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Bis-Type Cobalt(III) and Chromium(III) Complexes with Related Compounds of Nitrilotriacetic Acid*1

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β-Amino-*n*-butyric-*N*,*N*-diacetic acid (β-ABDA) and γ-amino-*n*-butyric-*N*,*N*-diacetic acid (γ-ABDA) were prepared as compounds related to nitrilotriacetic acid (NTA). Bis-type cobalt (III) and chromium(III) complexes with these ligands, *viz.*, $K_3[Co(\beta\text{-abda})_2]$ (I), $K[Co(H\text{-}\gamma\text{-abda})_2]\cdot 2H_2O$ (II) and $K[Cr(H\text{-}\gamma\text{-abda})_2]\cdot 2H_2O$ (III), and the same type cobalt(III) complex with β-aminoethylsulfonic-*N*,*N*-diacetic acid (AEDA), *viz.*, $K_3[Co(aeda)_2]\cdot 4H_2O$ (IV), were also synthesized. Chemical properties of the above complexes were compared with those of the chromium (III) complex corresponding to IV and of the cobalt(III) and chromium(III) complexes with NTA and NPDA. From the analysis of electronic spectra, it was found that the new complexes, I, II, III and IV have the *trans* form with respect to the nitrogn atoms in the ligands. A spectrochemical series of these ligands, containing iminodiacetic acid (IDA), methyliminodiacetic acid (MDA) and ethyliminodiacetic acid (EDA), was determined to be:

IDA>MDA>NPDA>β-ABDA>EDA>AEDA>NTA>γ-ABDA.

Most active works on the aminetricarboxylic acid complexes may be classified into four categories. The first deals with the formation constants of the bivalent metal complex species, *e,g.*, those with NTA[1,2] and nitrilopropionicdiacetic acid (NPDA).[3] The second deals with the reaction kinetics of

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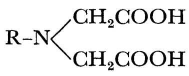
1) G. Schwarzenbach, H. Ackermann and P. Ruckstul, *Helv. Chim. Acta*, **32**, 1175 (1949).

2) G. Schwarzenbach, E. Kampitish and R. Steiner, *ibid.*, **28**, 828 (1945).

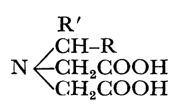
3) S. Chaberek, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **75**, 2888 (1950).

TABLE 1. CHELATING AGENTS AND THEIR ABBREVIATIONS

A. Iminodiacetic Acid and Related Compounds

Rational formula	R	Name	Abbreviation
	H	Iminodiacetic acid	IDA
	CH_3	Methyliminodiacetic acid	MDA
	C_2H_5	Ethyliminodiacetic acid	EDA

B. Nitrilotriacetic Acid and Related Compounds

Rational formula	R	R′	Name	Abbreviation
	COOH	H	Nitrilotriacetic acid	NTA
	CH_2COOH	H	Nitrilopropionicdiacetic acid	NPDA
	CH_2SO_3H	H	*β*-Aminoethylsulfonic-*N*,*N*-diacetic acid	AEDA
	CH_2COOH	CH_3	*β*-Amino-*n*-butyric-*N*,*N*-diacetic acid	*β*-ABDA
	CH_2CH_2COOH	H	*γ*-Amino-*n*-butyric-*N*,*N*-diacetic acid	*γ*-ABDA

bivalent metals with NTA.[4,5] The third deals with the preparation of cobalt(III) and chromium(III) complexes containing NTA[6-8] or its related compounds, *e.g.*, NPDA,[9,10] AEDA,[11] nitriloisopropionicdiacetic acid (NIPDA),[12] and *l*-leucine-*N*,*N*-diacetic acid (LDA).[13] The fourth deals with the thermal reaction in the solid-state.[14] Study on the geometrical isomerism of the mixed cobalt(III) complexes with NTA and natural amino acids[15] might also be included.

