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The Chromium(III) Complexes with Ammoniatriacetic Acid. II. The Mixed-ligand Complexes[*1]

Akira UEHARA, Eishin KYUNO and Ryokichi TSUCHIYA

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

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The following chromium(III) complexes containing ammoniatriacetic acid (ATA) and other reagents as "mixed-ligands" were newly prepared: $NH_4[Cr(ata)(acac)]\cdot H_2O$ (brown black)(I), $[Cr(ata)(o\text{-phen})]\cdot 4H_2O$ (brown) (II), $[Cr(ata)(dipy)]$ (red brown)(III), $(NH_4)_2[Cr(ata)\cdot(NCS)_2]\cdot H_2O$ (purple black)(IV, and $K_2[Cr(ata)(ox)]\cdot 2H_2O$(purple)(V), where ata, acac, *o*-phen, dipy and ox are the abbreviations of the ammoniatriacetate ion, acetylacetone, *o*-phenanthroline, α, α-dipyridyl, and the oxalate ion respectively. On the basis of the chemical analyses, the thermal analyses, and the measurements of the electronic absorption spectra, it may be considered that ATA was coordinated as a tetradentate ligand in all these complexes obtained. Further information on the conductivity in an aqueous solution suggested that the IV and V complexes are aquated instantly to form the complex ion as $[Cr(OH)(ata)(H_2O)_2]^-$. The values of the effective magnetic moments for these complexes were 3.7—3.9 B. M., nearly equal to the spin-only values of tervalent chromium.

In the preceding paper,1) the preparation of the chromium(III) complexes containing ammoniatriacetic acid (ATA) as a tridentate or a tetradentate ligand was reported, and their structures were discussed. In these complexes, the two or three residual coordinating positions left from the coordination by ATA in the octahedron were occupied by H_2O or OH^-. Moreover, it was found that, in a few of these complexes, the coordinating structures between a complex in a crystal state and that in an aqueous solution were different from each other.

The purposes of this paper were to prepare mixed-ligand complexes containing ATA and other reagents at the same time in order to find how ATA could behave to a chromium(III) ion in them, and to find out whether or not there are different structures between when the complexes are in a crystal and when they are in an aqueous solution.

Experimental

Preparation. *1) Ammonium Acetylacetonatoammoniatriacetatochromate(III) Monohydrate,* $NH_4[Cr(ata)(acac)]\cdot H_2O$ (I). All five complexes obtained were derived from ammonium hydroxoammoniatriacetatoaquochromate(III) dihydrate, $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$ (I′), which was newly prepared by the present authors for the preceding paper.1) Ten grams of the I′ complex as a starting material were dissolved in 50 m*l* of water, and the mixture was warmed on waterbath. When a few drops of concentrated hydrochloric acid were poured into this green solution, it turned purple. After about 3 g of acetylacetone had been added to this solution, it was refluxed (in a flask equipped with a reflux condenser in order to prevent the acetylacetone from vaporization) until no flotation of the acetylacetone could be seen. When the solution was cooled to 0°C, brown-black crystals were separated out. They were recrystallized from a concentrated methanol solution. Yield, about 5 g.

Found: Cr, 13.52; N, 7.14; C, 34.63; H, 4.89; H_2O, 4.69%. Calcd for $NH_4[Cr(ata)(acac)]\cdot H_2O$: Cr, 13.86; N, 7.47; C, 35.21; H, 4.80; H_2O, 4.80%.

2) Ammoniatriacetato-o-phenanthrolinechromium(II) Tetrahydrate, $[Cr(ata)(o\text{-phen})]\cdot 4H_2O$ (II). Six grams of *o*-phenanthroline and 2.6 m*l* of concentrated hydrochloric acid were added to about 50 m*l* of an aqueous solution containing 10 g of the I′ complex. After the solution had been heated for a few minutes on a water-bath, brown crystals were separated out. The recrystallization was achieved from water. Yield, about 6 g.

Found: Cr, 10.44; N, 8.47; C, 44.41; H, 4.04; H_2O, 14.41%. Calcd for $[Cr(ata)(o\text{-phen})]\cdot 4H_2O$: Cr, 10.58; N, 8.55; C, 44.01; H, 4.47; H_2O, 14.62%.

