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Preparation of the Co(III) Complexes with a Tridentate Hexaniobato and a Bi- or Tri-dentate Amino Carboxylato Ligand

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Twelve new Co(III) complexes containing a hexaniobate ion $Nb_6O_{19}^{8-}$ as a tridentate ligand were synthesized. The hexaniobato ligand coordinates facially, and the remaining three coordination sites are occupied by a tridentate amino carboxylato ligand or by a bidentate amino carboxylato ligand and NH_3 or H_2O. Two glycinato complexes, $[Co(Nb_6O_{19})(gly)(X)]^{6-}$ ($X=NH_3$ or H_2O), were optically resolved, and a L-valinato complex $[Co(Nb_6O_{19})(L\text{-}val)(NH_3)]^{6-}$ was separated into two diastereomers. The structures of these complexes were determined from their visible and ultraviolet absorption, circular dichroism, and proton magnetic resonance spectra.

Several papers have appeared for the heteropoly-condenced compounds containing Co(III) ion, but only a few concerned to a hybrid type between ordinary metal complex and heteropoly oxoanion, such as $K_5[SiCoW_{11}O_{39}(NH_3)]\cdot 14H_2O$,[1] $(+)_{589}$-$Na_4[Co_4I_3O_{18}(OH_2)_4(L\text{-}ala)]\cdot 8H_2O$,[2] and $Na_5[CoNb_6O_{19}(OH_2)(en)]\cdot 17H_2O$.[3] The last named compound was prepared by Flynn and Stucky in a reaction of *trans*-$[CoCl_2(en)_2]Cl$ with $Na_7HNb_6O_{19}\cdot 15H_2O$. They assumed that the hexaniobate ion $Nb_6O_{19}^{8-}$ coordinates to the central Co(III) ion through three niobium-bridging oxygen atoms and the remaining three coordination sites of Co(III) octahedron are occupied by ethylenediamine (en) and H_2O. This means that the hexaniobate ion is functioning as a bulky tridentate ligand. This kind of coordination was confirmed from an X-ray study on the crystal of $Na_{12}[Mn(Nb_6O_{19})_2]\cdot 15H_2O$.[4] The free ligand $Nb_6O_{19}^{8-}$ consists of six NbO_6 octahedra condenced by edge-sharing and has a m3m(O_h) point group symmetry as in Fig. 1.[5] The present study is concerned with the preparation of new hexaniobato Co(III) complexes with some kinds of tridentate or bidentate ligands and with subsequent electronic absorption and circular dichroism (CD) investigations of the complexes. The tridentate ligands used are iminodiacetate(ida), L-aspartate(L-asp), L-methioninate(L-methio), and diethylenetriamine(dien), and the bidentate ligands glycinate (gly), L-valinate (L-val), and L-alaninate(L-ala).

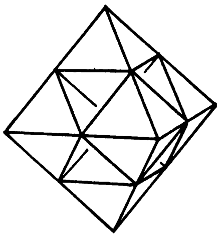

Fig. 1, Structure of $Nb_6O_{19}^{8-}$

Experimental

Preparation. (1) *$Na_5[Co(Nb_6O_{19})(dien)]$*: This complex was prepared by the similar method to that of $Na_5[Co(Nb_6O_{19})(OH_2)(en)]\cdot 17H_2O$.[3] Sodium hydrogenhexaniobate $Na_7HNb_6O_{19}\cdot 15H_2O$ (1.3 g; 1 mmol) and *mer*-$[CoCl_3(dien)]$ (0.27 g; 1 mmol) were dissolved in 40 cm³ of boiling water. After a 10 cm³ portion of 1 M NaOH had been added to the resulting violet-red solution, it was concentrated to about two-thirds of its original volume on a water bath. The concentrated solution was boiled for 1 hr. The solution was cooled to room temperature, filtered, and an appropriate amount of methanol was gradually added to the filtrate. After the filtrate had been kept in a refrigerator overnight, the purple product deposited was separated by a centrifuge, recrystallized from water by adding methanol and dried in a desiccator over $CaCl_2$. Found: C, 4.22; H, 1.90; N, 3.63%. Calcd for $Na_5[Co(Nb_6O_{19})(dien)]$: C, 4.22; H, 1.26; N, 3.69%.

