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The Chromium(III) Complexes with Anthranilicdiacetic Acid[*1]

Takeshi TOMITA, Eishin KYUNO and Ryokichi TSUCHIYA

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

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The following chromium(III) complexes containing the anthranilicdiacetic acid (ATDA) were prepared: $[Cr(atda)^*(H_2O)_2]\cdot 3H_2O$ (reddish-violet) (I), $K[Cr(OH)(atda)(H_2O)]$ (bluish-violet) (II), $[Cr(atda)(phen)^*]\cdot 3H_2O$ (red) (III), $[Cr(atda)(dipy)^*\cdot 2H_2O$ (red) (IV), $[Cr(atda)(en)^*]\cdot 2H_2O$ (red) (V) and $K[Cr(atda)(acac)^*]$ (violet) (VI). From the results of electronic spectra, molar conductivities, chemical and thermal analyses and IR spectra, it was concluded that the Complexes I, II and VI belong to the $[CrO_5N]$, and III, IV and V belong to the $[CrO_3N_3]$ type. ATDA in all these complexes obtained was found to behave only as a quadridentate ligand. The values of the effective magnetic moments were found to be 3.7—3.9 B. M., nearly equal to the spin-only values of the tervalent chromium.

(* atda, phen, dipy, en and, acac are the basic forms of anthranilic acid, *o*-phenanthroline, 2,2′-dipyridyl, ethylenediamine and acetylacetone respectively.)

The syntheses of the chromium(III) complexes with ammoniatriacetic acid (ATA)[1] and with its derivatives, ammoniapropionicdiacetic acid (APDA)[2] and ammoniaisopropionicdiacetic acid (AIPDA)[3] in the solid state have been reported and the coordinating structures of these complexes both in a solid state and in an aqueous solution have been discussed in previous papers. On the other hand, there are few papers on the synthesis of the complexes with the carboxylmethyl derivatives of the anthranilic acid as the aromatic amino acids.

The formation constants in aqueous solution may serve as an important guide for preparing metal coordination compounds. A series of stabilities of the complexes with anthranilic acid and its derivatives have been given by Young *et al.*,[4] who pointed out that the effect of attaching acetic groups to the amino nitrogen upon the stability is seen to grow up in the sequence: anthranilic acid < anthranilicmonoacetic acid < anthranilicdiacetic acid. It may be due to the fact that the number of the chelate rings increases as the carboxylmethyl groups are introduced step by step to anthranilic acid.

In this study, the authors took the anthranilicdiacetic acid (abbreviated as ATDA) as the ligand relating to ATA, but differing from it in that ATDA contains the aromatic ring, and studied the chromium(III) complexes with this ATDA.

The present work was undertaken, i) to prepare the single- and mixed-ligand complexes containing ATDA, ii) to find out how ATDA could behave towards a chromium(III) ion in complex formation, and iii) to discuss their structures based on the comparison with those of the corresponding ATA complexes.

Experimental

Syntheses. *1) Anthranilicdiacetic Acid Hydrochloride* (ATDA·HCl), $C_{11}H_{11}NO_6\cdot HCl$. Anthranilicdiacetic acid hydrochloride was prepared by the reaction of excess monochloroacetic acid with anthranilic acid in the presence of alkali hydroxide solution enough to neutralize the above acids.[4]

2) Anthranilicdiacetatodiaquochromium(III) Trihydrate, $[Cr(atda)(H_2O)_2]\cdot 3H_2O$ (I). To two liters of aqueous solution of 20 g of chromium(III) chloride hexahydrate, 20 g of anthranilicdiacetic acid hydrochloride was added. After the mixture was heated on a boiling water bath for about two hours, the color of the solution gradually turned from green to violet. Evaporating the resulting solution for one hour, the solution was stood at room temperature overnight. Reddish-violet needle crystals precipitated were filtered, and then recrystallization was done in water. Yield, about 12 g. The compound is poorly soluble in both water (M/200) and ethanol.