3) Ammoniatriacetato-α, α′-dipyridylchromium(III), $[Cr(ata)(dipy)]$ (III). Five grams of α, α'-dipyridyl and 2.6 m*l* of concentrated hydrochloric acid were added to about 50 m*l* of an aqueous solution containing 10 g of I′. After the solution had been heated on the water bath for a few minutes, red-brown crystals were separated out. The recrystallization was achieved from water. Yield, about 4 g.

Found: Cr, 12.69; N, 10.40; C, 47.31; H, 3.65%. Calcd for $[Cr(ata)(dipy)]$: Cr, 12.71; N, 10.26; C, 47.12; H, 3.43%.

4) Ammonium Diisothiocyanatoammoniatriacetatochromate (III) Monohydrate, $(NH_4)_2[Cr(ata)(NCS)_2]\cdot H_2O$ (IV). Ten grams of I′ were dissolved into about 50 m*l* of water containing a few drops of concentrated hydrochloric acid, and then 4.5 g of ammonium thiocyanate was added. The resultant solution was heated

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1) Part I of this series: A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **40**, 2317 (1967).

on the waterbath for several minutes. As soon as purple-black crystals had been separated out, the solution was quickly filtered. The purple-black color of this crystal instantaneously turned green in an aqueous solution. However, when a few drops of concentrated hydrochloric acid were added to the solution, it turned purple-black again, from which state the product was recrystallized. Yield, about 3 g.

Found: Cr, 12.82; N, 17.32; C, 23.78; H, 3.50; H_2O, 4.02%. Calcd for $(NH_4)_2[Cr(ata)(NCS)_2]\cdot H_2O$: Cr, 12.67; N, 17.03; C, 23.41; H, 3.89; H_2O, 4.39%.

5) *Potassium Oxalatoammoniatriacetatochromate(III) Dihydrate,* $K_2[Cr(ata)(ox)]\cdot 2H_2O$ (V). Ten grams of I′ were dissolved into 50 m*l* of water containing 2.4 g of potassium hydroxide and 5.5 g of oxalic acid. When the resultant solution was heated on the water bath about 15 minutes, the color gradually turned from green to purple. When this solution was cooled to 0°C for several days, purple, scale-like crystals were obtained. Although those crystals instantly turned green when dissolved into water, the color was turned back from green to purple by adding a few drops of concentrated hydrochloric acid. After the solution had stood at 0°C for several days, the recrystallized crystals were separated out. Yield, about 3.5 g.

Found: Cr, 11.76; N, 3.21; C, 21.47; H, 2.32; H_2O, 8.17%. Calcd for $K_2[Cr(ata)(ox)]\cdot 2H_2O$: Cr, 11.68; N, 3.18; C, 21.76; H, 2.26; H_2O, 8.15%.

The thermogravimetric measurements, molar conductivities, spectrophotometric and magnetic measurements were carried out with the same apparatuses as were described in the preceding paper.[1)]

The crystalline-water content in these complexes was estimated from the weight loss in the respective thermogravimetric curves.

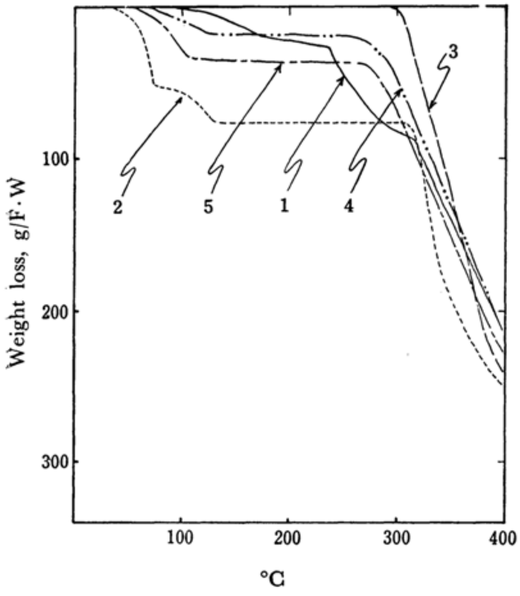

Fig. 1. Thermogravimetric curves for
1: $NH_4[Cr(acta)(acac)]\cdot H_2O$,
2: $[Cr(ata)(o\text{-phen})]\cdot 4H_2O$,
3: $[Cr(ata)(dipy)]$,
4: $(NH_4)_2[Cr(ata)(NCS)_2]\cdot H_2O$,
5: $K_2[Cr(ata)(ox)]\cdot 2H_2O$.