(2) *$Li_7[Co(Nb_6O_{19})(L\text{-}asp)]\cdot 13H_2O$, $Li_7[Co(Nb_6O_{19})(L\text{-}asp)(OH_2)]\cdot 16H_2O$, $Li_7[Co(Nb_6O_{19})(L\text{-}asp)(NH_3)]\cdot 13H_2O$*: A solution of 2.7 g (10 mmol) of $K[Co(CO_3)_2(NH_3)_2]$ in 80 cm³ of water was added to a solution of 13.7 g (10 mmol) of $K_7HNb_6O_{19}\cdot 13H_2O$ in 200 cm³ of water, and to this mixture was added 0.6 g (10 mmol) of KOH. The color of solution changed from violet to blue green and then dark green. The pH was about 10.6. The solution was evaporated to about 50 cm³ and a small amount of light green precipitate resulted, which seemed to be a salt of unreacted $Nb_6O_{19}^{8-}$, was filtered off. After a little amount of methanol had been added to the filtrate, it was kept in a refrigerator overnight. The viscous dark green product deposited was dried on a vacuum desiccator, after the supernatant had been decanted. The crude product was crystallized from water by addition of ethanol. This complex, which seems to be $K_7[Co(Nb_6O_{19})(CO_3)(NH_3)]$, is very useful as a starting material for the syntheses of amino carboxylato complexes (2)—(5).

To a solution of 1.2 g of $K_7[Co(Nb_6O_{19})(CO_3)(NH_3)]$ in 80 cm³ of water was added a mixed solution of 0.12 g (0.9 mmol) of L-aspartic acid and 0.1 g of KOH in 40 cm³ of water. The mixture was gradually evaporated almost to dryness on a water bath at about 70 °C. The resulting material was dissolved in a little amount of water and the solution was poured into a column (3 cm × 60 cm) of strong base anion-exchanger (QAE Sephadex A-25, chloride form). The adsorbed band was eluted with 0.35 M LiCl solution at a rate of about 0.5 cm³/min. Three colored bands, blue one, blue green one and green one, were eluted in this order. The three eluates were separately concentrated to about 20 cm³ at 30 °C in a rotatory evaporator, and a large volume of ethanol was added to each of the concentrated solutions. After the solution had been kept in a refrigerator overnight, the product deposited was collected by a centrifuge and washed several times with ethanol and then acetone–water mixture. Each of the complexes was recrystallized from water by adding

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ethanol and washed repeatedly with ethanol and ether. Found for the blue complex: C, 3.69; H, 2.13; N, 2.21%. Calcd for $Li_7[Co(Nb_6O_{19})(L\text{-asp})(NH_3)]\cdot 13H_2O$: C, 3.76; H, 2.13; N, 2.19%. Found for the blue green complex: C, 3.53; H, 2.46; N, 1.19%. Calcd for $Li_7[Co(Nb_6O_{19})(L\text{-asp})]\cdot 13H_2O$: C, 3.60; H, 2.35; N, 1.05%. Found for the green complex: C, 3.35; H, 2.73; N, 1.07%. Calcd for $Li_7[Co(Nb_6O_{19})(L\text{-asp})(OH_2)]\cdot 16H_2O$: C, 3.41; H, 2.80; N, 0.99%.

(3) $Li_7[Co(Nb_6O_{19})(ida)]\cdot 14H_2O$: The same procedure to that of the L-aspartato complex (2) was adopted using iminodiacetic acid instead of L-aspartic acid. In this case, however, the reaction was carried out at 65 °C. The column chromatography showed only one green band. Found: C, 4.28; H, 2.39; N, 0.99%. Calcd for $Li_7[Co(Nb_6O_{19})(ida)]\cdot 14H_2O\cdot 1/2C_2H_5OH$: C, 4.29; H, 2.60; N, 0.99%.

(4) $Li_6[Co(Nb_6O_{19})(\text{S.C-methio})]\cdot 8H_2O$: This complex was prepared by a similar method to (2). The column chromatography showed only a bluish-green band. Found: C, 4.75; H, 2.80; N, 1.20%. Calcd for $Li_6[Co(Nb_6O_{19})(L\text{-methio})]\text{-}8H_2O$: C, 4.72; H, 2.16; N, 1.10%.