Found: Cr, 13.08; C, 33.83; H, 4.46; N, 3.46; H_2O, 23.5%. Calcd for $[Cr(C_{11}H_8NO_6)(H_2O)_2]\cdot 3H_2O$: Cr, 13.30; C, 33.68; H, 4.62; N, 3.57; H_2O, 23.0%.

Other complexes newly prepared in the present study were derived from this I as a starting material.

3) Potassium Hydroxoanthranilicdiacetatoaquochromate(III), $K[Cr(OH)(atda)(H_2O)]$ (II). To a solution of 5 g of the Complex I, potassium hydroxide solution was added to adjust the solution to pH 8 and the mixture

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[*1] Presented at the 17th Symposium on Coordination Compounds, Hiroshima, December, 1967.

1) A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **40**, 2317, 2322 (1967).

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

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

4) A. Young and T. R. Sweet, *J. Am. Chem. Soc.*, **80**, 800 (1958).

was heated on a water bath. After cooling it to room temperature, bluish-violet powder was precipitated and then filtered. The recrystallization was achieved from water. The solubility of this compound in water was about 5 g per liter.

Found: Cr, 13.68; C, 36.66; H, 2.71; N, 3.70%. Calcd for K[Cr(OH)($C_{11}H_8NO_6$)(H_2O)]: Cr, 13.83; C, 35.11; H, 2.93; N, 3.72%.

4) Anthranilicdiacetato - o - phenanthrolinechromium(III) Trihydrate, [Cr(atda)(phen)]·$3H_2O$ (III). Five grams of I and 2.5 g of *o*-phenanthroline monohydrate were added to 200 m*l* of water. Heating the mixture on a boiling water bath, pH of the solution was controlled at 8 by dropping the alkali hydroxide solution into it. The color of the solution turned to dark-red from violet in the reaction process. After cooling the solution at 0°C overnight, the red compound was crystallized out. It was filtered and fully washed with water and ethanol. Recrystallization was carried out from the diluted hydrochloric acid solution. Yield, about 1 g. The complex is a little soluble in water.

Found: Cr, 9.74; C, 52.37; H, 4.19; N, 7.97; H_2O, 10.1%. Calcd for [Cr($C_{11}H_8NO_6$)($C_{14}H_{10}N_2$)]·$3H_2O$: Cr, 10.03; C, 53.28; H, 4.28; N, 8.14; H_2O, 10.4%.

5) Anthranilicdiacetato-2,2'-dipyridylchromium(III) Dihydrate, [Cr(atda)(dipy)]·$2H_2O$ (IV). Two grams of 2,2'-dipyridyl were dissolved in 400 m*l* of I solution placed on a boiling water bath. The pH of the mixture was adjusted to about 8 and concentrated for about an hour. After cooling it to 0°C, red crystalline compound was precipitated and was recrystallized from water. Yield, about 1.5 g.

Found: Cr, 10.27; C, 51.07; H, 4.50; N, 8.66; H_2O, 7.8%. Calcd for [Cr($C_{11}H_8NO_6$)($C_{12}H_8N_2$)]·$2H_2O$: Cr, 10.52; C, 51.01; H, 4.08; N, 8.50; H_2O, 7.3%.

6) Anthranilicdiacetatoethylenediaminechromium(III) Dihydrate, [Cr(atda)(en)]·$2H_2O$ (V). Five grams of I were dissolved in 400 m*l* of water and 4 g of ethylenediamine dihydrochloride was added to it. The alkali hydroxide solution was poured drop by drop until a suitable pH was attained and the solution was concentrated to 100 m*l* on a boiling water bath. When the solution was cooled to 0°C, a small amount of red crystals was precipitated. It was filtered and recrystallized from methanol. Yield, about 0.5 g.