In the previous paper,[16] the bis-type cobalt(III) and chromium(III) complexes with iminodiacetic acid (IDA) and its related compounds were reported from the viewpoint of geometrical isomerism. As a continuation of the work, investigations were carried out (1) to prepare bis-type cobalt(III) and chromium(III) complexes with nitrilotriacetic acid (NTA) or its related compounds, *β*-amino-*n*-butyric-*N*,*N*-diacetic acid (*β*-ABDA) and *γ*-amino-*n*-butyric-*N*,*N*-diacetic acid (*γ*-ABDA), the structures of these ligands being shown in Table 1, where those of IDA and its related compounds are also included, (2) to assign the geometrical structures of the complexes; *i. e.*, *cis* or *trans* with respect to the nitrogen atoms in ligands, (3) to inspect the difference in coordinating behaviors of these ligands, (4) to determine the spectrochemical series of all the ligands shown in Table 1, and (5) to compare the properties of cobalt(III) complexes with those of the corresponding chromium(III) ones.

Experimental

Preparation of Ligands. *β-Amino-n-butyric-N,N-diacetic Acid (β-ABDA)*, $N(CH(CH_3)CH_2COOH) (CH_2COOH)_2$. Five grams of *β*-amino-*n*-butyric acid was neutralized with 30 m*l* of water containing 3 g of potassium hydroxide. Fifty milliliters of water containing 10 g of monochloroacetic acid was gradually neutralized with 10 g of potassium hydrogen carbonate. The two solutions were mixed and heated on a water bath. When the temperature of solution was raised to *ca.* 70°C, 30 m*l* of water containing 6 g of potassium hydroxide was added, and heating was continued for 1—2 hr. The solution was cooled at room temperature. After potassium chloride deposited was filtered off, the pH of the solution was adjusted to *ca.* 5 by adding concentrated hydrochloric acid. The solution was then concentrated to about half its volume. After potassium chloride deposited was filtered off, the pH of the solution was adjusted to about 3. By scrubbing the wall of the reaction vessel with a glass rod, white powdered crystals were obtained. The crude products were recrystallized from water. Yield about 4 g.

Found: N, 6.31; C, 43.56; H, 5.82%. Calcd for $C_8H_{13}O_6N$: N, 6.39; C, 43.83; H, 5.98%.

γ-Amino-n-butyric-N,N-diacetic Acid (γ-ABDA), $N(CH_2CH_2CH_2COOH)(CH_2COOH)_2$. The preparative method closely resembles to that of *β*-ABDA; *i. e.*, in the preparation, *γ*-amino-*n*-butyric acid was used as a starting material in place of *β*-amino-*n*-butyric acid. Yield about 2 g.

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4) N. Tanaka and M. Kimura, This Bulletin, **41**, 2375 (1968).

5) M. Kimura, *ibid.*, **42**, 407 (1969).

6) M. Mori, M. Shibata, E. Kyuno and Y. Okubo, *ibid.*, **31**, 940 (1958).

7) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **40**, 2317 (1967).

8) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **40**, 2322 (1967).

9) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 2385 (1968).

10) M. Tachibana, A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **43**, 1061 (1970).

11) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **42**, 2835 (1969).

12) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 2393 (1968).

13) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **43**, 414 (1970).

14) R. Tsuchiya, A. Uehara and E. Kyuno, *ibid.*, **42**, 1886 (1969).

15) N. Koine, N. Sakota, J. Hidaka and Y. Shimura, *ibid.*, **42**, 1583 (1969).

16) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **43**, 1394 (1969).

Found: N, 6.29; C, 43.92; H, 5.73%. Calcd for $C_8H_{13}O_6N$: N, 6.39; C, 43.83; H, 5.98%.

Preparation of Complexes. *Potassium Bis-(β-amino-n-butyric-N,N-diacetato)cobaltate(III)*, $K_3[Co(\beta\text{-abda})_2]$ (I). Five grams of β-ABDA was added to 100 m*l* of aqueous solution containing 3 g of cobalt(II) chloride hexahydrate and the solution was then gradually neutralized with about 5 g of potassium hydrogen carbonate. After a few m*l* of 28% hydrogen peroxide solution was added, the solution was heated on a water bath and concentrated to about half its volume. After cooling pink crystals were obtained and recrystallized from water. Yield about 2 g.

Found: N, 4.74; C, 31.92; H, 3.31%. Calcd for $K_3[Co(\beta\text{-abda})_2]$: N, 4.60; C, 31.57; H, 3.29%.

Potassium Bis-(hydrogen-γ-amino-n-butyric-N, N-diacetato)-cobaltate(III) Dihydrate, $K[Co(H\text{-}\gamma\text{-abda})_2]\cdot 2H_2O$ (II). Five grams of γ-ABDA was added to 100 m*l* of aqueous solution containing 3 g of cobalt(II) chloride hexahydrate, and then about 3 g of potassium hydrogen carbonate was gradually added. A few m*l* of 28% hydrogen peroxide solution was dropped to oxidize the solution which was concentrated to half its volume on a water bath. After cooling pink crystals were obtained. The crude products were recrystallized from water. Yield about 1.5 g.

Found: N, 4.87; C, 33.42; H, 4.60%. Calcd for $K[Co(H\text{-}\gamma\text{-abda})_2]\cdot 2H_2O$: N, 4.93; C, 33.80; H, 4.61%.

Potassium Bis-(hydrogen-γ-amino-n-butyric-N, N-diacetato)-chromate(III) Dihydrate, $K[Cr(H\text{-}\gamma\text{-abda})_2]\cdot 2H_2O$ (III). To 100 m*l* of water containing 3 g of chromium(III) chloride hexahydrate, 5 g of γ-ABDA was added and 5 g of potassium hydrogen carbonate was then gradually added. The solution was heated on a water bath until the color of solution turned to pink from violet. From the solution pink crystals were obtained. Recrystallization was carried out from water. Yield about 3 g.

Found: N, 4.99; C, 33.85; H, 4.56%. Calcd for $K[Cr(H\text{-}\gamma\text{-abda})_2]\cdot 2H_2O$: N, 4.99; C, 34.22; H, 4.63%.

Potassium Bis-(β-aminoethylsulfonic-N,N-diacetato)cobaltate(III) Tetrahydrate, $K_3[Co(aeda)_2]\cdot 4H_2O$ (IV). 12 g of cobalt(II) chloride hexahydrate was dissolved in 200 m*l* of water and then 24 g of AEDA was added. 25 g of potassium hydrogen carbonate was gradually added to the mixture, which was then heated on a water bath until the solution turned from pink to red. After the solution was cooled to room temperature, about 5 m*l* of 28% hydrogen peroxide solution was added for oxidation. Reddish violet crystals were obtained from the cold solution. Recrystallization was carried out from water. Yield about 8 g.

Found: N, 3.83; C, 20.07; H, 3.27%. Calcd for $K_3[Co(aeda)_2]\cdot 4H_2O$: N, 3.86; C, 19.89; H. 3.31%.

Potassium Bis-(β-aminoethylsulfonic-N,N-diacetato) chromate(III) Tetrahydrate, $K_3[Cr(aeda)_2]\cdot 4H_2O$ (V),[11] *Potassium Bis(nitrilotriacetato)cobaltate(III) Trihydrate*, $K_3[Co(nta)_2]\cdot 3H_2O$ (VI),[10] *Potassium Bis-(hydrogennitrilotriacetato)cobaltate(III) Dihydrate*, $K[Co(Hnta)_2]\cdot 2H_2O$ (VII),[10] *Potassium Bis-(nitrilotriacetato)chromate(III) Tetrahydrate*, $K_3[Cr(nta)_2]\cdot 4H_2O$ (VIII),[7] *Potassium Bis-(hydrogennitrilotriacetato)chromate(III) Dihydrate*, $K[Cr(Hnta)_2]\cdot 2H_2O$ (IX),[7] *Potassium Bis(nitrilopropionicdiacetato)cobaltate(III) Dihydrate*, $K_3[Co(npda)_2]\cdot 2H_2O$ (X).[10] and *Potassium Bis-(nitrilopropionicdiacetato)chromate (III) Dihydrate*, $K_3[Cr(npda)_2]\cdot 2H_2O$ (XI)[9] were prepared by the similar method as in the corresponding ammonium salts given in literature and were identified by elemental analysis in order to compare their properties with those of complexes I, II, III and IV.

Apparatus. The same instruments as described previously were used.[16]

Results and Discussion

IR Spectra. Infrared absorption spectra were measured in Nujol mull state in order to see how carboxylate groups behave toward central metals. The band assignments with respect to carboxylate groups were carried out by the method of Busch and Bailar.[17] Numerical data of spectra arising from the free carboxylic acid (–COOH), the coordinated carboxylate (–COO–M) and the ionic carboxylate groups ($-COO^-$) are given in Table 2.

