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THE ISOLATION OF FAC(N)-D-ASPARTATO-L-ASPARAGINATOCOBALT(III) COMPLEX

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An isomeric complex of cobalt(III) containing a D-aspartate ion and a L-asparaginate ion as tridentate ligands has been isolated and identified as fac(N) isomer on the basis of IR, PMR and absorption spectra. The absorption spectrum in an alkaline solution revealed double maxima in the second absorption band region.

Both aspartic acid and asparagine are potentially tridentate ligands. Some works on the cobalt(III) complexes of L-aspartic acid functioning as tridentate ligand have recently been reported,[1-4)] but no study has been reported on cobalt (III) complex of asparagine acting as tridentate ligand. Now, we found a novel complex of cobalt(III) containing both D-aspartate ion (D-asp) and L-asparaginate ion (L-aspNH$_2$) as tridentate ligands.

To a green solution of potassium tricarbonatocobaltate(III) (Co(NO$_3$)$_2$·6H$_2$O, 5.80 g (0.02 mol) scale)[5)] was added L-asparagine monohydrate (6.00 g, 0.04 mol), the mixture being stirred at 40°C for 2 hr. Then D-aspartic acid (5.32 g, 0.04 mol) and activated charcoal (1 g) were added to the mixture, the whole being stirred at 50°C for 1 hr. After the resulting solution was once filtered, the pH was adjusted to ca. 7.0 with aqueous perchloric acid, and the solution was again filtered. A portion of the filtrate was charged on a column of Sephadex QAE-A25 in chloride form (3.0 X 120 cm). Non-charged and cationic species were eluted when the column was washed with water. The band adsorbed at the top of the column was then eluted with a 0.01 M CaCl$_2$ solution at a rate of about 0.5 ml/min. Six bands of univalent anionic species descended, of which the last band was to be desired (the others were mainly isomeric species of the [Co(D-asp)(L-aspNH$_2$)$_2$]$^-$). This separation procedure was applied to the remainder of the filtrate in order to collect the desired fraction. The eluate was concentrated to a small volume with a rotary evaporator at ca. 30°C. The concentrated solution thus obtained was passed through a column of Dowex 50W X 8 resin in hydrogen form (3.0 X 20.0 cm). The effluent was concentrated to a small volume and then kept in a refrigerator for a day in order to deposite the desired complex. The red-violet crystals thus deposited were not sufficiently soluble in water. The recrystallization was performed by dissolving the crystals in water containing a small amount of sodium hydroxide and then acidifying the solution with aqueous perchloric acid.

Found: C, 27.84; H, 4.43; N, 12.13%. Calcd for [Co(D-asp)(L-aspNH$_2$)]·1.5H$_2$O=

$CoC_8H_{12}N_3O_7\cdot 1.5H_2O$: C, 27.69; H, 4.34; N, 12.07%.

The IR spectrum of the present complex was compared with the spectra of fac-Δ-[Co(L-Hasp)$_3$][6] and fac-Δ-[Co(L-aspNH$_2$)$_3$].[7] The spectra in the 1500~1800 cm^{-1} region are illustrated in Fig. 1. The spectrum of the tris(L-hydrogenaspartato) complex exhibits a band at 1710 cm^{-1} which can be assigned to uncoordinated COO stretching,[3,8] and the spectrum of the tris(L-asparaginato) complex also shows a band near 1710 cm^{-1}. On the other hand, the present complex has no absorption in the 1710~1700 cm^{-1} region. This fact is regarded as an evidence for that both ligands act as tridentates in the present mixed ligand complex.

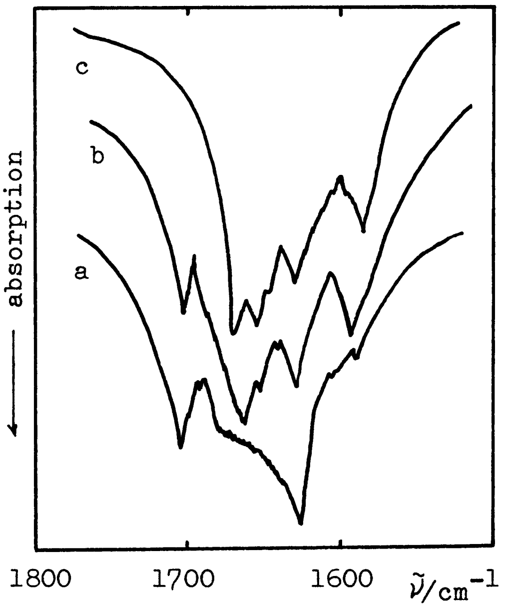

Fig.1 IR spectra of;

a. fac-Δ-[Co(L-Hasp)$_3$],

b. fac-Δ-[Co(L-aspNH$_2$)$_3$], and

c. [Co(D-asp)(L-aspNH$_2$)].