Found: Cr, 12.88; C, 39.25; H, 5.32; N, 10.51; H_2O, 9.3%. Calcd for [Cr($C_{11}H_8NO_6$)($C_2H_8N_2$)]·$2H_2O$: Cr, 13.05; C, 39.20; H, 5.06; N, 10.60; H_2O, 9.1%.

7) Potassium Anthranilicdiacetatoacetylacetonatochromate-(III), K[Cr(atda)(acac)] (VI). Five grams of I were dissolved in 400 m*l* of water, and 4.7 g of potassium acetylacetonate was added. The mixture was warmed on a water bath and then heated in a flask equipped with a reflux condenser for two hours in order to prevent the vaporization of acetylacetone during the reaction. After the solution was concentrated to 200 m*l*, the mixed solution was placed in a desiccator. If the crystal of trisacetylacetonatochromium(III) as the impure substance was deposited, it should be excluded by filtration. When the desired violet powder was precipitated, it was collected on the filter. The recrystallization was carried out from the concentrated aqueous solution. The complex is very soluble in water. Yield, about 0.5 g.

Found: Cr, 11.66; C, 43.71; H, 3.49; N, 2.97%. Calcd for K[Cr($C_{11}H_8NO_6$)($C_5H_7O_2$)]: Cr, 11.50; C, 43.65; H, 3.43; N, 3.18%.

Apparatus. The molar conductivity, the visible, UV and IR spectra, reflectance spectra and the magnetic susceptibility were measured with a Yokogawa Universal Bridge BV-Z-13A, a Hitachi EPS Spectrophotometer, a Jasco DS-301 IR Spectrophotometer, a Hitachi EPU-2A Spectrophotometer equipped with the standard Hitachi Reflectance Attachment and a Gouy Balance, respectively. The quantity of the crystal-water contained in these complexes was estimated from TGA curves measured with a Shimadzu Thermano Balance.

Results and Discussion

Behaviors toward Ion Exchangers and Molar Conductivities. The behaviors of the complexes newly prepared in the present work toward ion exchangers and their molar conductivity data measured in the 1×10^{-3} molar aqueous solution are shown in Table 1. Both the Complexes II and VI were adsorbed by Cl-form exchanger and their molar conductivities were 89.1 and 92.2 mho cm^{-1} respectively. This suggests that both complexes are 1 : 1 valency type and negatively charged electrolytes. All other complexes were adsorbed by neither Na- nor Cl-form exchanger, indicating that all exist as nonelectrolyte state.

Visible and UV Absorption Spectra. The electronic spectra of the Complexes I, II, IV and

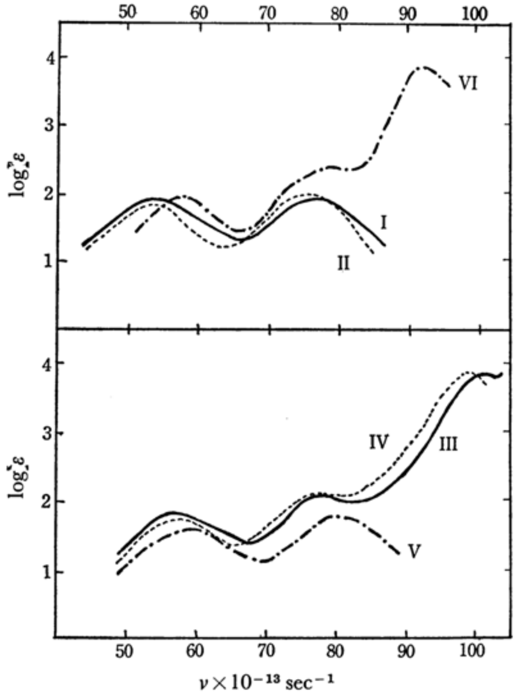

Fig. 1. Electronic absorption spectra.
Measured in aqueous solution for I, II, IV and VI; methanol solution for V; dimethylformamide solution for III.

