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PREPARATION OF A NOVEL AMMINEBROMOCYANO[1,4,7-TRIAZACYCLO-NONANE]COBALT(III) COMPLEX

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A new complex [Co(Br)(CN)(NH_3)(1,4,7-triazacyclononane)]Cl, which exhibits a novel optical isomerism due to the arrangement of unidentate ligands, has been prepared, and the optical resolution of the complex has been achieved by means of column chromatography.

There have been many studies on the optically active metal complexes whose chirality owes to the presence of the chelate rings about a central ion. On the other hand, there have been a few studies on the complexes that derive their chirality solely from the arrangement of unidentate ligands. Up to this time, some complexes of the cis,cis-[Co(a)$_2$(b)$_2$(CC)][1], all-cis-[Co(a)$_2$(b)$_2$(c)$_2$][1] and fac(D)-[Co(a)(BC)(DDD)][2,3] types have been reported. The paucity of the research seems mainly due to the lack of preparative methods. Now, we succeeded in preparing a novel amminebromocyano[1,4,7-triazacyclononane]cobalt(III) complex through two steps of ligand substitutions. Since the 1,4,7-triazacyclononane (=TACN) is a cyclic terdentate ligand, the chirality of the complex is derived from the arrangement of three unidentates, as shown in Fig.1.

At the first step, an intermediate [Co(CN)(SO_3)(NH_3)(tacn)] was prepared; the ligand TACN·3HCl (3.5g, 0.015mol), prepared by the literature method[4], was dissolved in a minimum amount of water and neutralized with an aqueous KOH solution. The resulting solution was added dropwise to a solution containing [Co(CN)(SO_3)(NH_3)$_4$][5] (5g, 0.02mol in 150cm^3 H_2O). The mixed solution was adjusted to pH 9 and stirred at 50°C for 24h. After cooling the solution to room temperature, precipitated material was removed by filtration. A portion, 25cm^3, of the filtrate was poured into a column of SP-Sephadex C-25 (4 x 45cm) and the adsorbed species was eluted with water. Three bands of non-charged species descended, after descent of anionic species. By repeating this procedure for the residual portion, every eluate of the third band was collected. The eluates were concentrated by means of a rotary evaporator at ca. 35°C. Upon keeping the concentrated solution in a refrigerator after addition of ethanol, powdery yellow crystals deposited. The yield was about 1g. $\tilde{\nu}_{Imax}$ =24,000cm^{-1}, log ε =2.21. Found: C, 26.13; H,5.80; N,22.00%. Calcd for [Co(CN)(SO_3)(NH_3)($C_6H_{15}N_3$)]·0.5H_2O: C,26.25; H,5.99; N,21.87%.

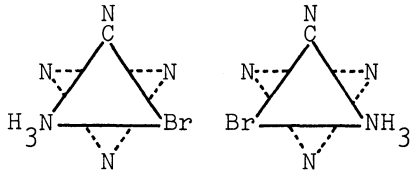

Fig.1. Enantiomers of [Co(Br)(CN)(NH_3)(tacn)]$^+$.

To an aqueous suspension of the above complex (1g, 0.003mol in 2cm^3 H_2O), was added 10cm^3 of 47% HBr dropwise and the mixed solution was allowed to stand at 50°C

for 6h, whereupon the color of the solution turned red. After cooling to room temperature, large amounts of ethanol and ether were successively added to the solution. Precipitated material was filtered and dissolved in water (500cm^3). The solution was chromatographed on a column of SP-Sephadex C-25 (4 x 25cm), using a 0.05M NaCl eluent. The effluent was concentrated by a rotary evaporator below 40°C, with simultaneous removals of the eluting agent precipitated. After addition of a small amount of ethanol to the final filtrate, the reddish crystals deposited on standing the whole in a refrigerator. The crude product was recrystallized from water. The yield was about 0.5g. Found: C,24.16; H,5.35; N,19.96%. Calcd for $[Co(Br)(CN)(NH_3)(C_6H_{15}N_3)]Cl$: C, 24.26; H,5.25; N,20.21%.

An aqueous solution of this complex was charged on a column containing SP-Sephadex C-25 in the Na^+ form. When the adsorbed band was descended to four fifth of the column height by elution with a 0.05M $K_2[Sb_2(d\text{-tart})_2]$ solution at a rate of 0.7cm^3/min, the band was washed with water and then eluted with a 0.05M NaCl solution, whereby the counter ions were changed into the chloride form. The effluent was successively collected with five fractions (each amount was ca. 50cm^3). The earliest fraction exhibited $(+)_{589}$ optical rotation.

The IR spectrum of the chloride complex indicated the coordinations of CN^-, TACN and NH_3. The fact that this complex behaved as an univalent cation against the chromatographic elution was a proof of the coordination of Br^-. The absorption spectrum of the complex is shown in Fig.2. An absorption maximum was observed at 19,400cm^{-1} (log ε =1.84) and a clear shoulder at ca. 23,000cm^{-1} (log ε =ca.1.6). The CD spectrum of the earliest fraction is also shown in Fig.2. The extrema observed in the first absorption band region were as follows; 17,300cm^{-1} (Δε = -0.01), 20,000cm^{-1} (Δε = +0.12) and 23,400cm^{-1} (Δε = -0.07) (the Co(III) concentration was determined from the absorption spectral data, and then the Δε values were evaluated). The CD spectrum of the last fraction was mirror image of that of the earliest one within experimental errors. The magnitude of the Cotton peaks is comparable to that of the all-cis-$[Co(CN)_2(NH_3)_2(H_2O)_2]^+$ complex[1].

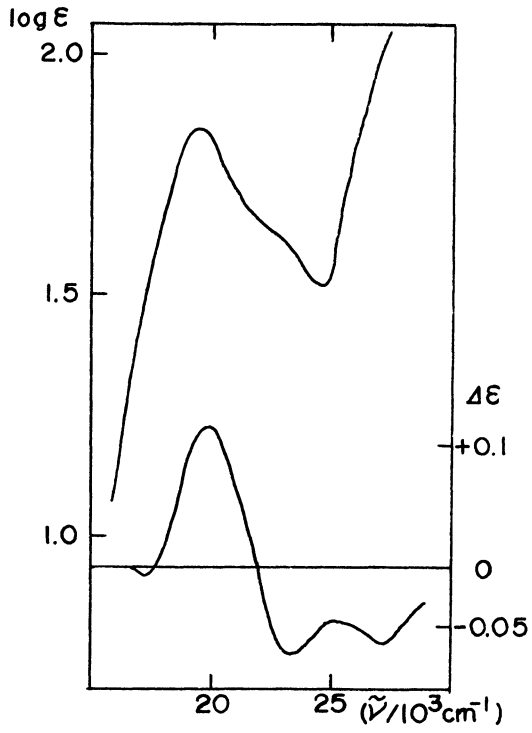

Fig.2. Absorption and CD spectra of $[Co(Br)(CN)(NH_3)(tacn)]^+$.

References

1) T.Ito and M.Shibata, Inorg. Chem., 16, 108 (1977).
2) K.Yamanari, J.Hidaka, and Y.Shimura, Bull, Chem. Soc. