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Preparation of Chromium(III) and Cobalt(III) Complexes with *l*-Leucine-*N*,*N*-diacetic Acid[*1]

Akira UEHARA, Eishin KYUNO and Ryokichi TSUCHIYA

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

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l-Leucine-*N*,*N*-diacetic acid (abbreviated as LDA) and the complexes thereof were prepared as follows: $K[Cr(OH)(lda)(H_2O)]\cdot 3H_2O$ (violet) (I), $[Cr(lda)(H_2O)_2]$ (bluish violet) (II), $[Cr(lda)(H_2O)_2]\cdot 2H_2O$ (grayish violet) (III), $(enH_2)_{1/2}[Cr(OH)(lda)(H_2O)_2]$ (green) (IV), $[Cr(lda)(o\text{-phen})]\cdot 2H_2O$ (brownish orange) (V), $K[Cr(lda)(acac)]\cdot H_2O$ (blackish violet) (VI) and $K[Co(OH)(lda)(H_2O)]\cdot H_2O$ (bluish violet) (VII), where *l*da, en, *o*-phen and acac are the abbreviations of *l*-leucine-*N*,*N*-diacetate ion, ethylenediamine, *o*-phenanthroline and acetylacetonate ion, respectively. Except for Complex IV, LDA behaves as a quadridentate ligand. In Complex IV, it acts as a terdentate one. It was found from electronic absorption spectra that in Complex I, LDA behaves as a quadridentate in a solid state and as a terdentate ligand in an aqueous solution, whereas in cobalt(III) complex VII corresponding to I, LDA behaves as a quadridentate. Stepwise liberation of the coordinated water molecules in Complexes II and III could be detected by means of Derivatograph. Complex VII showed "Dehydration-Dimerization Reaction" upon being heated.

Preparation and properties of chromium(III) complexes with ammoniatriacetic acid (ATA) or with its derivatives have been reported.[1–5] Although these agents have a maximum of four coordinating sites, the coordinating behaviors somewhat differ from each other due to the slight differences in their structures and chemical properties. As an example, the ligands which can form three five-membered chelate rings such as ATA or AIPDA act not only as a quadridentate of $N–O_3$ type but also as a terdentate ligand of O_3 type.[1,4] ATA, APDA and AEDA can also behave as a terdentate ligand of $N–O_2$ type.[1,3,5] In spite of the analogous structure of APDA and AEDA, the latter behaves with difficulty as a quadridentate due to the weaker coordinating ability of oxygen atom in the sulfonic than that in carboxylic group.

In a series of studies on chromium(III) and cobalt(III) complexes with ATA and its derivatives, the preparation of *l*-leucine-*N*,*N*-diacetic acid and the complexes thereof were undertaken in order to investigate how LDA behaves toward the two metals.

For the sake of convenience, the rational formula of LDA is given in Table 1 with respect to ATA as the mother chelating agent and the other related agents.[1,3,5]

Experimental

Preparation of *l*-Leucine-*N*,*N*-diacetic Acid, $C_{10}H_{17}O_6N$. Thirteen grams of *l*-leucine was dissolved in 50 m*l* of water containing 6 g of sodium hydroxide

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

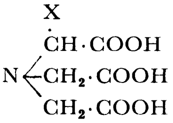
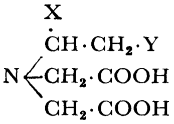
2) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **40**, 2322 (1967).

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

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

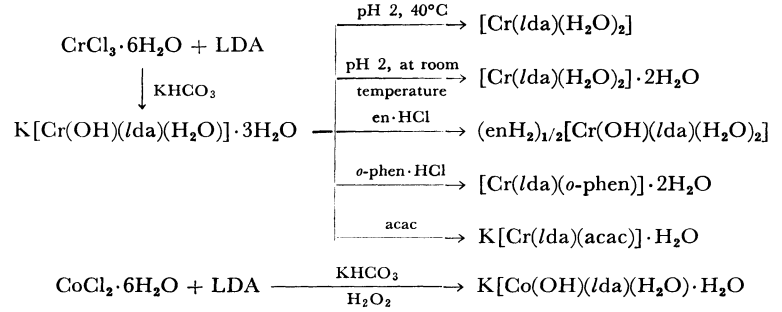
5) A. Uehara, E. Kyuno and Tsuchiya, *ibid.*, **42**, 2835, (1969).

