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Preparation and Resolution of (4-Aminobutanoic acidato)bis(ethylenediamine)cobalt(III) Ion

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Synopsis. A new complex containing a seven-membered chelate ring, $[Co(amb)(en)_2]^{2+}$ (amb=4-aminobutanoato ion) was prepared and resolved. The complex is decomposed in 1.0 M $HClO_4$ at room temperature to give $[Co(H_2O)(Hamb)(en)_2]^{3+}$ in which the Hamb acts as a unidentate ligand with a free carboxyl group.

Although complexes of the type, $[Co(am)(en)_2]^{2+}$ (am=amino acidate ion) have been prepared and resolved for a variety of amino acids, no complex has been reported for 4-aminobutanoato ion (amb) which forms a seven-membered chelate ring. This Note will describe the preparation and resolution of $[Co(amb)(en)_2]^{2+}$ and compare the absorption and circular dichoism(CD) spectra with those of the corresponding glycinato and β-alaninato complexes. Koine *et al.*[1)] prepared a complex containing amb, *trans*(*N*)-K[Co(nta)(amb)]·$3H_2O$(nta =nitrilotriacetate ion). However, no evidence was given for the formation of a seven-membered chelate ring. Such large chelate ligands as amb tend to coordinate to a metal ion as a unidentate ligand or to two metal ions as a bridging ligand.[2,3)]

Experimental

Ligands. Guaranteed reagent grade 4-aminobutanoic acid, β-alanine, and glycine were obtained from Wako Pure Chemical Industries Co. and used without further purification.

[Co(amb)(en)₂]Cl₂·2.5H₂O. A solution of sodium methoxide (0.16 g, 3.0 mmol) and 4-aminobutanoic acid (0.31 g, 3.0 mmol) in methanol (7 cm^3) was added to a solution of *trans*-$[CoCl_2(en)_2]ClO_4$ (0.9 g, 3.0 mmol) in DMSO(250 cm^3). The solution was stirred for 20 h at 40 °C, and then diluted with 3 dm^3 of water. This was passed through an SP-Sephadex column (ϕ4.5×30 cm), and the adsorbed complexes were chromatographed with a 0.2 M Na_2SO_4 solution. The column showed seven separate bands. The effluent of the first red band was diluted with 3 dm^3 of water and poured again on an SP-Sephadex column (ϕ2.7×3 cm). The adsorbed complex was eluted with a 1.0 M $CaCl_2$ solution, and the effluent was concentrated to a syrup in a vacuum desiccator over P_2O_5. The excess $CaCl_2$ was extracted repeatedly with a small amount of isopropyl alcohol until the complex began to crystallize. The complex was dissolved in a small amount of water, and isopropyl alcohol was added to the solution. Purplish red crystals which formed on cooling the mixing solution in a refrigerator were filtered off and washed with isopropyl alcohol. The complex was recrystallized from water by the addition of isopropyl alcohol. Found: C, 24.24; H, 7.38; N, 18.10%. Calcd for $CoC_8H_{29}N_5O_{4.5}Cl_2$=$[Co(amb)(en)_2]Cl_2\cdot 2.5H_2O$: C, 24.19; H, 7.36; N, 17.63%.

[Co(gly)(en)₂](ClO₄)₂ and [Co(β-ala)(en)₂](ClO₄)₂·H₂O. $[Co(gly)(en)_2](ClO_4)_2$ was prepared by the method of Shimura and Tsuchida.[4)] $[Co(\beta\text{-ala})(en)_2](ClO_4)_2\cdot H_2O$ was obtained from the corresponding chloride.[5)] The complex chloride adsorbed on SP-Sephadex was eluted with a 1.0 M $NaClO_4$ solution, and the effluent was concentrated to a small volume in a vacuum desiccator over P_2O_5. The concentrate was mixed with ethanol, and cooled. Red crystals were filtered off, washed with ethanol, and recrystallized from water by the addition of ethanol. Found: C, 17.40; H, 4.99; N, 14.46%. Calcd for $CoC_7N_5H_{24}O_{11}Cl_2$=$[Co(\beta\text{-ala})(en)_2](ClO_4)_2\cdot H_2O$: C, 17.36; H, 5.00; N, 14.46%.