(5) $Li_6[Co(Nb_6O_{19})(am)(OH_2)]\cdot nH_2O$ *and* $Li_6[Co(Nb_6O_{19})(am)(NH_3)]\cdot nH_2O$ *(am=amino carboxylate)*: The complex with glycinate, L-valinate or L-alaninate was prepared by the same method as that of L-aspartato complex described in (2). The reaction temperature was 65 °C. Each of the products separated on the column gradually into two colored bands, blue one and green one, when eluted with 0.30 M LiCl solution. In the case of L-valinato complex, however, the blue band further separated gradually into two bands F_1 and F_2 (denoted by the elution order), with the formation ratio $F_1/F_2=2$. Each of the complexes isolated was purified by the same method as that of the L-aspartato complex. Found for the blue glycinato complex: C, 2.13; H, 2.87; N, 2.18%. Calcd for $Li_6[Co(Nb_6O_{19})(gly)(NH_3)]\cdot 12H_2O\cdot 1/8C_2H_5OH$: C, 2.12; H, 2.53; N, 2.19%. Found for the green glycinato complex: C, 1.95; H, 2.18; N, 1.29%. Calcd for $Li_6[Co(Nb_6O_{19})(gly)(OH_2)]\cdot 10H_2O$: C, 1.95; H, 2.18; N, 1.13%. Found for the blue L-valinato complex (F_1): C, 4.69; H, 3.15; N, 2.05%. Calcd for $Li_6[Co(Nb_6O_{19})(L\text{-val})(NH_3)]\cdot 13H_2O$: C, 4.58; H, 2.98; N, 2.11%. Found: for the blue L-valinato complex (F_2): C, 7.31; H, 3.67; N, 1.82%. Calcd for $Li_6[Co(Nb_6O_{19})(L\text{-val})(NH_3)]\cdot 19H_2O\cdot 9/4C_2H_5OH$: C, 7.42; H, 3.84; N, 1.82%. Found for the green L-valinato complex: C, 4.51; H, 2.93; N, 1.09%. Calcd for $Li_6[Co(Nb_6O_{19})(L\text{-val})(OH_2)]\cdot 13H_2O$: C, 4.51; H, 2.89; N, 1.09%. Found for the blue L-alaninato complex: C, 2.74; H, 2.53; N, 2.24%. Calcd for $Li_6[Co(Nb_6O_{19})(L\text{-ala})(NH_3)]\cdot 11H_2O$: C, 2.84; H, 2.21; N, 2.47%. Found for the green L-alaninato complex: C, 2.83; H, 2.58; N, 1.16%. Calcd for $Li_6[Co(Nb_6O_{19})(L\text{-ala})(OH_2)]\cdot 10H_2O$: C, 2.88; H, 2.27; N, 1.16%.

(6) Resolution of $[Co(Nb_6O_{19})(gly)(X)]^{6-}$ *(X=*NH_3 *or* H_2O*)*: A solution of 0.12 g of $(+)_{589}$-$[Co(en)_3]Br_3$ in 500 cm^3 of water was gradually added with mechanical stirring to a solution of 0.35 g of $Li_6[Co(Nb_6O_{19})(gly)(NH_3)]\cdot 12H_2O$ in 1 dm^3 of water. The mixed solution was evaporated to about 300 cm^3 in air stream. The dark yellow-green diastereomer deposited was isolated by filtration and washed with water and then methanol several times. This sparingly soluble diastereomer was stirred mechanically in an aqueous solution containing cation-exchange resin (Dowex 50 W×8, Na^+ form). When the color of solution changed to blue, the solution was filtered to remove the resin, and the filtrate was concentrated to obtain the blue sodium salt, $\Delta\varepsilon_{546}=+0.61$, $\Delta\varepsilon_{589}=-0.028$.

The resolution of $[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$ was made by the same method; $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$ which was derived from the less soluble diastereomer has $\Delta\varepsilon_{546}=+0.061$ and $\Delta\varepsilon_{589}=-0.012$.

Measurements. Electronic absorption spectra of the complexes in the visible and near ultraviolet regions were measured by a Shimadzu UV-200 spectrophotometer in aqueous solutions. Circular dichroism spectra were recorded on a Jasco Model J-20 spectropolarimeter with a CD attachment. A Yanagimoto spectropolarimeter was used to check the optical rotations. The proton magnetic resonance spectra were measured in deuterium oxide with a Varian XL-100-15 NMR spectrophotometer, using *tert*-butyl alcohol (TBA) as an internal reference. The infrared spectra were obtained with a Hitachi EPI-001 infrared photometer with NaCl prisms using KBr disks. All measurements were made at room temperature.