Results and Discussion

Thermogravimetric Measurements. The thermogravimetric curves for the five complexes newly prepared in the present work are shown in Fig. 1. It can be seen from this figure that all the complexes were dehydrated easily up to 150°C, and that then the complexes were decomposed at about 300°C except for the I complex, which was decomposed step by step at 220°C and 330°C.

In the case of the II complex, 3 mol of the crystalline water were dehydrated at 90°C, and then last one mole was dehydrated at 140°C.

Visible and Ultraviolet Absorption Spectra. The visible and ultraviolet absorption spectra for all the complexes, as measured in an aqueous solution, are shown in Fig. 2 and Fig. 3, while their absorption maxima are given in Table 1 together with those for the related complexes, trisoxalato chromate(III) and hexaaquochromium(III) complexes.

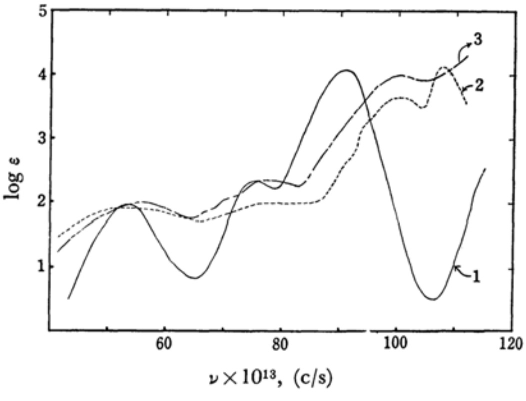

Fig. 2. Electronic absorption spectra for
1: $NH_4[Cr(ata)(acac)]\cdot H_2O$,
2: $[Cr(ata((o\text{-phen})]\cdot 4H_2O$,
3: $[Cr(ata)(dipy)]$.

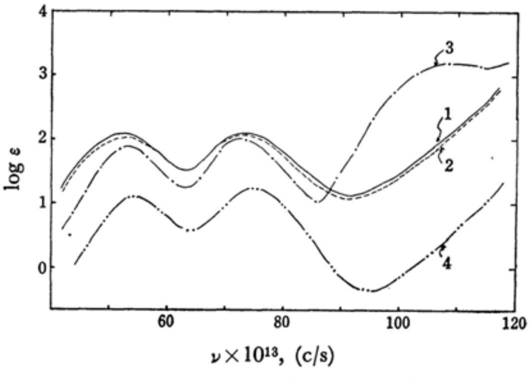

Fig. 3. Electronic absorption spectra for
1: $(NH_4)_2[Cr(ata)(NCS)_2]\cdot H_2O$,
2: $K_2[Cr(ata)(ox)]\cdot 2H_2O$,
3: $K_3[Cr(ox)_3]\cdot 3H_2O$,
4: $[Cr(H_2O)_6]\cdot K(SO_4)_2\cdot 6H_2O$.

TABLE 1. ABSORPTION MAXIMA

Complex		$\nu_1(10^{13}/\text{sec})(\log \varepsilon_1)$	$\nu_2(10^{13}/\text{sec})(\log \varepsilon_2)$	$\nu_3(10^{13}/\text{sec})(\log \varepsilon_3)$
$NH_4[Cr(ata)(acac)]\cdot H_2O$	(I)	53.9 (1.99)	77.9 (2.37)	91.9 (3.89)
$[Cr(ata)(o\text{-phen})]\cdot 4H_2O$	(II)	55.5 (1.89)	76.1 (2.06)	99.0 (3.69)
$[Cr(ata)(dipy)]$	(III)	56.6 (1.95)	76.7 (2.39)	97.4 (4.10)
$(NH_4)_2[Cr(ata)(NCS)_2]\cdot H_2O$	(IV)	51.5 (2.06)	73.5 (2.13)	
$K_2[Cr(ata)(ox)]\cdot 2H_2O$	(V)	51.5 (2.05)	73.5 (2.11)	
$K_3[Cr(ox)_3]\cdot 2H_2O$[2]		52.6 (1.87)	71.4 (2.11)	
$[Cr(H_2O)_6]K(SO_4)_2\cdot 6H_2O$[3]		52.6 (1.02)	73.6 (1.20)	

TABLE 2. BEHAVIORS TO THE ION EXCHANGER AND MOLER CONDUCTIVITIES

Complex	Color of crystal	Color of solution	Adsorption to the ion exchanger		Molar conductivity (mho cm^{-1})
			Na-form	Cl-form	
I	Brown black	Brown black	−	+	104.7
II	Brown	Brown	−	−	—
III	Red brown	Red brown	−	−	—
IV	Purple black	Green	−	+	493.3
V	Purple	Green	−	+	422.6

