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The Chromium(III) Complexes with Ammoniatriacetic Acid. I.[*1] The Complexes with Ammoniatriacetic Acid as a Tridentate or Tetradentate Ligand

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The following chromium(III) complexes, each containing ammoniatriacetic acid (ATA) as a tridentate or a tetradentate ligand, were newly prepared: $(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$ (pale red) (I), $NH_4[Cr(ataH)_2]\cdot 2H_2O$ (pink) (II), $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$ (purple) (III) and $NH_4[Cr(OH)(ata)(H_2O)]\cdot 3H_2O$(green)(IV), where ata is an abbreviated form of $N(CH_2COO^-)_3$. On the basis of the chemical and thermal analyses and the measurement of electronic absorption spectra, it was considered that the I and II complexes belong to the $[Cr\cdot N_2\cdot O_4]$ type, III belongs to the $[Cr\cdot N\cdot O_5]$ type, and IV to the $[Cr\cdot O_6]$ type. The further information on the conductivity in an aqueous solution suggested that the II and III complexes are gradually aquated to form the $[Cr\cdot N\cdot O_5]$ and $[Cr\cdot O_6]$ types respectively. The X-ray powder diffraction patterns show that all these complexes have crystals of the tetragonal system. The values of the effective magnetic moments for these complexes were 3.7—3.9 B. M., nearly equal to the spin-only magnetic moments of tervalent chromium.

The preparation of the cobalt(III) complexes with ammoniatriacetic acid (ATA) has already been reported1); here ATA could behave toward a cobalt(III) ion only as a tetradentate ligand, not as a tridentate ligand.

The purposes of this study were to find how ATA could behave toward a chromium(III) ion, to find if ATA coordinates to chromium not only as a tetradentate, but also as a tridentate ligand, to prepare various complexes in which ATA behaves

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1) M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, **31**, 940 (1958).

as a tetradentate or a tridentate ligand, and to investigate the conditions connected with the formation of these complexes.

Experimental

Preparation. *1) Ammonium Bis-(ammoniatriacetato)-chromate(III) Tetrahydrate,* $(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$. Approximately 4 g of ATA and an appropriate amount of chromium(III) hydroxide newly prepared from 10 g of chromium alum were mixed in 40 m*l* of water; then the mixed solution was evaporated almost to dryness on a water bath. The residue was dissolved in 30 m*l* of warm water, and the resultant purple solution was filtered from the residue undissolved. By using this purple solution as a starting material, the four complexes which shall be described in this paper could be prepared.

Another 4 g of ATA were dissolved in 10 m*l* of water containing about 3 g of ammonium carbonate; this mixture was added to the above purple solution and again evaporated to dryness. The residue was treated with 10 m*l* of an ethanol-water mixture (1 : 1), and the crude product was recrystallized from a 1% ammonium carbonate solution. The crystals were pale red needles. Yield, about 5 g.

Found: Cr, 9.32; N, 12.64; C, 25.10; H, 5.52; H_2O, 13.50%. Calcd for $(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$: Cr, 9.06; N, 12.21; C, 25.81; H, 5.96; H_2O, 13.01%.

2) Ammonium Bis-(hydrogenammoniatriacetato)chromate-(III) Dihydrate, $NH_4[Cr(ataH)_2]\cdot 2H_2O$. To the purple solution mentioned above, about 0.5 g of ammonium carbonate was added, the pH was adjusted to 3—4, and the mixture was cooled to 0°C. Pink powdered crystals were separated out and then recrystallized with water. The aqueous solution was purple and stable for several weeks. Yield, about 2 g.

Found: Cr, 10.82; N, 8.28; C, 29.75; H, 4.59; H_2O, 7.09%. Calcd for $NH_4[Cr(ataH)_2]\cdot 2H_2O$: Cr, 10.73; N, 8.68; C, 29.75; H, 4.54; H_2O, 7.44%.

3) Ammonium Hydroxoammoniatriacetatoaquochromate-(III) Dihydrate, $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$. To the purple solution, about 1.5 g of ammonium carbonate was added and the pH was adjusted to 5—6. After it was cooled to 0°C, purple scale-like crystals came out. The product was recrystallized from its concentrated greenish solution. Yield, about 1.5 g.