Results and Discussion

The hexaniobato Co(III) complexes obtained are summarized in Table 1 with their d–d absorption data and the representative absorption curves are shown in Figs. 3 and 4. It is expected stereochemically that only one complex is possible for each of $[Co(Nb_6O_{19})(dien)]^{5-}$, $[Co(Nb_6O_{19})(ida)]^{7-}$, $[Co(Nb_6O_{19})(L\text{-asp})]^{7-}$, and $[Co(Nb_6O_{19})(L\text{-methio})]^{6-}$, and this was chromatographically confirmed. Two diastereomers (Fig. 2) are possible for $[Co(Nb_6O_{19})(L\text{-val})(NH_3)]^{6-}$ and this was also confirmed by the chromatographic separation of F_1(earlier eluted) and F_2 (later eluted) isomers. In addition, the corresponding glycinato complexes, $[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ and $[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$, were resolved into their optical isomers. These facts support the Flynn and Stucky's inference for the structure of ethylenediamine complex $[Co(Nb_6O_{19})(OH_2)(en)]^{5-}$. Diastereomers are also expected for the other complexes with L-aminocarboxylate as a bidentate ligand, but the present chromatographic separation procedure was uneffective for the separation of the isomers. As is seen in Fig. 3 and Table 1, the first and second absorption bands of the complexes shift to shorter wave lengths reasonably in the order of complex type $CoO_5N \rightarrow cis\text{-}CoO_4N_2 \rightarrow fac\text{-}CoO_3N_3$. The first absorption band of CoO_5N type complex shows a vague shoulder at lower energy of the absorption maximum and that of cis-CoO_4N_2 type at higher energy. These are in accordance with the facts that $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$ shows three CD components in the first absorption band region, and $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ two CD components (Table 2 and Fig. 5). The fac-CoO_3N_3 type complex shows a sharp first

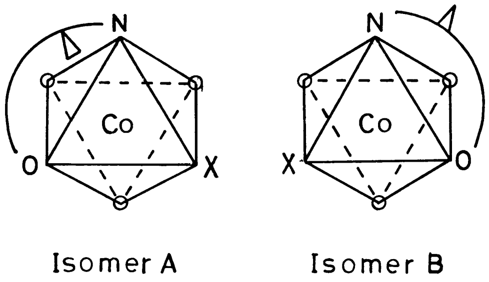

Fig. 2. Diastereomers of $[Co(Nb_6O_{19})(L\text{-am})X]^{6-}$: X=$OH_2$ or NH_3; N–O=L-ala or L-val. The circled three apices are occupied by $Nb_6O_{19}{}^{8-}$.

TABLE 1. ABSORPTION DATA OF THE COMPLEXES

Type	Complex	σ_{max}[a] (log ε)	
		I band	II band
CoO_5N	$[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$	16.5 (1.87)	23.8 (1.95)
	$[Co(Nb_6O_{19})(L\text{-val})(OH_2)]^{6-}$	16.6 (1.89)	23.9 (1.95)
	$[Co(Nb_6O_{19})(L\text{-ala})(OH_2)]^{6-}$	16.7 (1.86)	23.7 (1.87)
	$[Co(Nb_6O_{19})(L\text{-asp})(OH_2)]^{7-}$	16.7 (1.92)	23.6 (1.88)
	$[Co(Nb_6O_{19})(L\text{-asp})]^{7-}$	16.9 (1.95)	23.9 (1.94)
	$[Co(Nb_6O_{19})(ida)]^{7-}$	16.9 (1.98)	23.9 (2.11)
cis-CoO_4N_2	$[Co(Nb_6O_{19})(en)(OH_2)]^{5-}$	16.8 (1.84)	24.7 (1.73)
	$[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$	17.0 (1.89)	24.8 (1.95)
	$[Co(Nb_6O_{19})(L\text{-val})(NH_3)]^{6-}$	17.0 (1.90)	24.4 (1.95)
	$[Co(Nb_6O_{19})(L\text{-ala})(NH_3)]^{6-}$	17.0 (1.87)	24.5 (1.86)
	$[Co(Nb_6O_{19})(L\text{-asp})(NH_3)]^{7-}$	17.1 (1.89)	24.7 (1.94)
fac-CoO_3N_3	$[Co(Nb_6O_{19})(dien)]^{5-}$	18.2 (1.80)	25.6 (1.80)
CoO_4NS	$[Co(Nb_6O_{19})(L\text{-methio})]^{6-}$	17.1 (2.06)	*ca.* 24 (shoulder)

a) In the unit of 10^3 cm^{-1}.