Chromatographic Resolution of the Complexes. A solution containing about 0.1 mmol of the amb complex (or the β-ala or the gly complex) was poured on an SP-Sephadex column (ϕ2.7×120 cm) and the adsorbed band was eluted with a 0.1 M sodium $(+)_{589}$-tartrate or a 0.08 M sodium $(+)_{589}$-tartratoantimonate(III) solution. Two bands, the $(+)_{589}$- and $(-)_{589}$-isomers, were eluted in this order. Each eluate was passed through an SP-Sephadex column (ϕ1.5×3 cm) after dilution with water and the adsorbed complex was eluted with a 1.5 M $NaClO_4$ solution.

Measurements. Absorption and CD spectra were obtained on a Hitachi 323 spectrophotometer and a JASCO J-20 spectropolarimeter, respectively.

Results and Discussion

$[Co(gly)(en)_2]^{2+}$ and $[Co(\beta\text{-ala})(en)_2]^{2+}$ can easily be prepared by the reactions of *trans*-$[CoCl_2(en)_2]^+$ with gly or β-ala, respectively in water at fairly high concentration of the reactants. A reaction with amb under a similar condition is not expected to give the desired complex, since such large chelate ligands as amb or tmd(tetramethylenediamine) tend to act as a bridging

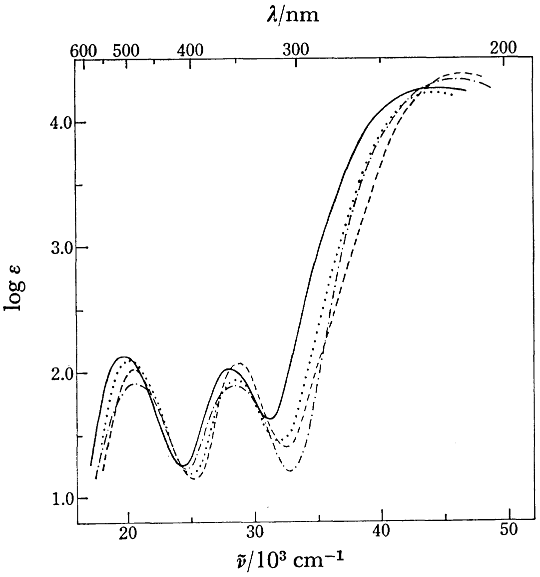

Fig. 1. Absorption spectra of $[Co(gly)(en)_2]^{2+}$(----), $[Co(\beta\text{-ala})(en)_2]^{2+}$(······), and $[Co(amb)(en)_2]^{2+}$(——) in water, and $[Co(H_2O)(Hamb)(en)_2]^{3+}$(—·—) in 1.0 M $HClO_4$.

Table 1. Absorption and CD spectral data

Complex	Absorption[a)]		CD[b)]	
	$\tilde{\nu}$/cm^{-1}	log ε	$\tilde{\nu}$/cm^{-1}	Δε
$(+)_{589}[Co(gly)(en)_2]^{2+}$	20450	2.00	19690	+2.26
	28800	2.03	27000	+0.09
			30300	+0.15
	45900	4.15	46700	−27
$(+)_{589}[Co(\beta\text{-ala})(en)_2]^{2+}$	20160	2.09	19270	+1.28
			21800	−0.52
	28400	1.93	27300	+0.21
	44100	4.22	44100	−12
$(+)_{589}[Co(amb)(en)_2]^{2+}$	19800	2.11	18690	+1.27
			21470	−0.71
	27900	2.03	27400	+0.20
	44100	4.27	47200	−17
$(+)_{589}[Co(H_2O)(Hamb)(en)_2]^{3+}$	20530	1.90	20620	+0.31
	28500	1.89	26400	+0.10
			30300	+0.03
	45500	4.32	45700	−8.5

a) In water except for $(+)_{589}[Co(H_2O)(Hamb)(en)_2]^{3+}$ which was measured in 1.0 M $HClO_4$. b) In 1.5 M $NaClO_4$ except for $(+)_{589}[Co(H_2O)(Hamb)(en)_2]^{3+}$ which was measured in 1.0 M $HClO_4$.