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

Complex	-COOH	-COO-Cr	-COO$^-$	-COOH	Complements
$ataH_3$	1968 (vs)			1233 (m)	
$ataH(NH_4)_3$			1623 (vs)		
I		1673 (sh)—1611 (vs)			1573 (vs), 1528 (vs), 1198 (s), 1225 (s)*
II		1683 (sh)—1613 (vs)			1525 (s), 1550 (s), 1569 (s), 1603 (s), 726 (s), 858 (s)**
III		1683 (sh)—1615 (vs)			1491 (s), 1563 (s), 1598 (s), 780 (s), 897 (s)***
IV		1678 (sh)—1613 (vs)			2085 (vs)****
V		1681 (sh)—1610 (vs)			

* The absorption arising from acetylacetone.
** Those from *o*-phenanthroline.
*** Those from α, α'-dipyridyl.
**** Those from NCS.

The spectrum for the I complex has three absorption peaks, at 53.9, 77.9 and 91.9×10^{13}/sec. The third absorption band must be due to the charge transfer from acetylacetone coordinated to the central metal.

The spectra for the II and III complexes give complicated curves based on the α, α'-dipyridyl and *o*-phenanthroline. That is, for the II complex, little splits can be seen on the band at 76.1×10^{13}/sec, while similar splits appear on the band at 97.4×10^{13}/sec for the III complex.

The IV and V complexes both have two absorption bands, at 56.5 and 73.5×10^{13}/sec; their spectra are quite analogous to those of $[Cr(ox)_3]^{3-}$ and $[Cr(H_2O)_6]^{3+}$, in which all the coordinating positions are occupied by six oxygen atoms.[2,3] This suggests that the nitrogen atom of ata does not immediately coordinate to chromium, as will be proposed in more detail later in this paper. Furthermore, on the basis of the information already known, that the coordinated NCS^- shows a specific absorption band at about 100×10^{13}/sec, while non-coordinated NCS^- does not,[4] the spectrum of IV indicates that the NCS^- in it does not coordinate with the chromium.

Behavior toward the Ion Exchanger and Molar Conductivities. Table 2 shows the behavior of the complexes toward the ion exchanger and the values of their molar conductivities in a

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

[3] R. Tsuchida and M. Kobayashi, *ibid.*, **64**, 1268 (1943).

[4] R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 471 (1938).

1/1000 mol/*l* solution. The I complex had a brown-black color in an aqueous solution as well as in the crystalline state; it was adsorbed to a Cl-form anion exchanger, and its molar conductivity was 104.7 mho cm^{-1}, suggesting that it is a 1:1-type electrolyte. Neither complex II or III showed any color change on being dissolved into water, and nor could be adsorbed to either the Na-form cation or the Cl-form anion exchanger, showing that they are non-electrolyte complexes.