Found: Cr, 15.73; N, 8.35; C, 21.02; H, 4.33; H_2O, 10.18%. Calcd for $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$: Cr, 15.81; N, 8.52; C, 21.96; H, 4.86; H_2O, 10.93%.

4) Ammonium Hydroxoammoniatriacetatodiaquochromate-(III) Trihydrate, $NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$. To the purple solution, about 2.5 g of ammonium carbonate was added and the pH was adjusted to 7—8. When it was cooled to 0°C, green scale-like crystals were obtained. Since it was sometimes contaminated with purple crystals, the pH had to be well adjusted to 7—8. The recrystallization was also achieved from its concentrated greenish solution, adjusting the pH to 7—8 by adding an appropriate amount of ammonium carbonate. Yield, about 1.5 g.

Found: Cr, 14.32; N, 7.90; C, 20.25; H, 5.03; H_2O, 14.13%. Calcd for $NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$: Cr, 14.25; N, 7.67; C, 19.71; H, 5.75; H_2O, 14.79%.

The content of the crystalline water in these complexes was estimated from the weight loss in the respective thermogravimetric curves, which are shown in Fig. 1. The weight loss was measured with a Shimadzu Thermano-Balance. It was found that all of these complexes were dehydrated at about 110°C and decomposed at about 250—280°C.

Interconversion among These Complexes. The four complexes obtained were also successively interconverted into each other under specific conditions. The interconversion was, of course, considerably affected by the pH values in the solution. Figure 2 shows schematically the preparative interconversion among these complexes.

Several procedures of interconversion are presented below:

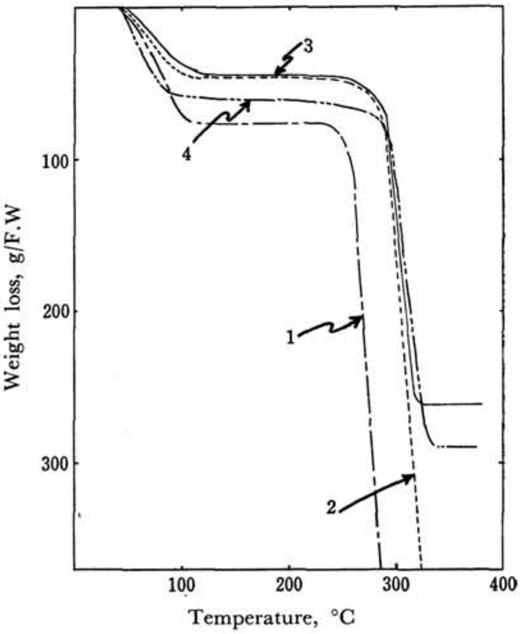

Fig. 1. Thermal decomposition curves.
1: $(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$
2: $NH_4[Cr(ataH)_2]\cdot 2H_2O$
3: $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$
4: $NH_4[Cr(OH)(ata)(H_2O)]\cdot 3H_2O$

A) The Interconversion from I to II. To the pale red aqueous solution of I (pH about 6), a few drops of concentrated hydrochloric acid were added and the pH was adjusted to 3—4. The solution turned purple, and pink powder crystals of II were separated out.

B) The Interconversion from II to I. One mole of ammonium carbonate was added to a purple solution containing one mole of II, and the resultant solution was evaporated to dryness. Pale red crystals of I were separated out.

C) The Interconversion from I to III or IV. When a pale red solution of I was cooled to 0°C, purple scale-like crystals III were obtained. After the pH of the pale red solution of I had been adjusted to 7—8 under cooling at 0°C by adding an appropriate amount of ammonium carbonate, greenish scale-like crystals were obtained.

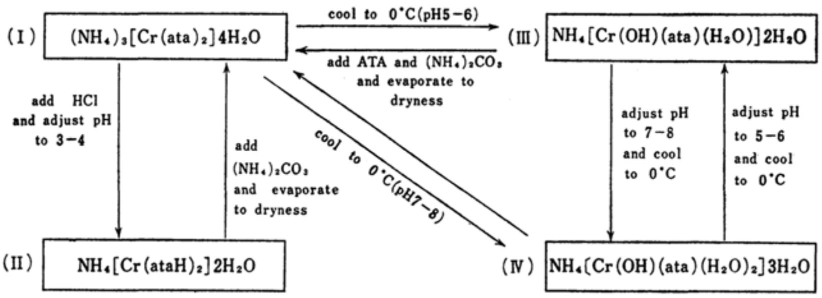

Fig. 2. Flow chart for the preparative interconversions of the complexes.