TABLE 1. BEHAVIOR TO THE ION EXCHANGER AND MOLAR CONDUCTIVITY

	Complex	Color	Adsorption to the ion exchanger		Molar conductivity (mho cm^{-1})
			Na-form	Cl-form	
I	$[Cr(atda)(H_2O)_2]\cdot 3H_2O$	red-violet	–*	–*	
II	$K[Cr(OH)(atda)(H_2O)]$	blue-violet	–	+	89.1
III	$[Cr(atda)(phen)]\cdot 3H_2O$	red	–	–	
IV	$[Cr(atda)(dipy)]\cdot 2H_2O$	red	–	–	
V	$[Cr(atda)(en)]\cdot 2H_2O$	red	–	–	
VI	$K[Cr(atda)(acac)]$	violet	–	+	92.2

* The sign + or – means the possibility or impossibility of the adsorption of the complex species against the exchanger respectively.

TABLE 2. ABSORPTION MAXIMA

Complex	$\nu_1(10^{13}/sec)$	$(\log \varepsilon_1)$	$\nu_2(10^{13}/sec)$	$(\log \varepsilon_2)$	$\nu_3(10^{13}/sec)$	$(\log \varepsilon_3)$
I	54.9 (56.6)*	(1.93)	75.8 (75.6)	(1.94)		
II	54.1 (56.3)	(1.88)	74.5 (75.2)	(2.03)		
III	57.7 (57.7)	(1.87)	76.9 (76.0)	(2.18)	101.4	(4.02)
IV	57.7 (58.8)	(1.83)	76.7 (76.0)	(2.14)	97.4	(4.02)
V	58.8 (60.9)	(1.83)	79.8 (80.1)	(1.94)		
VI	56.9 (58.7)	(1.96)	78.3 (77.5)	(2.31)	90.9	(3.87)

* The numerals under parentheses indicate the absorption peaks measured by means of the diffuse-reflectance method.

VI measured in aqueous solution and those of the Complexes III and V in DMF and methanol respectively are shown in Fig. 1, and all their absorption spectra obtained by diffuse-reflectance method in the solid state are in Fig. 2. The numerical data of their absorption maxima are summarized in Table 2.

It can be seen from Figs. 1 and 2 that every absorption spectrum in the solution closely coincides with the corresponding one in the solid state. It may indicate that all the complexes concerned exist in analogous form both in solution and in the crystalline state without any decomposition.

It has already been reported that the complexes, $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$[1] and $NH_4[Cr(OH)(aipda)(H_2O)]\cdot 4H_2O$,[3] corresponding to the Complex II, easily give rise to conversion to $NH_4[Cr(OH)(ata)(H_2O)_2]$ and $NH_4[Cr(OH)(aipda)(H_2O)_2]$ respectively as soon as dissolved in water and, at the same time, the color changes from purple in the crystal to green in aqueous solution, due to the liberation of nitrogen in ligands from coordination. Taking into account the result that the absorption maxima of II are larger than those of the corresponding ATA and AIPDA complexes cited above, it may be concluded that II is more stable than the ATA and AIPDA complexes.

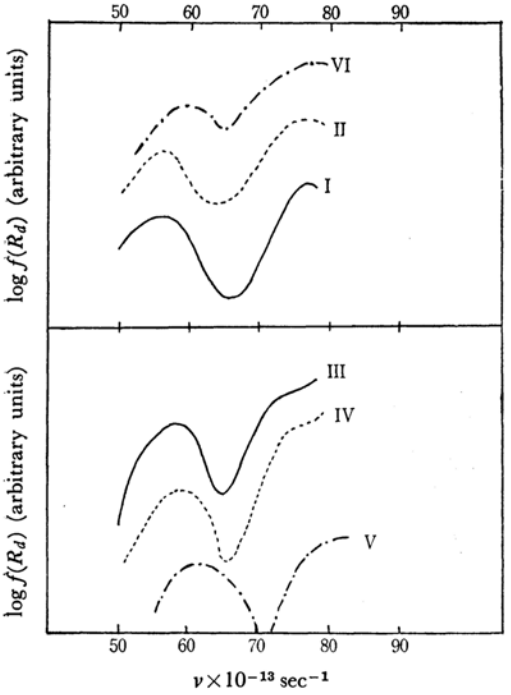

Fig. 2. Absorption spectra measured by the diffuse-reflectance method.
R_d: relative reflectance index