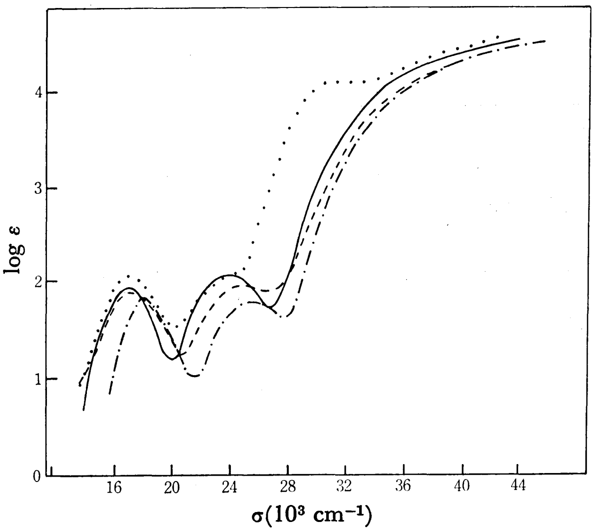

Fig. 3. Absorption spectra of $[Co(Nb_6O_{19})(ida)]^{7-}$ (——), $[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ (----), $[Co(Nb_6O_{19})(dien)]^{5-}$ (-·-·-) and $[Co(Nb_6O_{19})(L\text{-methio})]^{6-}$ (······).

absorption band. These spectral behaviors agree well with those which can be expected from the semi-empirical rule for d–d absorption bands.[6] The second absorption band of $[Co(Nb_6O_{19})(L\text{-methio})]^{6-}$ appears as a shoulder because of overlapping by the thioether charge transfer band,[7] which is located at 31300 cm^{-1} with log $\varepsilon=4.07$. For all the complexes studied, a strong absorption band due to the coordinated hexaniobate appears in a region of 38000—40000 cm^{-1}, and its position and intensity are independent of the pH change from 6.5 to 14, though a 41300 cm^{-1} band of the free $Nb_6O_{19}{}^{8-}$ ion depends strongly upon the pH. The two resembling complexes, $[Co(Nb_6O_{19})(L\text{-asp})]^{7-}$ and $[Co(Nb_6O_{19})(L\text{-asp})(OH_2)]^{7-}$, were distinguished from each other by the pmr spectra. The former complex shows an ABX pattern due to $-CHCH_2-$ protons of the tridentate L-aspartato ligand,[8] whereas the latter shows a more complicated pattern, which suggests the mixing of two ABX patterns resulted from the coexistene of two diastereomers.

The CD data of the present complexes are summarized in Table 2. The CD curve of $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ obtained from the less soluble diastereomer with $(+)_{589}$-$[Co(en)_3]Br_3$ is shown in Fig. 5. As is seen in Fig. 4, the CD curves of two L-valinato isomers differ remarkably from that of $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$, and the difference may be attributed to the vicinal contribution due to the L-valinato ligand. When the additivity rule for the configurational and vicinal CD contributions is applied for the CD curves of L-valinato diastereomers,[9,10] the calculated configurational CD curve does not agree well with the observed CD curve of $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ (Fig. 5). But the sign pattern suggests that the configuration of $(+)^{CD}_{546}$-$[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ corresponds to

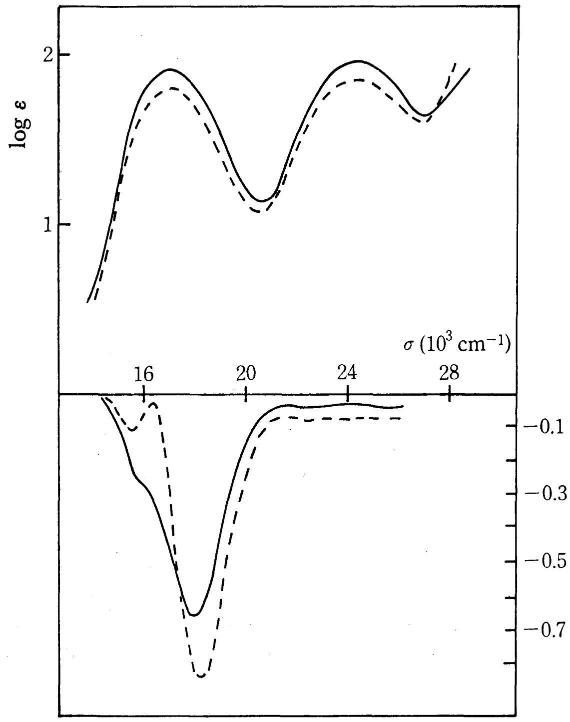

Fig. 4. Absorption and CD spectra of $[Co(Nb_6O_{19})(L\text{-val})(NH_3)]^{6-}$, F_1 (——) and F_2 (----).