The PMR spectrum measured with an alkaline solution of the present complex exhibits two kinds of ABX pattern arising from the chelated D-asp and L-aspNH$_2$ (Fig. 2). From the comparison with the PMR spectrum of fac(N)-[Co(L-2,4-dba)(D-asp)] (L-2,4-dba stands for L-2,4-diaminobutyrate ion),[4] the signals centered at 3.54 ppm ($J_{AX} + J_{BX}$ = 7.6 cps) were assigned to the signals of a methin portion of the chelated D-asp. This result gives another evidence for the tridentate D-asp.

The absorption spectra for the present complex were measured with solutions freshly prepared in pH 9.0 and pH 2.0. The spectrum measured under the mild

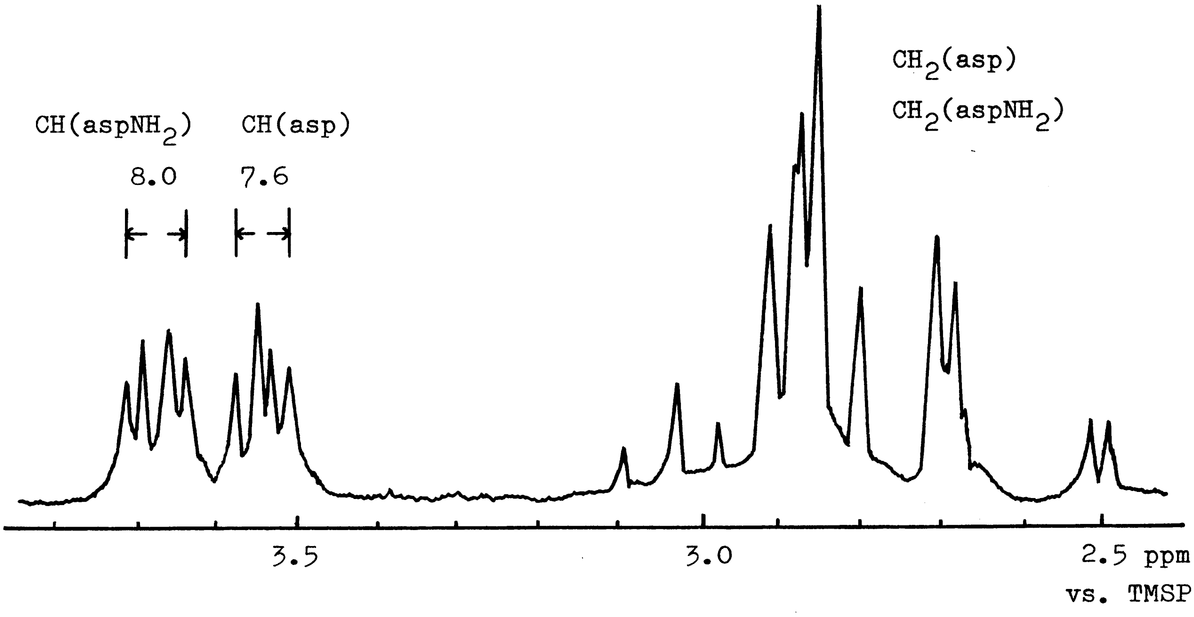

Fig.2 PMR spectrum of [Co(D-asp)(L-aspNH$_2$)] in D_2O (pD 9.4).

alkaline condition reveals a maximum at 19100 cm^{-1} and double maxima at ca. 25500 and ca. 27100 cm^{-1} (Fig. 3). The spectrum under the mild acidic condition shows a maximum at 19300 cm^{-1} and a maximum at 27100 cm^{-1} (Fig. 3). The reversible change was recognized between the two spectra. The observed maximum values except for 25500 cm^{-1} belong to normal values for the fac-$[Co(N)_3(O)_3]$-type complexes.[9] On this basis, the present complex can be identified as fac(N)-isomer (Fig. 4).