Complex IV shows the bands due to the coordinated carboxylate and the free sulfonate groups ($-SO_3^-$). The shoulder originating from the ionic carboxylate groups ($-COO^-$), besides the band assigned to a coordinated group, is also detected in the case of complex I. Complexes II and III give the bands assigned to the free carboxylate groups in addition to the coordinated groups.

Molar Conductivities. In order to examine to what kind of valency-type the new complexes belong, the molar conductivities were measured at 25°C in a 10^{-3} mol/*l* aqueous solution. The numerical values are given in Table 3.

The values of complexes I and IV fairly show that they are 1 : 3 type electrolytes. Complexes II and III show considerably high values which suggest partial dissociation of hydrogen ions in

Table 2. IR data (cm^{-1})

Complex	-COOH	-COO-M	-COO-	Complement
IV		1640 vs, br		1200 s, br*
V		1630 vs, br		1190 s, br*
I		1635 vs, br	1602 sh,	
II	1730 s	1655 vs, br		
III	1731 s	1660 vs, br		

* Absorptions arising from sulfonate groups (SO_3^-).
Abbreviations: s, strong; vs, very strong; br, broad; sh, shoulder.

Table 3. Molar conductivities (mho cm^{-1})

Complex	Molar conductivity* (mho cm^{-1})
IV	311.2
I	284.5
II	430.8
III	442.6

* 10^{-3} mol/*l* aqueous solution was used.

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

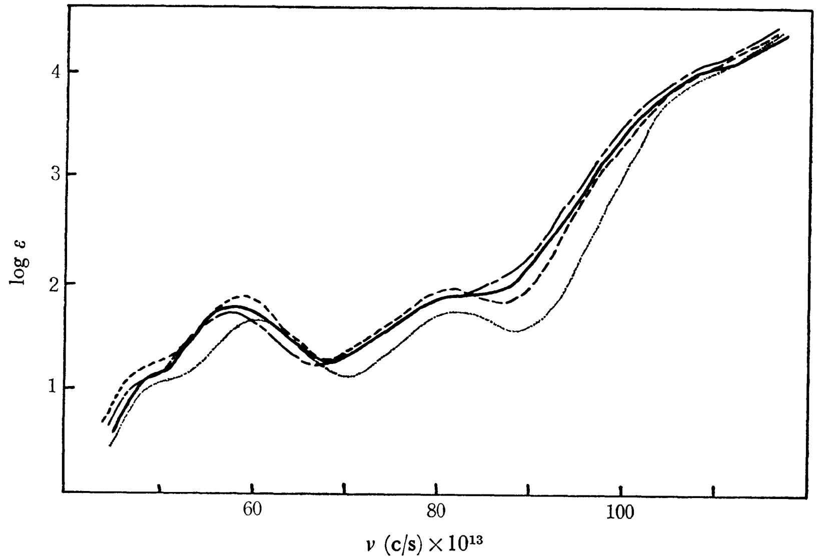


Fig. 1. Electronic spectra for complexes IV (———), I (– – – –), II (—·—) and *trans*-K[Co(ida)$_2$]·H$_2$O (·········).

