Preparation and Properties of Oxo-Centered Trinuclear Chromium(III) Complexes with Bridging Optically Active Amino Acids, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-amino-acid})_6(H_2O)_3]^{7+}$ [1)]

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Synopsis. Trinuclear chromium(III) complexes with optically active amino acids as bridging groups, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}RCH(NH_3)COO)_6(H_2O)_3]X_7$ (R=CH_3, $(CH_3)_2CH$, $(CH_3)_2CHCH_2$, $C_6H_5CH_2$; X=Cl^-, NO_3^-), were prepared, and the X-ray structure of the L-valine complex was determined. Their electronic spectra and magnetic moments are similar to those of analogous carboxylate-bridged trichromium(III) complexes.

Oxo-centered triangular trinuclear metal complexes with bridging carboxylates ($RCOO^-$) between each pair of metal ions are known for various tervalent metal ions such as V, Cr, Mn, Fe, Co, Ru, Rh, and Ir.[2)] They have a general formula, $[M_3(O)(RCOO)_6L_3]^+$ (hereafter abbreviated as M_3, and L stands for a monodentate ligand such as H_2O, pyridine, and so on). Amino acids are also known as bridging ligands (μ-O,O'-$RCH(NH_3)COO$) for the Fe_3 complexes[3-7)] and some mixed Fe_nCr_{3-n} analogs.[8-10)] Complexes with bridging amino acids are important to extend the chemistry of trinuclear complexes. The Fe_3 amino acid complexes are not stable in aqueous solution,[11)] and not suitable for extending their chemistry further particularly in solution. We thought it important to prepare amino acid bridged derivatives of the trinuclear metal complexes with substitution inert metal ions such as Cr(III), Ru(III), and Rh(III). Amino acid complex for these metal ions reported before we started the present study was only $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-glyH})_6(H_2O)_3]^{7+}$ (Hgly=glycine).[9)] The present paper describes the preparation and some properties of new trinuclear chromium(III) complexes with optically active amino acid bridges. Very recently, alanine and α-aminobutane chromium(III) complexes were reported by Fisher et al.[12,13)]

Experimental

Preparation of the Complexes. L-Alanine Complex, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-}CH_3CH(NH_3)COO)_6(H_2O)_3]Cl_7\cdot 5H_2O$ (1). $Cr(NO_3)_3\cdot 9H_2O$ (4.00 g, 0.01 mol) dissolved in absolute ethanol (20 cm^3) was added to the suspension of L-alanine (1.78 g, 0.02 mol) in water (20 cm^3). After pH was adjusted to 2 with diluted nitric acid, the mixture was kept at 70—80 °C for 10 h, during which time L-alanine was dissolved completely. Volume of the solution was then reduced to ca. 20 cm^3 on a rotatory evaporator. The solution was then treated with Sephadex G-10 column chromatography (35 mmϕ×400 mm). The green eluate of 0.1 M HCl (1 M=1 mol dm^{-3}) was concentrated to dryness. The green residue was dissolved in a small amount of ethanol. Green powder was obtained on addition of diethylether, and was collected by filtration and dried under vacuum. Yield, 1.02 g (26%). Anal. Found: C, 19.87; H, 4.68; N, 7.37%. Calcd for $C_{18}H_{58}N_6O_{21}Cl_7Cr_3$: C, 19.67; H, 4.59; N, 7.65%. IR (cm^{-1}): $COO(\nu_a)$, 1655; $COO(\nu_s)$, 1436.

L-Valine Complex, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-}(CH_3)_2CHCH(NH_3)COO)_6(H_2O)_3](NO_3)_7\cdot 5H_2O$ (2). This was prepared similarly as **1** by using L-valine (2.38 g, 0.02 mol) in place of L-alanine. After reducing the volume to ca. 20 cm^3, the solution was set aside for a few days at room temperature instead of treating with the column. Large green crystals were collected by filtration and dried under vacuum. Yield, 1.78 g (36%). Anal. Found: C, 24.53; H, 5.26; N, 13.16%. Calcd for $C_{30}H_{82}N_{13}O_{42}Cr_3$: C, 24.80; H, 5.69; N, 12.53%. IR (cm^{-1}): $COO(\nu_a)$, 1658; $COO(\nu_s)$, 1452.