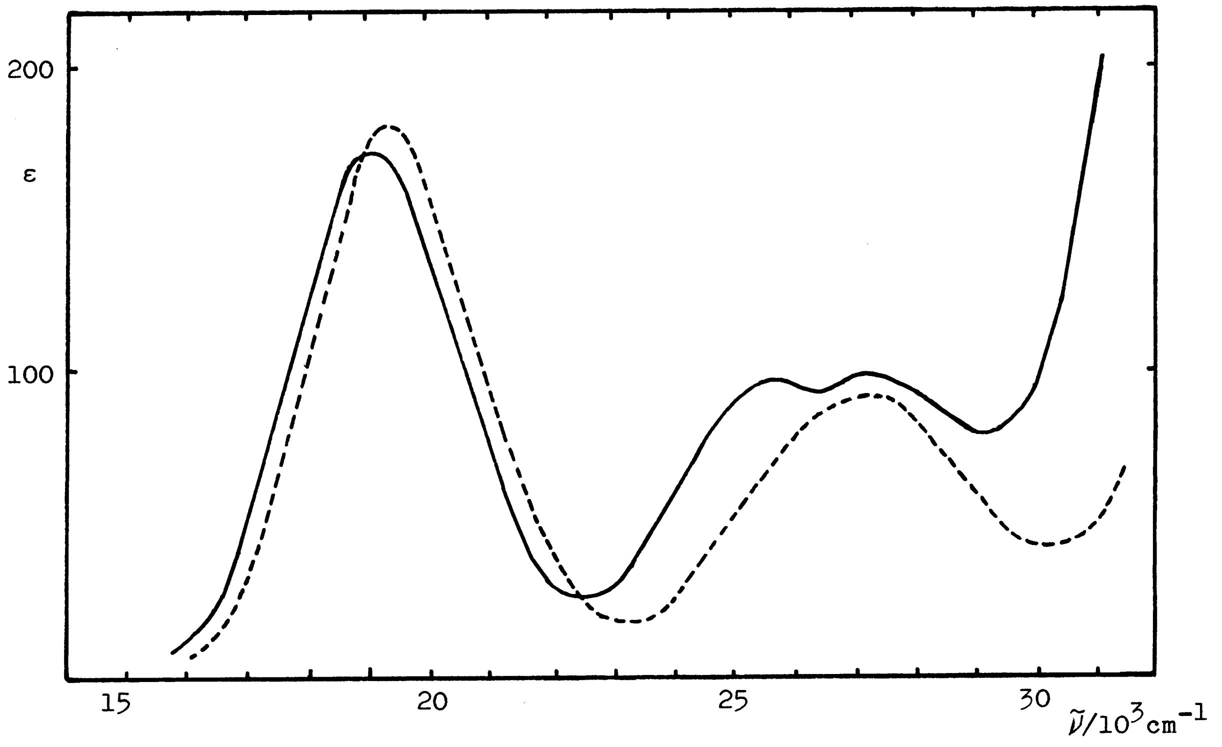

Fig.3 Absorption spectra of $[Co(D\text{-}asp)(L\text{-}aspNH_2)]$ in pH 9.0 solution (———) and pH 2.0 solution (-----).

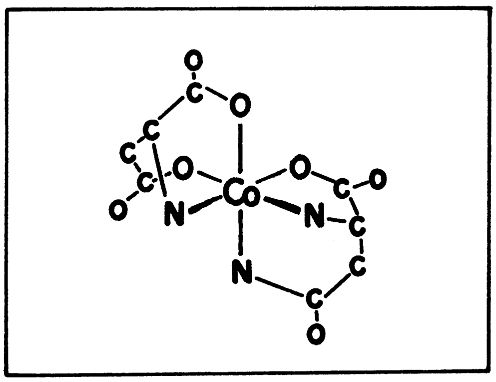

Fig.4 Fac(N) structure.

The CD spectrum measured with the alkaline solution reveals only one peak with minus sign, while the spectrum measured with the acidic solution shows two peaks with different signs in the first absorption band region (Fig. 5). The CD spectra in the second absorption band region somewhat differ between the alkaline solution and the acidic solution.

Corresponding to these different patterns in the absorption and CD spectra under the alkaline and acidic conditions, the complex species behave as univalent

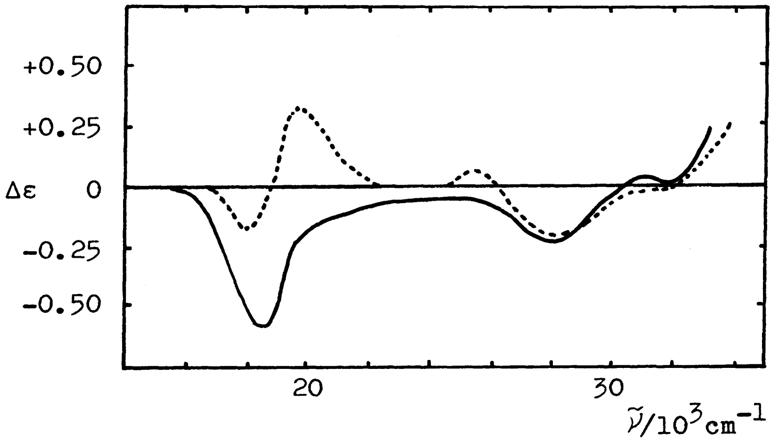

Fig.5 CD spectra of $[Co(D-asp)(L-aspNH_2)]$ in pH 9.0 solution (———) and pH 2.0 solution (-----).

anion on a Sephadex column in Cl-form and also as non-charged species on a Dowex 50 resin column in H-form. The former fact suggests that the deprotonation of the β-$CONH_2$ group of the chelated L-$aspNH_2$ takes place in the alkaline solution and consequently the coordination through the N atom of the β-$CONH^-$ participates in the tridentate chelation of the L-asparaginate ion.

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