ligand to yield polymeric complexes.[3)] Thus, we have carried out the reaction in a highly dilute solution as described in the Experimental part. The use of organic solvent, DMSO is known to be useful for preparing complexes containing large chelate rings.[6)]

The formation of the amb chelate ring is evidenced by the following observations. The absorption spectrum of the amb complex in a 1.0 M $HClO_4$ solution changes with isosbestic points(416, 458 nm), the change at room temperature(25 °C) being completed in a day. Since the first absorption band (487 nm) of the final spectrum is nearly the same as that (485 nm) of *cis*-$[Co(H_2O)(NH_3)(en)_2]^{3+}$,[7)] the spectral change may correspond to a ring-opening reaction of the amb chelate to give *cis*-$[Co(H_2O)(Hamb)(en)_2]^{3+}$ (Fig. 1). The absorption spectra of the gly and β-ala complexes in 1.0 M $HClO_4$ remained unchanged over a prolonged heating. Further, the amb complex adsorbed on SP-Sephadex is eluted with a 0.2 M Na_2SO_4 solution with a similar R_f value to those of the gly and β-ala complexes.

As Fig. 1 and Table 1 show, the d-d absorption bands of the present series of complexes, $[Co(am)(en)_2]^{2+}$ shift to longer wavelengths as the number of ring members of the amino acidate ligands increases. A similar shift was observed for complexes of the type, $[Co(en)_2(diamine)]^{3+}$; the first absorption bands of $[Co(en)_3]^{3+}$, $[Co(en)_2(tn)]^{3+}$(tn=trimethylenediamine), and $[Co(en)_2(tmd)]^{3+}$ are at 21.3, 21.0, and 20.9×10³ cm^{-1}, respectively.[3)]

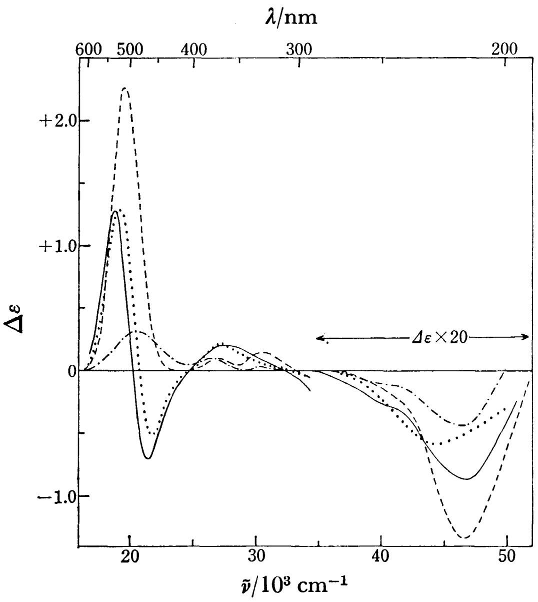

Fig. 2. CD spectra of $(+)_{589}[Co(gly)(en)_2]^{2+}$(----), $(+)_{589}[Co(\beta\text{-ala})(en)_2]^{2+}$(······), and $(+)_{589}[Co(amb)(en)_2]^{2+}$(——) in 1.5 M $NaClO_4$, and $(+)_{589}[Co(H_2O)(Hamb)(en)_2]^{3+}$(—·—) in 1.0 M $HClO_4$.

All the complexes have been completely resolved by SP-Sephadex column chromatography. Figure 2 shows the CD spectra of the $(+)_{589}$-isomers. The CD spectrum of the gly complex agrees well with that reported previously.[8)] All the $(+)_{589}$-isomers give a main positive and a strong negative CD band in the first absorption and the charge transfer region, respectively. Therefore, it can be concluded that these isomers have the same absolute configuration, *Λ*. The β-ala and the amb complexes exhibit negative CD components at a shorter wavelength side of the first absorption band. Although no such a component is observed for the gly complex, these negative components seem to increase the strength as the number of ring member of the amino acidate ligand increases.

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