L-Leusine Complex, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-}(CH_3)_2CHCH_2CH(NH_3)COO)_6(H_2O)_3]Cl_7\cdot H_2O$ (3), and L-Phenylalanine Complex, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-}C_6H_5CH_2CH(NH_3)COO)_6(H_2O)_3]Cl_7\cdot 6H_2O$ (4). These compounds were synthesized in a similar way to the preparation for **1**. Yield of green powder, 1.08 g (26%) for **3** and 0.33 g (7%) for **4**. Anal. Found for **3**: C, 32.42; H, 7.02; N, 6.53%. Calcd for $C_{36}H_{92}N_6O_{20}Cl_7Cr_3$: C, 32.43; H, 6.95; N, 6.30%. Found for **4**: C, 41.21; H, 5.37; N, 5.32%. Calcd for $C_{54}H_{84}N_6O_{22}Cl_7Cr_3$: C, 41.21; H, 5.34; N, 5.34%. IR (cm^{-1}): $COO(\nu_a)$ 1655, $COO(\nu_s)$ 1445 for **3**; $COO(\nu_a)$ 1660, $COO(\nu_s)$ 1450 for **4**.

Measurements. Electronic and CD spectra were measured with a Hitachi 340 spectrophotometer and a JASCO J-40A spectropolarimeter, respectively. Infrared absorption spectra were recorded on a JASCO IR-810 spectrophotometer by KBr method. Magnetic susceptibilities at room temperature were measured in methanol-d_4 by the Evans method.[14)]

X-Ray Structure Determination for 2. A green crystal of the L-valine complex (**2**) with dimensions 0.3×0.3×0.4 mm was used for the X-ray work. X-Ray data were collected on a Rigaku AFC-5R four circle diffractometer equipped with a rotating Mo anode (40 kV, 200 mA, λ=0.71069 Å). Intensity data were corrected for Lorentz and polarization factors. No absorption correction was applied. Crystallographic data are: monoclinic, $P2_1$, a=13.104(5), b=21.460(7), c=12.218(4) Å, β=110.99(3)°, V=3207(2) Å^3, Z=2, ρ_{obsd}=1.47, ρ_{calcd}=1.50 g cm^{-3}.

The structure was solved by the direct method and refined by use of the block-diagonal least-squares method. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the calculation. Final R value was 0.099 for 6394 independent reflections ($F_o \geqslant 3\sigma(F_o)$) and 794 parameters.[15)] All the calculations were performed with the Universal Crystallographic Computer Program System UNICS III[16)] on an ACOS-1000 computer at the Computer Center of Tohoku University.

Results and Discussion

Preparation and Stability of the New Complexes. Desired complexes with neutral amino acid (zwitter ion

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form) bridges have high electric charge of 7+. In spite of this, preparation and isolation of the complexes were straightforward. Chromium(III) ions and amino acids appear to undergo self-assembly to give desired trinuclear complexes in acidic aqueous ethanol solution. Similar trinuclear complexes would be easily prepared with other amino acids than those used in this study. The complexes are stable in acidic solution. However they decompose slowly in neutral solution and immediately in alkaline solution as evidenced by electronic spectral change. They are soluble in certain organic solvents such as methanol and ethanol. Attempts to prepare complexes with pyridine ligands at the terminal positions were unsuccessful. It is probabbly because the compounds are unstable in basic media.

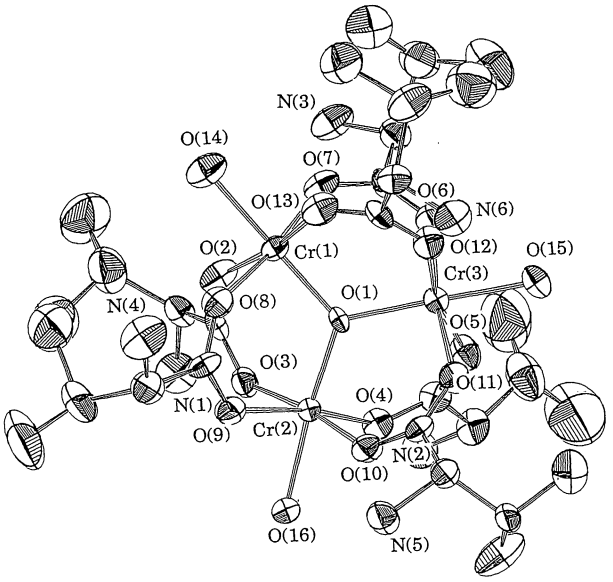

Fig. 1. Structure of $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-}(CH_3)_2CHCH(NH_3)COO)_6(H_2O)_3]^{7+}$ (**2**) and atomic labelling scheme.