TABLE 2. CD DATA OF THE COMPLEXES

Complex	σ_{ext} a) ($\Delta\varepsilon$)	
	I band	II band
$[Co(Nb_6O_{19})(L\text{-methio})]^{6-}$	17.2(+1.23)	25.0(−0.22)
$[Co(Nb_6O_{19})(L\text{-asp})]^{7-}$	14.8(−0.1)	*ca.* 24 (+0.06)
	16.4(+0.14)	
	18.5(−0.11)	
$(+)^{CD}_{546}\text{-}[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$	14.6(+0.20)	23.5(−0.06)
	16.0(−0.26)	27.4(+0.05)
	17.9(+0.08)	
$[Co(Nb_6O_{19})(L\text{-val})(OH_2)]^{6-}$ b)	15.8(−0.29)	24.0(−0.03)
$[Co(Nb_6O_{19})(L\text{-ala})(OH_2)]^{6-}$ b)	16.8(−0.31)	22.5(+0.01)
$[Co(Nb_6O_{19})(L\text{-asp})(OH_2)]^{7-}$ b)	15.6(−0.21)	*ca.* 23 (+0.02)
$(+)^{CD}_{546}\text{-}[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$	16.4(−0.21)	22.7(+0.04)
	18.3(+0.61)	24.6(−0.06)
$[Co(Nb_6O_{19})(L\text{-val})(NH_3)]^{6-}$: F_1	*ca.* 16 (−0.25)	
	18.1(−0.66)	
F_2	15.6(−0.11)	
	18.4(−0.84)	
$[Co(Nb_6O_{19})(L\text{-ala})(NH_3)]^{6-}$ b)	17.9(−0.26)	*ca.* 22 (−0.03)
$[Co(Nb_6O_{19})(L\text{-asp})(NH_3)]^{7-}$ b)	16.2(+0.10)	22.5(−0.02)
	18.3(−0.40)	*ca.* 25 (+0.01)

a) In the unit of 10^3 cm^{-1}. b) Unresolved complex.

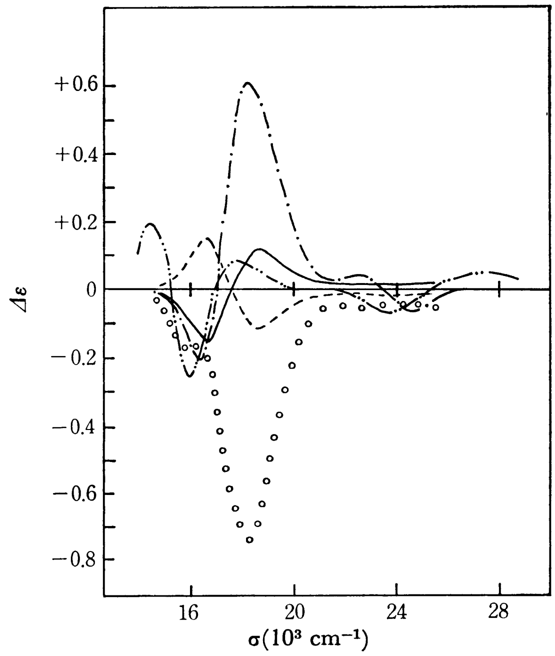

Fig. 5. Calculated configurational (F_1' ——, F_2' ----) and vicinal (○○○○) CD curves of $[Co(Nb_6O_{19})(L\text{-val})(NH_3)]^{6-}$. Observed CD spectra of $(+)^{CD}_{546}\text{-}[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ (-·-·-) and $(+)^{CD}_{546}\text{-}[Co(Nb_6O_{19})(gly)(OH_2)]^{6-}$ (-··-).

the L-valinato F_1 isomer. The formation ratio of F_1 to F_2 is about 2 as described in Experimental section. This fact suggests that the F_1 diastereomer is (A) in Fig. 2, since a less interaction is expected between the $-CH(CH_3)_2$ substituent and the coordinated hexaniobato ligand in the isomer (A) than in (B).

The configurational chirality in the present complexes is the same type as in the $[Co(am)NH_3(tame)]^{2+}$ complexes recently studied in this laboratory,[11] where the ligand tame is 1,1,1-tris(aminomethyl)ethane. In this $CoON_5$ type complexes the additivity of the configurational and vicinal CD contributions was reasonably well in contrast to the present hexaniobato complexes. The reason for such difference between the $CoON_5$ and the present CoO_4N_2 types still remaines unknown.

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