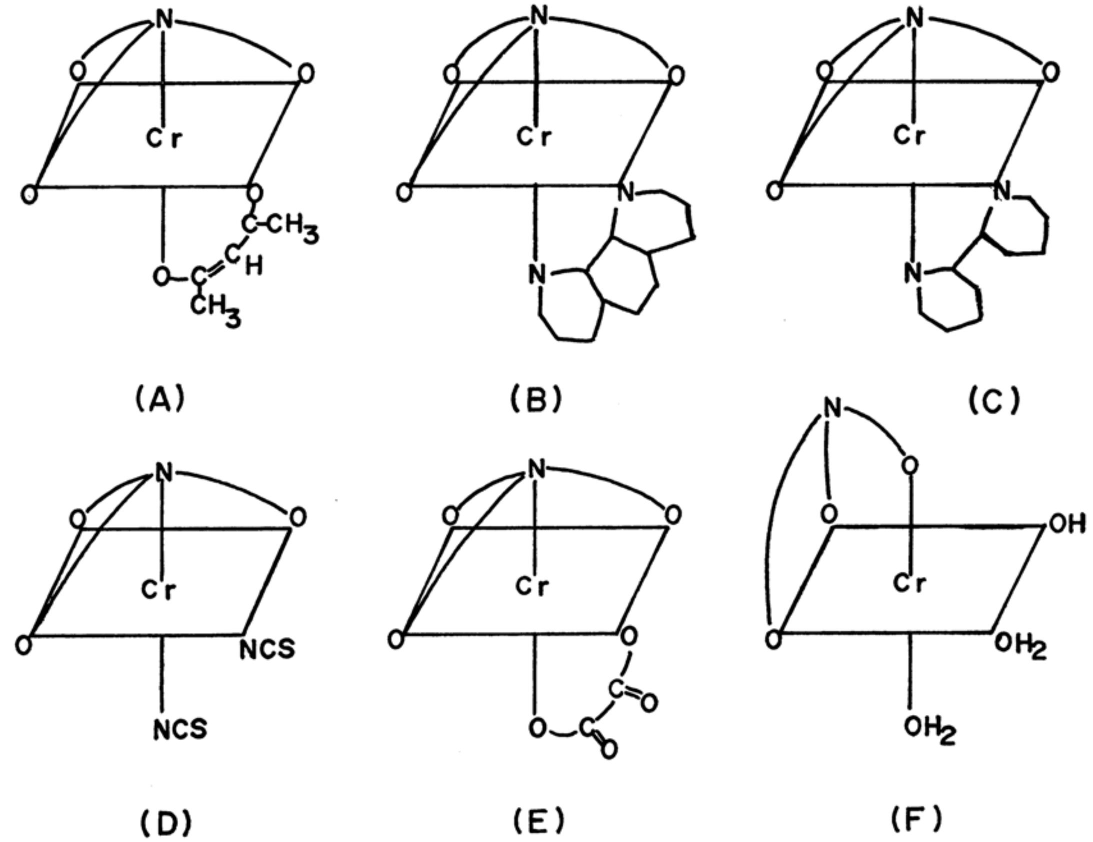
As has been mentioned above, the IV and V complexes were decomposed in an aqueous solution. The complex species formed in the solution were adsorbed to the Cl-form anion exchanger and gave the molar conductivities as 493.3 and 422.6 mho cm^{-1} for the solutions of IV and V respectively. On the basis of these results it may be better to consider that the IV and V complexes are easily aquated in the solution by losing NCS$^-$ and ox^{2-} respectively.

Infrared Spectra. The infrared absorption spectra were measured in order to determine whether the mixed ligands and three carboxyl groups in the ATA were coordinating or not. Typical absorption bands arising from the mixed ligands and the carboxyl groups are listed in Table 3. The characteristic bands for the complexes in question occur in the 1600—1680 cm^{-1} region; this shows that all the complexes have coordinated carboxyl groups. In addition, the I complex gives the specific absorption bands representing the C=C, C=O, and C–H vibrations in the acetylacetone included. The II and III complexes show the bands concerned with the vibrations of C=C, C=N, and C–H in coordinated *α*, *α*′-dipyridyl or *o*-phenanthroline. For the IV complex, the strong absorption could be detected at 2085 cm^{-1} assigned to the stretching vibration of C–N in NCS. For the V complex, only the band due to the coordinated carboxyl groups could be seen.

Magnetic Moments. The magnetic susceptibility for the complexes was measured by the

TABLE 4. MAGNETIC MOMENTS (B.M.)

Complex	B.M.
I	3.76
II	3.72
III	3.77
IV	3.82
V	3.80



(A) (B) (C)

(D) (E) (F)

Fig. 4. Possible structures.

Gouy method. The numerical data of the magnetic moment, as evaluated from the above value, are summarized in Table 4. The values for these complexes are 3.7—3.9 B. M., nearly equal to their spin-only values for chromium (III).

Summary of the Structures. As all the complexes possess ATA as a tetradentate ligand, at least in the crystalline state, the two residual coordinating positions have to be occupied by other ligands in the octahedron. The possible structures for the mixed-ligand complexes newly prepared in the present work are shown in Fig. 4. The A, B, C, D, and E structures may be proposed for the I, II, III, IV, and V respectively. As has been mentioned above, the coordination structures of the IV and V complexes changed in an aqueous solution, their electronic spectra were quite similar to those of $[Cr(ox)_3]^{3-}$ and $[Cr(H_2O)_6]^{3+}$, and their molar conductivities were far from that of the 1 : 2-type electrolyte. It may be reasonably concluded that, in an aqueous solution, they will have the F structure, illustrated in Fig. 4, which contains ATA as a tridentate ligand and that the other coordinating positions are occupied by the H_2O and OH^- ligands, though their positions may be arbitrary.