The Structure of the L-Valine Complex. Figure 1 shows the structure of the complex cation. Selected bond distances and angles are summarized in Table 1.[15] The complex contains a triangular Cr_3 unit with an oxide ion in the center of the triangle. Each pair of Cr atoms are doubly bridged by carboxylate groups of two L-valine ligands. Overall skeletal structure is very similar to those of other trinuclear chromium carboxylates.[17-19] Each chromium ion takes slightly distrorted octahedral geometry, shifting towards the central oxide ion from the plane defined by four carboxylate oxygens (0.13—0.20 Å). This is also seen in other trichromium complexes. The Cr···Cr distance is 3.30(2) Å and the Cr–(μ_3-O) distance is 1.90(1) Å. The core structure is similar to amino-acid-bridged trinuclear iron(III) complexes.[20] No regularity is found in the orientation of $(CH_3)_2CHCH$ residue of the bridged L-valine.

Electronic and Circular Dichroism Spectra. Table 2 summarizes electronic absorption and circular dichroism spectral data of the new complexes in aqueous solutions. Spectra of the L-valine and L-phenylalanine complex are shown in Fig. 2. Two absorption peaks in visible region are seen as other trichromium complexes,[21] and are assigned from longer wavelengths to $^4A_{1g}\rightarrow{}^4T_{2g}$ and $^4A_{1g}\rightarrow{}^4T_{1g}$ transitions of octahedral chromium(III) center. Circular dichroism peaks are weak as expected from the fact that the asymmetric centers are apart from the chromophoric center. It is noted that the main CD peaks corresponding to the $^4A_{1g}\rightarrow{}^4T_{2g}$ transition is negative for the L-valine and L-leusine complexes, whereas positive for other two complexes. The reason

Table 1. Selected Bond Distances (Å) and Angles (°) for $[Cr_3(\mu_3\text{-}O)(\mu\text{-}O,O'\text{-}(CH_3)_2CHCH(NH_3)COO)_6(H_2O)_3](NO_3)_7\cdot5H_2O$ (**2**)

Distances/Å				Angles/°			
Cr(1)–O(1)	1.880(9)	Cr(1)–O(8)	1.979(10)	O(1)–Cr(1)–O(14)	177.38(46)	O(1)–Cr(2)–O(10)	91.27(38)
Cr(2)–O(1)	1.961(12)	Cr(1)–O(13)	1.976(12)	O(1)–Cr(1)–O(2)	92.92(45)	O(1)–Cr(3)–O(15)	178.54(41)
Cr(3)–O(1)	1.942(9)	Cr(2)–O(3)	1.996(10)	O(1)–Cr(1)–O(7)	93.04(43)	O(1)–Cr(3)–O(5)	96.52(39)
Cr(1)–Cr(2)	3.273(3)	Cr(2)–O(4)	1.951(10)	O(1)–Cr(1)–O(8)	94.66(39)	O(1)–Cr(3)–O(6)	94.46(41)
Cr(2)–Cr(3)	3.317(3)	Cr(2)–O(9)	1.993(10)	O(1)–Cr(1)–O(13)	96.61(43)	O(1)–Cr(3)–O(11)	93.86(40)
Cr(1)–Cr(3)	3.298(3)	Cr(2)–O(10)	1.948(10)	O(1)–Cr(2)–O(16)	175.00(39)	O(1)–Cr(3)–O(12)	96.02(40)
Cr(1)–O(14)	2.038(13)	Cr(3)–O(5)	1.955(10)	O(1)–Cr(2)–O(3)	96.49(38)	Cr(1)–O(1)–Cr(2)	120.68(45)
Cr(2)–O(16)	2.048(10)	Cr(3)–O(6)	1.952(11)	O(1)–Cr(2)–O(4)	94.89(39)	Cr(1)–O(1)–Cr(3)	119.26(44)
Cr(3)–O(15)	2.005(11)	Cr(3)–O(11)	1.968(10)	O(1)–Cr(2)–O(9)	96.06(40)	Cr(2)–O(1)–Cr(3)	120.06(44)
Cr(1)–O(2)	1.961(12)	Cr(3)–O(12)	1.955(10)				
Cr(1)–O(7)	1.963(11)						