Table 1. Chelating agents

Rational formulas	Chelate rings	Chelating agents
	5, 5, 5	X=H : ATA* X=CH_3 : AIPDA* X=$CH_2 \cdot CH \cdot (CH_3)_2$: LDA*
	5, 5, 6	X=H, Y=COOH : APDA* X=H, Y=SO_3H : AEDA* X=COOH, Y=COOH : ASDA*

* ATA: Ammoniatriacetic acid, AIPDA: Ammoniaisopropionicdiacetic acid, LDA: *l*-Leucine-*N*,*N*-diacetic acid, APDA: Ammoniapropionicdiacetic acid, AEDA: *β*-Aminoethylsulfonic-*N*,*N*-diacetic acid, ASDA: Aspartic-*N*,*N*-diacetic acid

Table 2. Preparative scheme for Cr-, Co-LDA complexes



(A). 70 m*l* of water containing 19 g of monochloroacetic acid was gradually neutralized with 17 g of sodium hydrogen carbonate (B). B had to be added gradually to A since rapid addition produces deposit of *l*-leucine. The mixture was heated on a water bath, 30 m*l* of water containing 12 g of KOH being added. Heating was continued for about 1 hr till the condensation reaction was completed. After the solution was cooled, concentrated hydrochloric acid was added little by little to the solution with scrubbing of the wall of the reaction vessel with a glass rod, when white powdered crystals were deposited. Recrystallization was achieved by dissolving the crude products in sodium hydrogen carbonate solution and by adjusting the pH of the solution to 3. Yield about 8 g.

Found: N, 5.66; 48.49; H, 6.86%. Calcd for $C_{10}H_{17}O_6N$: N, 5.63; C, 48.57; H, 6.92%.

Preparation of Complexes. Preparation of the complexes is schematically shown in Table 2.

Potasium Hydroxo-*l*-leucine-*N*,*N*-diacetatoaquochromate(III) Trihydrate, K[Cr(OH)(*l*da)(H_2O)]·$3H_2O$ (I). Twenty five grams of chromium chloride hexahydrate and 24 g of LDA were added to about 300 m*l* of water. The mixture was heated on a water bath until LDA was completely dissolved. To the resulting violet solution, about 10 g of potassium hydrogen carbonate were added, when vigorous bubbling took place. Heating of the solution was continued until the bubbles subsided. When the solution was concentrated, a tar-like residue was deposited out. The supernatant layer was discarded by decantation. The residue was dissolved in about 300 m*l* of water. The pH of the violet solution was then adjusted to 6—7 by adding an appropriate amount of potassium hydrogen carbonate. The resulting solution was concentrated to about 200 m*l* and was stood in a refrigerator. Violet crystals were obtained. Recrystallization was carried out from water. Yield about 5 g. The crystals were used as material to prepare the following complexes, II to VI.

Found: N, 3.31; C, 28.31; 5.43%. Calcd for K[Cr(OH)(*l*da)(H_2O)]·$3H_2O$: N, 3.47; C, 28.58; H, 4.84%.

The use of ammonium carbonate, instead of potassium hydrogen carbonate as described above, produced the corresponding ammonium salt which is also violet.

Found: N, 7.28; C, 31.18; H, 6.48%. Calcd for NH_4[Cr(OH)(*l*da)(H_2O)]·$2H_2O$: N, 7.25; C, 30.90; H, 6.51%.

***l*-Leucine-*N*,*N*-diacetatodiaquochromium(III), [Cr(*l*da)(H_2O)$_2$] (II).** Five grams of Complex I was dissolved in 200 m*l* of hot water and then a few drops of hydrochloric acid were added. As the solution was gradually concentrated at about 40°C, violet crystals were depo-sited out. The crude crystals were recrystallized from a concentrated hot aqueous solution. Yield about 1.5 g.

Found: N, 4.22; C, 36.18; H, 5.43%. Calcd for [Cr(*l*da)(H_2O)$_2$]: N, 4.51; C, 35.56; H, 5.42%.

***l*-Leucine-*N*,*N*-diacetatodiaquochromium(III) Dihydrate, [Cr(*l*da)(H_2O)$_2$]·$2H_2O$ (III).** Preparation was carried out in a manner similar to that used for II, except that the solution was stood at room temperature instead of 40°C. The crystals have a grayish violet color. Recrystallization was achieved from water. Yield about 2 g.

Found: N, 3.81; C, 32.62; H, 5.38%. Calcd for $[Cr(lda)(H_2O)_2]\cdot 2H_2O$: N, 3.88; V, 32.54; H, 5.19%.