Complexes III, IV and VI give the characteristic bands probably assigned to 2,2′-dipyridyl, *o*-phenanthroline and acetylacetone coordinated, respectively. When the aqueous solution of V was allowed to stand for several hours, a distinct frequency shift of the absorption peaks to lower wavelength region was observed, probably being attributed to the gradual aquation taking place in the complex.

The conclusion that the nitrogen atom of ATDA always coordinates to chromium(III) ion even in aqueous solution in the complexes concerned in this work, differing from that in the corresponding ATA and AIPDA complexes, may be supported by the information given above.

IR Spectra. The predominant peaks appearing in IR spectra on the complexes obtained are summarized in Table 3. With all complexes, the characteristic bands assigned to the stretching $\nu_{C=C}$ in benzene ring of atda are found near 1600 cm^{-1} and the bands for carboxyl groups of atda coordinated to chromium are shown within the wave number region of 1600—1700 cm^{-1}. By comparing these wave numbers with those observed in ATDA non-coordinated to chromium, 1730 cm^{-1}, it can be deduced that all the carboxyl groups in ATDA in every complex prepared in this work participate in coordination to the metal ion.

TABLE 3. IR DATA (cm^{-1})*

Complex	ν_{O-H}	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=C}$
atdaH$_3$			1680, 1730	1600
I	3320		1620, 1675	1600
II	3240		1660, 1680	1600
III	3380		1675, 1700	1600
IV	3500		1665, 1695	1600
V	3440	3200, 3270	1630, 1680	1600
VI			1665, 1695, 1560	1605, 1530

* Measured in Nujol mull state.

As is indicated in Table 3, Complexes I—V have O–H stretching band and, above all, V shows two band peaks due to N–H stretching vibration rising from ethylenediamine. Complex VI gives two characteristic peaks owing to the acetylacetone coordinated, as is cited in literature.[5]

Magnetic Susceptibility. The effective magnetic moments of the complexes evaluated from the magnetic susceptibility measurement at room temperature are listed in Table 4. All the complexes show the normal magnetic moments, 3.7—3.9 B. M., which are nearly equal to the spin-only values calculated for tervalent chromium.

Thermogravimetric Measurement. The thermogravimetric curves for the complexes are shown in Fig. 3. It can be seen that all the complexes are gradually dehydrated up to about 130°C and then decomposed at about 230—300°C, except for the Complex I which loses stepwise three moles of the crystal-water and then two moles of the coordinated water up to 160°C.

TABLE 4. MAGNETIC MOMENT OF THE COMPLEXES

Complex	Magnetic moment (B. M.)	(Temp. °C)
I	3.76	(18.0)
II	3.80	(19.2)
III	3.80	(29.5)
IV	3.81	(30.0)
V	3.76	(21.3)
VI	3.90	(20.0)