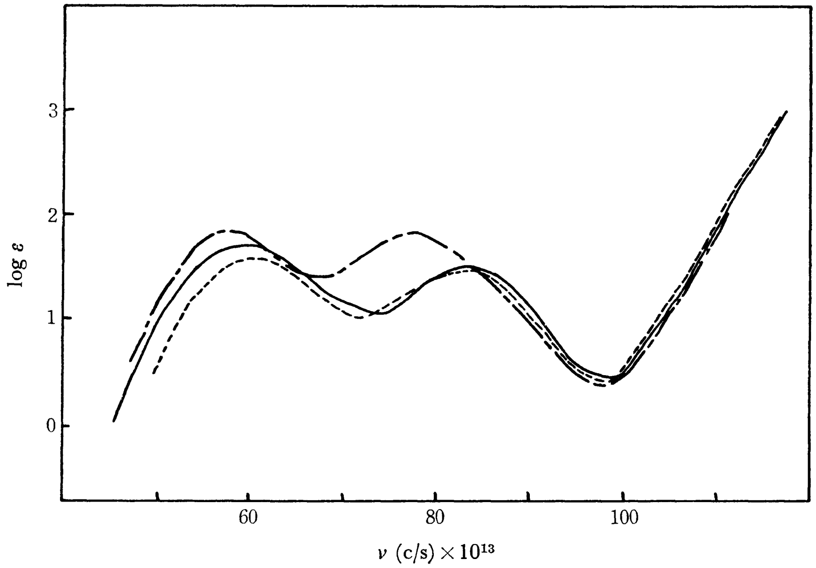


Fig. 2. Electronic spectra for complexes III (———), *trans*-[Cr(mda)$_2$] (– – – –) and *cis*-K[Cr(ida)$_2$]·3H$_2$O (—·—).

TABLE 4. ABSORPTION MAXIMA FOR BIS COBALT(III) COMPLEXES

Complex	mμ_1	($\nu_1 10^{-13}$/sec)	log ε_1	mμ_2	($\nu_2 10^{-13}$/sec)	log ε_2
VI	521	(57.58)	1.83	366	(81.97)	2.27
VII	521	(57.58)	1.81	367	(81.74)	2.25
X	511	(58.71)	1.90	362	(82.87)	2.10
IV	520	(57.69)	1.77	367	(81.74)	1.87
I	515	(58.25)	1.85	370	(81.08)	1.93
II	525	(57.14)	1.75	367	(81.74)	1.86
trans-K[Co(eda)$_2$]·H$_2$O	516	(58.14)	1.78	369	(81.30)	1.84
trans-K[Co(mda)$_2$]	509	(58.94)	1.74	367	(81.74)	1.84
trans-K[Co(ida)$_2$]·H$_2$O	500	(60.00)	1.70	365	(82.19)	1.74
cis-K[Co(ida)$_2$]·2H$_2$O	566	(53.00)	2.03	380	(78.95)	2.04

TABLE 5. ABSORPTION MAXIMA FOR BIS CHROMIUM(III) COMPLEXES

Complex	$m\mu_1$	$(\nu_1 10^{-13}/\text{sec})$	$\log \varepsilon_1$	$m\mu_2$	$(\nu_2 10^{-13}/\text{sec})$	$\log \varepsilon_2$
VIII	499	(60.12)	1.65	359	(83.57)	1.48
XI	492	(60.98)	1.62	362	(82.87)	1.43
V	500	(60.00)	1.54	360	(83.33)	1.39
III	508	(59.06)	1.66	363	(82.64)	1.47
trans-K[Cr(eda)$_2$]·H$_2$O	504	(59.52)	1.56	363	(82.64)	1.38
trans-K[Cr(mda)$_2$]	500	(60.00)	1.58	364	(82.42)	1.42
cis-K[Cr(ida)$_2$]·3H$_2$O	523	(57.36)	1.87	392	(76.53)	1.91

Abbreviations : eda, ethyliminodiacetate ion : mda, methyliminodiacetate ion.

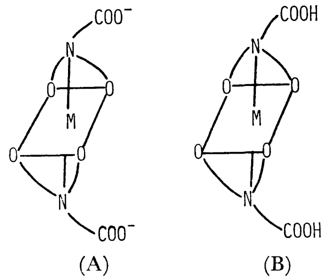
the complex species.

Electronic Spectra and Coordinating Structures. The electronic absorption spectra for the complexes were measured in aqueous solutions. Those for complexes VIII and XI were measured in a buffer solution of pH 6—7 in order to prevent aquation. Figure 1 shows the spectra for complexes I, II, IV and *trans*-K[Co(ida)$_2$]·H$_2$O, and Fig. 2, those for complexes III, *trans*-K[Cr(mda)$_2$] and *cis*-K[Cr(ida)$_2$]·3H$_2$O. For the sake of comparison, the values of absorption maxima due to *d–d* transition for cobalt(III) and chromium(III) complexes are summarized in Tables 4 and 5 respectively, together with those for related complexes.