Ethylenediamine Hydroxo-*l*-leucine-*N*,*N*-diacetatodiaquochromate(III) $(enH_2)_{1/2}[Cr(OH)(lda)(H_2O)_2]$ (IV). Five grams of Complex I was dissolved in 200 m*l* of water and then 4 g of ethylenediamine hydrochloride was added. Gradual concentration on a water bath gave a deposit of green crystals. Another crop of crystals were obtained from the resulting cool solution. Recrystallization was carried out from water. Yield about 2 g.

Found: N, 7.37; C, 34.79; H, 6.12%. Calcd for $(enH_2)_{1/2}[Cr(OH)(lda)(H_2O)_2]$: N, 7.22; C, 35.03; H, 5.93%.

***l*-Leucine-*N*,*N*-diacetato-*o*-phenanthrolinechromium(III) Dihydrate, $[Cr(lda)(o\text{-phen})]\cdot 2H_2O$ (V).** Two grams of *o*-phenanthroline was added to 200 m*l* of water containing 5 g of Complex I. After the pH of the solution was adjusted to 4—5, it was heated on a water bath. Heating was continued until brown crystals began to deposit. Although the crystals are slightly soluble in water, recrystallization can be made from hot water. Yield about 3 g.

Found: N, 8.21; C, 51.59; H, 5.08%. Calcd for $[Cr(lda)(o\text{-phen})].2H_2O$: N, 8.43; C, 51.91; H, 4.72%.

Potassium *l*-Leucine-*N*,*N*-diacetatoacetylacetonatochromate(III) Monohydrate, $K[Cr(lda)(acac)]\cdot H_2O$ (VI). Two-hundred milliliters of aqueous solution containing 5 g of Complex I and 1.5 g of acetylacetone was heated on a water bath and then was concentrated to about 50 m*l*. The solution being stood in a refrigerator for a few days, blackish violet crystals were obtained. The crude products were recrystallized from a water-alcohol mixture (1 : 4). Yield about 2 g.

Found: N, 3.09; C, 39.75; H, 5.29%. Calcd for $K[Cr(lda)(acac)].H_2O$: N, 3.03; C, 39.20; 5.19%.

Potassium Hydroxo-*l*-leucine-*N*,*N*-diacetatoaquocobaltate(III) Monohydrate, $K[Co(OH)(lda)(H_2O)]\cdot H_2O$ (VII). One-hundred grams of LDA was added to 300 m*l* of water containing 100 g of cobalt(II) chloride hexahydrate and then the mixture was heated on a water bath. About 50 g of potassium hydrogen carbonate was gradually added. After the pH of the solution was adjusted to 6—7, about 10 m*l* of 28% hydrogen peroxide solution was dropped into the solution in order to oxidize the cobalt(II) ion. Bluish violet crystals were obtained from the solution stood at room temperature. Recrystallization was achieved from water. Yield about 20 g.

Found: N, 3.54; C, 30.41; H, 4.82%. Calcd for $K[Co(OH)(lda)(H_2O)]\cdot H_2O$: N, 3.72; 30.78; H, 4.71%.

Apparatus. Molecular rotatory power was measured with Model MP-IT Polarimeter supplied by Applied Electric Lab., Ltd. The other apparatus used in this paper were the same as described previously.[1-5]

Results and Discussion

IR Spectra. The infrared absorption spectra were measured in their nujol mull state in order to ascertain whether or not the carboxylic group was coordinated. Table 3 shows their IR data. Assignments by Busch and Bailar[6] were also applied in this paper. The bands observed at 1738 and 1580 cm^{-1} in LDA itself were assigned to free carboxylic acid and carboxylate ion, respectively. Only one band was observed in all the complexes in the range ($\sim$1650 cm^{-1}) where the presence of the coordinated carboxylate groups can be detected.

Molar Conductivities. Molar conductivities were measured in an aqueous solution at 25°C for examination of the type of electrolytes for the complexes. The results are given in Table 4, together with their magnetic moments evaluated from magnetic susceptibilities measured at 20—23°C. Numerical data of conductivities for Complexes I, IV, VI and VII are within 110 to 160 mho cm^{-1}, indicating that these complexes are the 1 : 1 type electrolytes. The value for IV (157 mho cm^{-1}) is somewhat larger than that expected. This seems to be due to the partial dissociation of the hydrogen ion from enH_2^{2+}. Small conductivities for II, III and V suggest that they are non-electrolyte complex species.

Magnetic Moments. The effective magnetic moments of these complexes were evaluated from the magnetic susceptibilities measured by the Gouy method. The results are shown in Table 4. The magnetic moments for I to VI are in region of 3.75—

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

Complexes	-COOH	-COO-M	$-COO^-$	Complement
I		1069—1640		
II		1670—1610		
III		1665—1615		
IV		1660—1630		
V		1690—1640		1585, 1529, 860*[1]
VI		1680—1630		1573, 1528*[2]
VII		1690—1640		
LDA	1738		1580	

*[1] Absorptions arising from *o*-phenanthroline.
*[2] Absorptions arising from acetylacetone.