Table 2. Electronic Absorption (A) and Circular Dichroism (B) Spectral Data of the New Complexes in Aqueous Solution

Complex	(A) λ/nm (ε/M^{-1} cm^{-1})	(B) λ/nm ($\Delta\varepsilon$/M^{-1} cm^{-1})
$[Cr_3O(L\text{-ala})_6(H_2O)_3]Cl_7\cdot5H_2O$[a]	712(14)[s] 664(46)[s] 588(90) 438(113)	658(+0.15) 602(+0.36) 486(−0.14) 426(+0.11) 350(+0.07)
$[Cr_3O(L\text{-val})_6(H_2O)_3]Cl_7\cdot5H_2O$[b]	714(10)[s] 665(37)[s] 589(89) 440(104)	600(−0.50) 540(+0.11) 482(−0.03) 428(+0.10) 355(−0.05)
$[Cr_3O(L\text{-leu})_6(H_2O)_3]Cl_7\cdot5H_2O$[c]	714(9)[s] 664(40)[s] 588(86) 440(106)	606(−0.24) 550(+0.14) 488(−0.12) 430(+0.13)
$[Cr_3O(L\text{-phe})_6(H_2O)_3]Cl_7\cdot6H_2O$[d]	714(13)[s] 666(47)[s] 589(104) 442(136)	660(+0.23) 592(+0.41) 488(−0.24) 426(+0.17) 362(+0.05)

s=shoulder. a) L-ala=*O,O'*-$CH_3CH(NH_3)COO$. b) L-val=*O,O'*-$(CH_3)_2CHCH(NH_3)COO$. c) L-leu=*O,O'*-$(CH_3)_2CHCH_2CH(NH_3)COO$. d) L-phe=*O,O'*-$C_6H_5CH_2CH(NH_3)COO$.

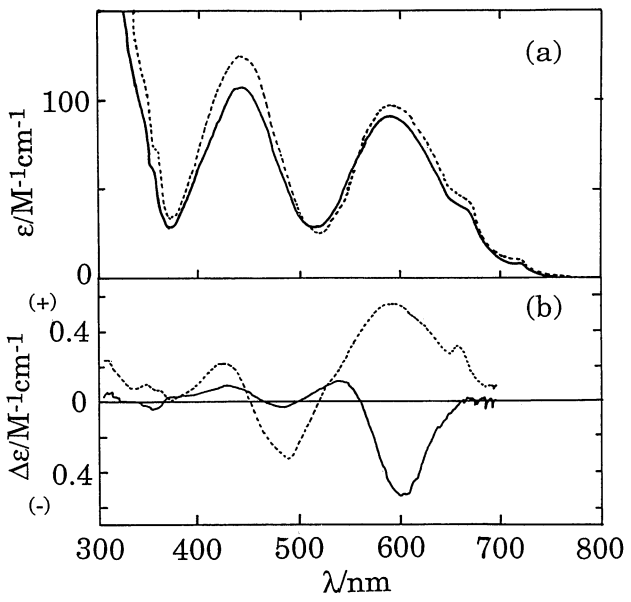

Fig. 2. Electronic absorption (a) and circular dichroism (b) spectra of (**2**) (—) and (**4**) (-----) in aqueous solution.

for this phenomena is not clear. CD spectra in other region are similar for all the four complexes.

Magnetic Properties. The μ_{eff} values obtained by the Evans method at room temperature were 3.39, 3.31, 3.37, and 3.38 (BM per Cr) for the L-alanine, L-valine, L-leusine, and L-phenylalanine complexes, respectively. These values are close to those reported for the carboxylate-bridged trichromium complexes (3.13–3.48 BM)[22] and glycine complex (3.34 BM).[10] These values are somewhat smaller than the spin-only value (3.87 BM), and may suggest weak antiferromagnetic interactions among the three chromium ions.[22]

Redox Properties. Cyclic voltammograms in methanol of the new complexes were measured in the range from −3.0 to +1.0 V vs. Ag/Ag^+ (0.1 M $AgClO_4$). No redox wave was observed in the range studied.

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