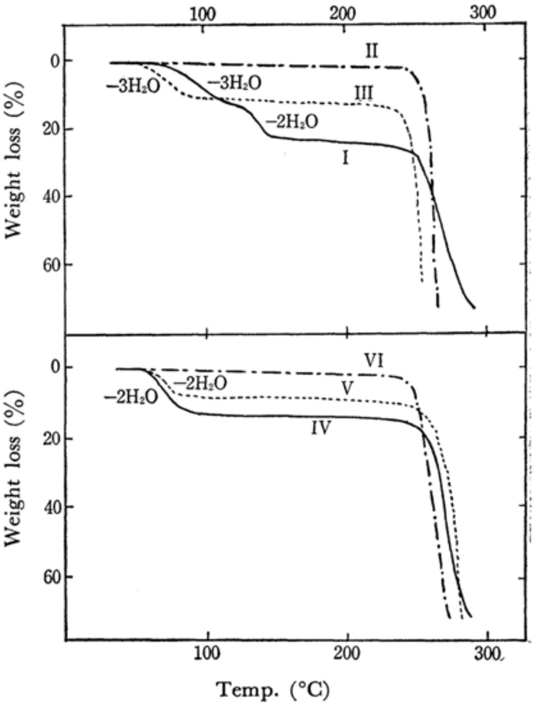

Fig. 3. Thermogravimetric curves.

Discussion on the Structures. The configuration of the ligands, ATA, APDA and ATDA, are sketched in Fig. 4. When ATA behaves toward chromium as a quadridentate ligand, it forms three five-membered chelate rings. However, since there are some steric strains on nitrogen atom, it can be easily left from coordination to chromium, acting as a terdentate one.

In the case of APDA, which is formed by introducing a methylene group into ATA, it can make one six-membered and two five-membered rings. Owing the such configuration, the steric strain focused on the nitrogen atom is, to some extent, reluxed, but one of the carboxyl groups is, in

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[5] J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

reverse, given the tendency to dislocate from coordination, differing from ATA. In short, both ATA and APDA can behave as terdentate ligands, the former acting without coordination of nitrogen atom and the latter having one of the free carboxyl group.

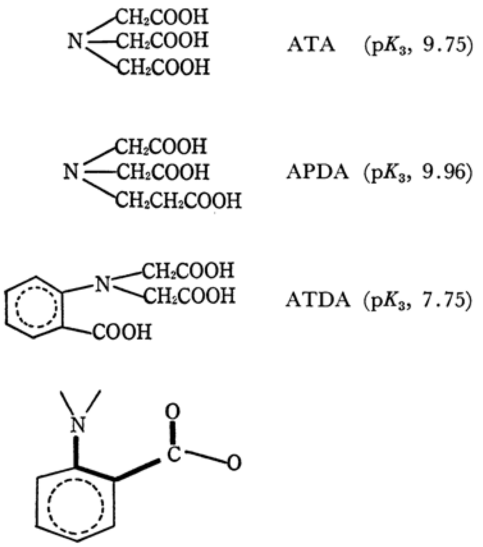

Fig. 4. The configurations of ATDA and related ligands.

On the other hand, ATDA behaves as a quadridentate ligand in all complexes treated in the present study; *i. e.*, it should be emphasized that all the four terminal atoms in the ligand, one nitrogen atom and three oxygen atoms, coordinate to the central metal ion even in an aqueous solution, although APDA sometimes behaves as terdentate ligand despite the fact that it has the analogous skeleton as ATDA. The reason for such difference will be attributed to the presence of the aromatic ring in ATDA. The available resonating interaction among one of the three carboxyls and the tertiary nitrogen group through the benzene ring may result in the shortening of the bond distances (shown by heavy lines in Fig. 4) with some extra stabilization energies and, therefore, the greater chelating power will be generated.[6] Thus, ATDA always behaves as a quadridentate ligand without the easy dissociation of the nitrogen atom from the coordination and without the formation of free carboxyl group even in solution, quite differing from ATA and APDA.

The difference of p*K* values among these three ligands (shown in Fig. 4) may allow an explanation for such coordinating characteristics in them as mentioned above. For example, the result that even one of the carboxyl groups in ATDA can not be easily released from the central metal in solution may be due to the smaller p*K* value in it.

In contrast to this stereochemical standpoint, the solubility sequence in water of each starting complex in the syntheses of a series of the mixed complexes, such as $NH_4[Cr(OH)(ata)(H_2O)] > [Cr(OH)(apdaH)(H_2O)] > [Cr(atda)(H_2O)_2]$, may play an important part in their preparation.

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[6] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," New York Prentice Hall, Inc., New York (1956), p. 156.