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

Table 4. Molar conductivities (λ) and magnetic moments (μ_{eff})

Complexes	λ* mho cm^{-1}	λ* (°K)	μ_{eff} B.M.	μ_{eff} (°K)
I	111.2	(298°)	3.76	(293°)
II	11.2	(298°)	3.81	(293°)
III	3.3	(298°)	3.83	(293°)
IV	157.0	(298°)	3.81	(294°)
V	19.6	(298°)	3.93	(294°)
VI	109.0	(298°)	3.86	(296°)
VII	117.8	(298°)	dia	(294°)

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

3.95 B.M., being near the spin-only values for tervalent chromium. Complex VII is diamagnetic, indicating that the cobalt is tervalent.

Molecular Rotatory Powers. As LDA is optically active, the measurements of molecular rotatory powers for LDA and each complex were carried out with a Na-D line. The data are summarized in Table 5.

Table 5. Molecular rotatory powers

Complexes	$[M]_D^{25}$	Condition
I	+373	0.3% aqueous solution
II	+298	0.3% aqueous solution
III	+260	0.4% aqueous solution
IV	+362	0.3% aqueous solution
V	+41	0.1% aqueous solution
VI	+299	0.4% aqueous solution
VII	+1132	0.4% aqueous solution
LDA	+22.5	8.7% (0.1 N $KHCO_3$) solution

Electronic Spectra. Electronic spectra of all the complexes were measured in an aqueous solution, and those for solid-state were carried out by a diffusion-reflection method. The spectra are shown in Figs. 1—5, and numerical values of absorption maxima are summarized in Table 6.

Table 6. Absorption maxima

Complexes	ν_1(10^{13}/sec)	(log ε_1)	ν_2(10^{13}/sec)	(log ε_2)
I	51.46	(1.96)	72.64	(2.00)
II	53.57	(2.03)	73.53	(2.01)
III	53.57	(2.04)	73.53	(1.99)
IV	51.46	(1.94)	72.64	(2.01)
V	56.39	(1.95)	76.14	(2.87)
VI	54.45	(1.98)	78.13	(2.28)
VII	53.10	(2.28)	75.38	(2.32)

The spectra for Complex I in an aqueous solution and in a solid state are shown in Fig. 1 together with those for the corresponding ATA complex in a solution. The spectra for Complex I and the corresponding ATA complex both in solution are quite similar, whereas the spectrum for Complex I in a solid state is considerably different from the former two. The facts suggest that, like the ATA complex, LDA actsas a quadridentate (N_1–O_3 type) in a solid state but as a terdentate (O_3 type) in an aqueous solution.

Figure 2 shows the spectra in an aqueous solution for Complexes II, III and $[Cr(ata)(H_2O)_2]$ in which ATA acts as a quadridentate ligand. Close resemblance between these spectra suggests that the structures of these complex species are analogous with each other and LDA behaves as a quadridentate.

Figure 3 shows the spectra in solution and solid state for Complex IV and those for the corresponding ATA complex in solution in which ATA behaves as a terdentate ligand (O_3 type). Similarity among these spectra suggests that the structures of Complex IV are identical in solid state and solution, and that LDA behaves toward metal as a terdentate

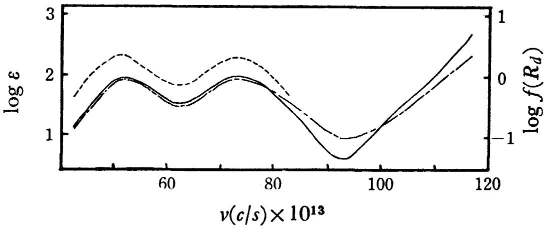


Fig. 1. Electronic Spectra for the solution (——) and the solid (- - -) of Complex I and for the solution of $K[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$ (—·—).

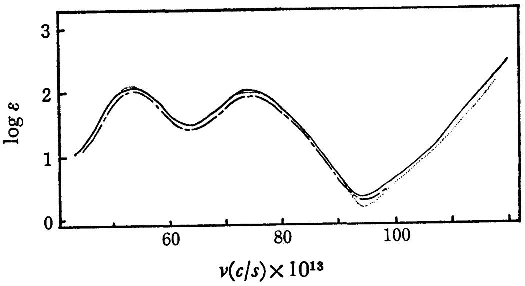


Fig. 2. Electronic spectra for the solutions of Complex II (——), Complex III (······) and $[Cr(ata)(H_2O_2)]$ (—·—).