D) The Interconversion from III or IV to I. One mole of ATA was dissolved in water containing one mole of ammonium carbonate, and the mixed solution was added to one mole of a greenish solution of III or IV. When the solution thus obtained was evaporated to dryness, pale red crystals of I were separated out.

E) The Interconversion from III to IV or IV to III. The pH of a greenish solution of III (pH about 7) was adjusted to 7—8 by adding small amount of ammonium carbonate; when it was then cooled to 0°C, green crystals of IV were obtained. On the other hand, when hydrochloric acid was used instead of ammonium carbonate, the pH of the greenish solution of IV (pH about 7) decreased to 5—6; after it was cooled to 0°C, purple crystals of III were obtained.

Apparatus. The conductivity, the ultraviolet, visible and infrared absorption spectra, the magnetic susceptibility, and the X-ray diffraction were measured with a Yokogawa Universal Bridge BV-Z-13A, a Hitachi EPS Spectrophotometer and a Nippon Bunko DS-301 Infrared Spectrometer, a Gouy Balance, and a Rigaku-denki Geiger-flex X-ray Analyzer respectively.

Results and Discussion

Reactions to the Ion Exchanger and Molar Conductivity. The reactions to the ion exchanger and molar conductivities of a 1/1000 mol solution of the samples are shown in Table 1, in which the symbol + indicates the possibility of the adsorption of the complexes by the resin, and −, the reverse.

The pale red aqueous solution of the I crystal, keeping for a while its original pale red color, was adsorbed by the Cl-form anion exchanger. Its molar conductivity was 288.0 mho cm^{-1}, which supports the idea that the I complex is a 1 : 3-type electrolyte. On standing overnight, I turned green.

The pink crystals of II turned purple in an aqueous solution as soon as they were dissolved, and they were adsorbed by neither Na-form nor Cl-form resin, showing that this complex species exists as non-electrolyte molecules.

In addition, the purple solution used as a starting material could not be adsorbed by either type of exchanger.

The solutions of the purple crystals of III and of the green crystals of IV were both greenish and were adsorbed by the Cl-form anion exchanger. Their molar conductivities were 119.3 and 116.5 mho cm^{-1} respectively, suggesting that they are 1 : 1-type electrolyte-complex ions.

Visible and Ultraviolet Absorption Spectra. The absorption spectrum for the pale red complex, I, was measured in a phosphate buffer with a pH of 6 in order to prevent gradual decomposition; the spectra for the other three, II, III, and IV, were measured in an aqueous solution. The spectra are shown in Fig. 3 and Fig. 4, and the numerical values of the first and the second absorption maxima are summarized in Table 2.

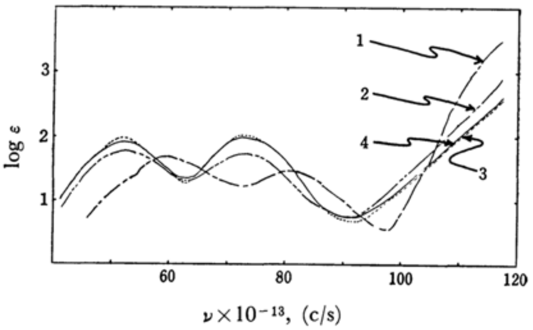

Fig. 3. Electronic absorption spectra.
1: $(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$
2: After decomposition of $(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$
3: $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$
4: $NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$

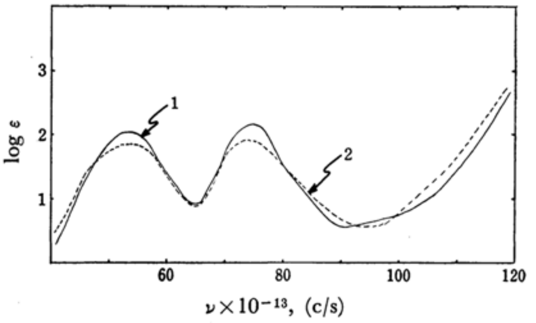

Fig. 4. Electronic absorption spectra.
1: $NH_4[Cr(ataH)_2]\cdot 2H_2O$
2: Purple solution used as a starting material.