Appearance of splitting in the first band at longer wavelength in [Co N$_2$O$_4$] type complexes has been assigned to *trans* form from MO theory.[18] We see from Fig. 1 that complexes I, II and IV show the splitting in the first band at longer wavelength side which suggests that all the complexes have the *trans* configuration with respect to nitrogen atoms as in the case of *trans*-K[Co(ida)$_2$]·H$_2$O.[19]

It can be seen from Fig. 2 and Table 5 that complex III shows a spectrum similar to that of *trans*-K[Cr(mda)$_2$][16] rather than to that of *cis*-K[Cr(ida)$_2$]·3H$_2$O.[16] This suggests that complex III has a *trans* structure rather than *cis*. The possibility of the presence of *cis*-configuration in the bis complexes with aminetricarboxylic acids seems to be slight because the steric hindrance due to the methyl or ethyl groups prevents the formation of *cis* complexes even in the case of the MDA[20,21] and EDA[16] complexes.

With the *trans* isomer, two types of configuration can be assumed, one is *trans facial* and the other *trans meridional*. It has been mentioned that the former may be preferred because of the relevant bond angles of these ligands coordinated[22] as in the case of the bis-type complexes with IDA and the related compounds.[16] Thus the structures of complexes I, II, III and IV might belong to *trans-fac* type. In Fig. 3, two types of *trans-fac* are depicted, one of which has noncoordinating –COO$^-$ (A) and the other, –COOH (B). From IR and molar conductivity data, complexes I and IV may have (A) structure, and II and III (B) structure.



(A) (B)

Fig. 3. Possible structures. M: Co(III) or Cr(III).

From a comparison of the spectra in Figs. 1 and 2, it can be seen that the first and second bands clearly appear in the case of the chromium(III) complexes, while the second band of the cobalt(III) complexes is not so distinct owing to the overlap of CT bands. Such a difference has been detected in the case of acidopentaammine complexes of cobalt(III) and chromium(III).[23,24]

Spectrochemical Series of the Ligands. Although all the complexes obtained show a band pattern very similar to each other, a careful inspection of data in Tables 4 and 5 reveals a small but distinct difference in the wavelength of absorption bands. The differences in a series of cobalt(III) complexes are much remarkable in contrast with those in the chromium(III) ones. A spectrochemical series in the cobalt(III) complexes will be settled as follows according to the sequences of weavelength of the first band in Table 4;

IDA>MDA>NPDA>β-ABDA>EDA>AEDA>NTA>γ-ABDA

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

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

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

[21] D. W. Cooke, *ibid.*, **5**, 1141 (1966).

[22] J. A. Weyh and R. E. Hamm, *ibid.*, **7**, 2431 (1968).

[23] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **266**, 49 (1951).

[24] M. Linhard and M. Weigel, *ibid.*, **271**, 101 (1952).

Table 6. Coordinating behaviors of ligands having (5,5,5)-, (5,5,6)- or (5,5,7)-membered chelate rings

Ligand	Chelate ring	Coordinating type	Coordination number	Cr(III)	Co(III)
NTA	5.5,5	N_1-O_3	4	○	○
		N_1-O_2	3	○	○
		O_3	3	○	×
NPDA	5,5,6	N_1-O_3	4	○	○
		N_1-O_2	3	○	○
		O_3	3	×	×
γ-ABDA	5,5,7	N_1-O_3	4	×	×
		N_1-O_2	3	○	○
		O_3	3	×	×

Difference in the Coordinating Behaviors of the Ligands. The relations between the coordinating behaviors in NTA, NPDA and γ-ABDA complexes which have three chelate rings consisting of (5,5,5)-, (5,5,6)-, (5,5,7)-members respectively are summarized in Table 6. Each complex is respectively classified into three groups owing to the possible coordinating types, N_1-O_3, N_1-O_2 and O_3, which represent the coordinating nitrogen and oxygen atoms and their number per one molecule of these ligands. The complexes which we succeeded in preparing are denoted by ○, and those in which we did not succeed by × in Table 6.

NTA could act as N_1-O_3, N_1-O_2 and O_3 types toward chromium(III), but not as O_3 type toward cobalt(III). This might be due to the smaller affinity of cobalt(III) to oxygen as compared with that of chromium(III).[10] NPDA could not behave as O_3 type to both metals.[9,10] It may be understood by empirical facts that the complexes with a ligand forming two five-membered and one six-membered chelate rings are more stable than those forming three five-membered rings.

γ-ABDA acted only as an N_1-O_2 type. In this case the butyric acid group may be uncoordinated, because the formation of a seven membered ring is difficult.

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