrared Spectrophotometer and with a Yokogawa Universal Bridge BV-Z-13A, respectively.

## Results and Discussion

**IR Spectra.** Infrared absorption spectra of the complexes were measured to confirm whether or not the carboxylate groups were coordinated.

It is well known that the characteristic band for the free carboxylic acid and that for the coordinated one in aminopolycarboxylic acid complexes appear at $\sim$1750 and $\sim$1640 cm$^{-1}$, respectively.[10)]

Since all the complexes showed the bands near $\sim$1640 cm$^{-1}$, it is obvious that the carboxylate groups are all coordinated.

**Molar Conductivities.** The molar conductivities of the complexes in $10^{-3}$ mol/*l* aqueous solution were measured at 25°C in order to ascertain the valency-type of the complexes. All the complexes except for IV showed the values of 92—98 mho·cm$^{-1}$, indicating that they are 1 : 1 type electrolyte. The value of 183.1 mho·cm$^{-1}$ for complex IV is fairly

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

reasonable for 1 : 2 type electrolyte.

**Electronic Spectra and Possible Structures.** The electronic spectra of all the complexes were measured in aqueous solutions. The spectra for the cobalt(III) complexes are depicted in Fig. 2, and those for the chromium(III) complexes in Fig. 3. The absorption maxima are also listed up in Table 1, together with those of reference substances.

Table 1. Absorption maxima

| Complex | m$\mu_1$($\nu_1 10^{-13}$/sec) log $\varepsilon_1$ | m$\mu_2$($\nu_2 10^{-13}$/sec) log $\varepsilon_2$ |
|---|---|---|
| A. for the cobalt complexes | | |
| I | 500(60.00)1.70 | 365(82.19)1.74 |
| II | 566(53.00)2.03 | 380(78.95)2.04 |
| V | 509(58.94)1.74 | 367(81.74)1.84 |
| VII | 516(58.14)1.78 | 369(81.30)1.84 |
| B. for the chromium complexes | | |
| III | 523(57.36)1.87 | 392(76.53)1.91 |
| IV | 524(57.25)1.85 | 393(76.34)1.92 |
| VI | 500(60.00)1.58 | 364(82.42)1.42 |
| VIII | 504(59.52)1.56 | 363(82.64)1.38 |
| [Cr(edta)]$^-$ [12] | 543 | 394 |
| [Cr(tmta)]$^-$ [9,13] | 509 | 385 |

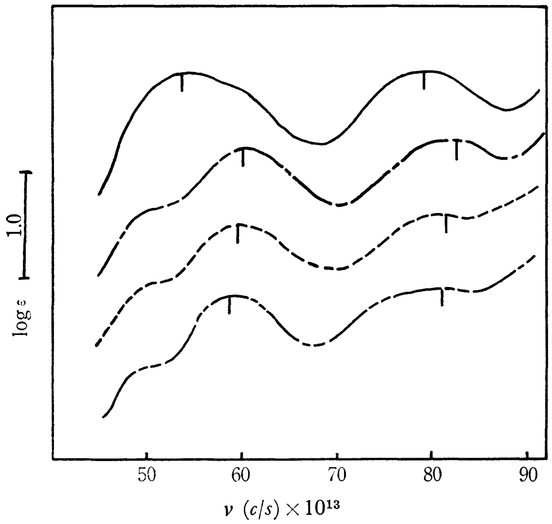

Fig. 2. Electronic spectra for *cis*-K[Co(ida)$_2$]·2$H_2O$ (II) (———) *trans*-K[Co(ida)$_2$]·$H_2O$ (I) (—·—), K[Co(mda)$_2$] (V) (------) and K[Co(eda)$_2$]·$H_2O$ (VII) (—··—).

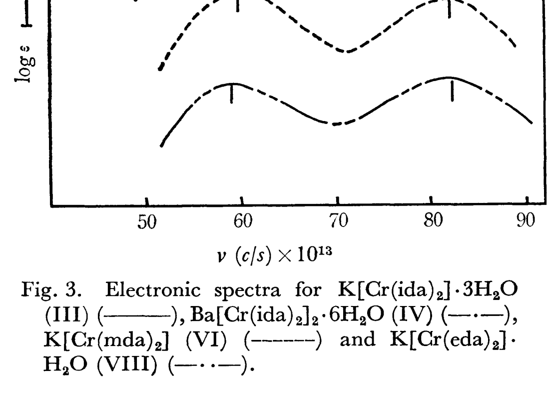

Fig. 3. Electronic spectra for K[Cr(ida)$_2$]·3$H_2O$ (III) (———), Ba[Cr(ida)$_2$]$_2$·6$H_2O$ (IV) (—·—), K[Cr(mda)$_2$] (VI) (------) and K[Cr(eda)$_2$]·$H_2O$ (VIII) (—··—).