TABLE 1. BEHAVIOR TO THE ION EXCHANGER AND MOLAR CONDUCTIVITY

Complex	Color of crystal	Color of solution	Adsorption of the ion exchanger		Molar conductivity (mho cm^{-1})
			Na-form	Cl-form	
$(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$	pale red	pale red	−	+	288.0
$NH_4[Cr(ataH)_2]\cdot 2H_2O$	pink	purple	−	−	
$NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$	purple	green	−	+	119.3
$NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$	green	green	−	+	116.5

TABLE 2. ABSORPTION MAXIMA

Complex	ν_1(10^{13}/sec)(log ε_1)	ν_2(10^{13}/sec)(log ε_2)
$(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$	60.1 (1.65)	83.6 (1.48)
$NH_4[Cr(ataH)_2]\cdot 2H_2O$	53.9 (2.02)	74.3 (2.06)
$NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$	51.5 (1.95)	73.5 (2.05)
$NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$	51.5 (1.92)	73.5 (2.00)

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

Complex	-COOH	-COO-Cr(III)	-COO$^-$
$ataH_3$	1698 (s) 1233 (m)		
$ataH(NH_4)_2$			1623 (vs)
$(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$		1658 (sh)—1629 (vs)	1603 (sh)
$NH_4[Cr(ataH)_2]\cdot 2H_2O$	1748 (s) 1225 (s)	1659 (sh)—1621 (vs)	
$NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$		1658 (sh)—1618 (vs)	
$NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$		1658 (sh)—1631 (vs)	

TABLE 4. MAGNETIC MOMENT AND RESULT OF X-RAY DIFFRACTION

Complex	Magnetic moment (B. M.)	Crystal system	a(Å)	c(Å)	a/c	d		Z
						Found	Calcd	
$(NH_4)_3[Cr(ata)_2]\cdot 4H_2O$	3.82	tetragonal	11.29	16.39	1.45	2.97	3.10	8
$NH_4[Cr(ataH)_2]\cdot 2H_2O$	3.93	tetragonal	15.12	19.55	1.29	2.24	2.19	16
$NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$	3.75	tetragonal	16.32	22.15	1.35	2.50	2.52	16
$NH_4[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$	3.90	tetragonal	15.06	19.35	1.28	1.99	2.12	16

The absorption spectrum for the I complex has two bands, at 60.1 and at 83.6×10^{13}/sec. So far as the first band, due to a d-d electron transition, is concerned, an indication of splitting is detected. As has been mentioned above, on standing overnight this pale red solution turned green, and it is reasonable that the spectrum is quite similar to that of IV.

The spectrum of the II complex agreed with that of the purple solution used as a starting material.

Though the III complex had purple crystals, it instantaneously turned green in an aqueous solution, and the spectrum was quite analogous to that of IV, in which the first and the second bands are at 51.5 and 73.5×10^{13}/sec respectively. This may mean that the instantaneous conversion of $[Cr(OH)(ata)(H_2O)]^-$ to $[Cr(OH)(ata)(H_2O)_2]^-$ and the gradual conversion of $[Cr(ata)_2]^{3-}$ to $[Cr(OH)(ata)(H_2O)_2]^-$ take place by aquation under the above conditions.

Infrared Absorption Spectra. The infrared absorption spectra of the complexes were measured in the mull state of Nujol. The characteristic absorption peaks for the complexes in question occur in the regions of 1700—1750, 1600—1660, and 1230 cm^{-1}, as listed in Table 3. The peaks in the first and the third wavelength regions mentioned above are assigned to the stretching vibration of carboxyl groups not coordinated to metal, while the peak in the second wavelength region is assigned to that of carboxyl groups coordinated to metals.