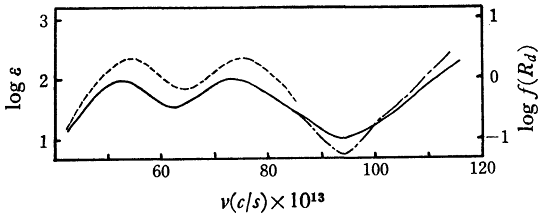


Fig. 3. Electronic spectra for the solution (——) and the solid (- - -) of Complex IV and for the solution of $K[Cr(OH)(ata)(H_2O)_2]\cdot 3H_2O$.

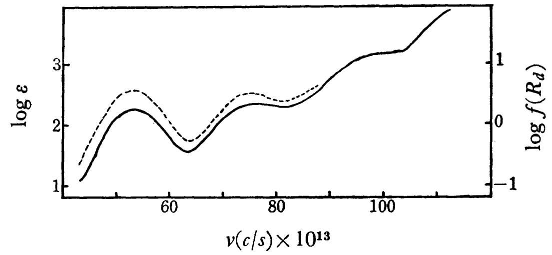


Fig. 4. Electonic spectra for the solution (——) and the solid (······) of Complex VII.

(O_3 type) as in the case of the ATA complex.

The spectra for Complex VII in a solid state and in an aqueous solution are shown in Fig. 4. We see that both spectra resemble each other, showing the same structures. This is different from Complex I. This might be mainly due to the ease of aquation in the latter complex, *viz.*, the chromium(III) complex may more easily undergo an aquation than the corresponding cobalt(III) complex.

Thermal Decomposition Processes in Complexes II, III and VII. Thermal decomposition of the complexes was measured with a Derivatograph[7,8] in a constant nitrogen stream with heating rate 1°C/min. Five-hundred milligrams of the samples was used in each experiment. The derivatograms for Complexes II, III and VII are given in Fig. 5.

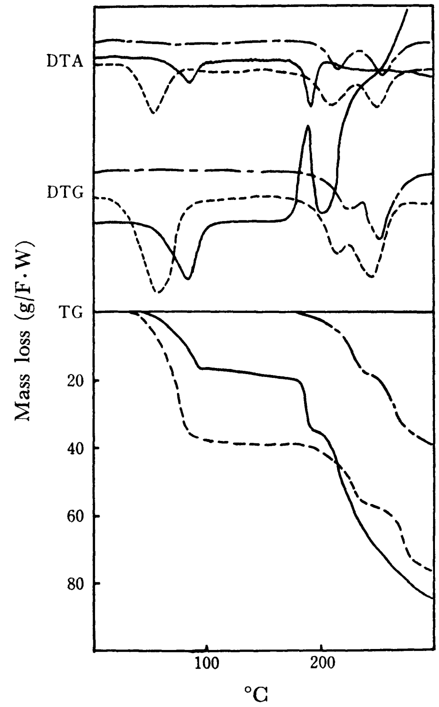
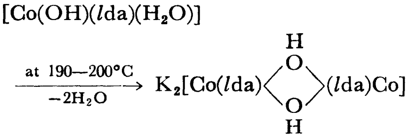


Fig. 5. Derivatograms for Complexes II (—·—), III (- - -) and VII (——).

Complex III, first, lost two moles of crystalline water at 100°C and liberated stepwise two moles of coordinated water at 190 to 230°C in the second step.

For Complex II having no crystalline water, a similar liberation of two moles of coordinated water could be detected at 190—235°C as in the second step of III.

Complex VII lost one mole of crystalline water at 100°C and the weight loss, corresponding to one mole of water, was detected at 190—200°C. It is of interest that an exothermic peak appears on DTA curve in the corresponding temperature range. At this step the color of the sample turned from bluish violet to reddish violet. From the results, the dimerization reaction seems to proceed at this step, resulting in the formation of the diol complex as shown by



$$2K[Co(OH)(lda)(H_2O)] \xrightarrow[-2H_2O]{\text{at } 190\text{—}200°C} K_2[Co(lda)\langle\overset{H}{O}\rangle\langle\underset{H}{O}\rangle(lda)Co].$$

A more detailed discussion and the kinetics for this reaction will be published elsewhere with illustrative examples.

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7) R. Tsuchira, Y. Kaji, A. Uehara and E. Kyuno, This Bulletin, **42**, 1881 (1969).

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