It has been discussed from MO treatments that, in the cobalt(III) complexes of $N_2$-$O_4$ type, the *trans* form with respect to the nitrogen atoms shows the splitting in the first band at the longer wavelength side.[11] The assignments of *trans*- or *cis*-K[Co(ida)$_2$] have been made from the above viewpoint.[4] The spectra for complexes V and VII show such a splitting in the first band as in the case of complex I, differing from that of II which shows no splitting. This indicates that the former two complexes are considered to have the *trans*-form. The frequencies of absorption maxima of the above three complexes in *trans*-form are seen from Fig. 2 and Table 1 to be raised in the order VII<V<I, suggesting that spectrochemical series of these ligands is concluded to follow the order, EDA<MDA<IDA. This is also in agreement with the fact that the stability of the complexes is lowered by *N*-alkyl substitution in the ligands.

Concerning *trans* configuration, two possible forms may be assumed; one is *trans-fac* (Fig. 1-A) and the other, *trans-mer* (Fig. 1-B). However, the former configuration seems to be reasonable in EDA complex of *trans* type, because the observation of the favorable angle of ∠C-N-C in the *trans* IDA and MDA complexes[4,6] suggested only the *trans-fac* configuration.

Preparation of the *cis*-isomer of the MDA or EDA complexes has not been successful probably because of the steric hindrance of methyl or ethyl groups, as reported by Weyh and Hamm.[9]

Although complexes VI and VIII do not show distinct splitting in the first band unlike cobalt complexes, it should be considered from the discussion of the corresponding cobalt complexes that they have also the same *trans-fac* configuration. As seen from Fig. 3, complex VIII has the absorption maxima at the longerwave length region than VI, as in the case of cobalt complexes.

Concerning the structures of complexes III and IV, if it is assumed that they have the *trans* configuration, their absorption maxima should be

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[11] H. Yamatera, This Bulletin, **31**, 95 (1958).

detected at ~500 and ~365 m$\mu$, and their log $\varepsilon_1$ are expected to be 1.5—1.6. As can be seen from Table 1, however, the experimental results seem to be inconsistent with the above expectation. On the other hand, $[Cr(edta)]^-$ ion prepared by the method given in literature[12] shows the bands at 543 and 394 m$\mu$. If III and IV are expected to have the same *cis*-form as $[Cr(edta)]^-$, the complexes should show the absorption maxima at 540—550 and 390—395 m$\mu$.

The trimethylenediaminetetraacetatochromate (III) ion ($[Cr(tmta)]^-$),[13] which has six-membered chelate ring through two nitrogen atoms, shows the maxima at 509 and 385 m$\mu$. These values are shorter than those of $[Cr(edta)]^-$ in spite of the fact that they have the same *cis*-configuration.

Studies of the metal chelate with diaminetetracarboxylic acids of the type $(HO_2CCH_2)_2N(CH_2)_n$-$N(CH_2CO_2H)_2$ indicated that the conformational strain becomes larger with the increase of $n$ over 2,[14] when the octahedral coordination structure is assumed to be kept without any distortion. We thus consider that, in TMTA complex (TMTA: trimethylenediaminetetraacetic acid), the normal octahedral coordination form is somewhat distorted so as to diminish the strain due to the chelate ring through nitrogen atoms. It may be understood that complexes III and IV, like the chromium TMTA complex, take the *cis* configuration without much strain in the chelate ring structure as imagined by the sketch (D) in Fig. 1.

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[12] D. T. Sawyer and J. M. Mckinnie, *J. Amer. Chem. Soc.*, **82**, 4191 (1960).

[13] R. Tsuchiya, A. Uehara and E. Kyuno, This Bulletin, **42**, 1886 (1969).

[14] G. Schwarzenbach and G. Anderegg, *Z. Anorg. Allg. Chem.*, **282**, 286 (1955).