The II complex has strong absorptions near 1750 and 1230 cm^{-1}, suggesting the presence of free carboxylic acid radicals. The shoulder at

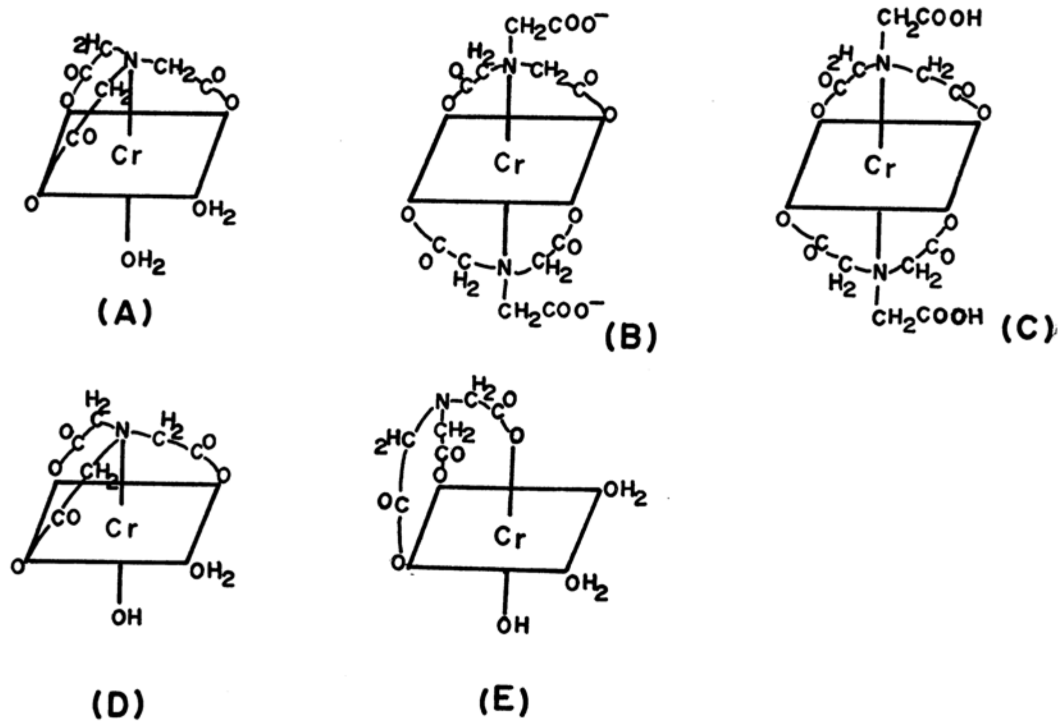

Fig. 5. Possible structures.

1603 cm^{-1}, which appeared only in the pale red crystals, may give evidence for the presence of free carboxylate ions in the complex.

Magnetic Moment and X-Ray Powder Diffraction Pattern. The effective magnetic moment of the complexes was evaluated from the magnetic susceptibility as measured by the Gouy-method. The numerical data, corrected by Pascal's constants,[2] are summarized in Table 4.

As may be seen in Table 4, the effective magnetic moments, 3.7—3.9 B. M., of these complexes are very close to those for the spin-only value of tervalent chromium.

The results of the X-ray diffraction measurement are shown in Table 4, together with the values of the magnetic moments. It is found in this table that all these complexes belong to a tetragonal system.

Determination and Discussion of the Possible Structures. Now, the possible structures of these complexes proposed on the basis of the above results are given in Fig. 5.

The purple solution used as the starting material of the preparation of these complexes may be considered to have the A structure (Fig. 5). For the pale red crystal, the trans structure, as illustrated by B, seems reasonable from the splitting at the long-wave side of the first band[3] and the presence of the free carboxylate ions.

For the pink crystals, which have the free carboxylic acids, C may be proposed. However, in an aqueous solution, the A structure will be proposed because this solution was non-electrolyte and showed a spectrum quite similar to that of the purple solution used as the starting material.

The purple crystals may be assigned a D structure in which the H_2O ligand is cis-position to the coordinated nitrogen atom, because the infrared spectrum of this complex is very analogous to that of the α-form of the corresponding cobalt-(III) complex,[1] which has been reported to have the $K[Co(OH)(ata)(H_2O)]\cdot 2H_2O$ formula and to be cis-form concerning the position of the OH^- and H_2O ligands.

For the green crystals, from the evidence that all of the carboxyl groups participate in coordination, the structure may be regarded as E, in which the coordinating positions of the octahedron are occupied by six oxygen atoms, although the positions of the OH^- and H_2O ligands are arbitrarily drawn.

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[2] P. E. Selwood, "Magnetochemistry," 2nd ed., Interscience Pub., New York.

[3] H. Yamatera, This Bulletin, **31**, 95 (1956).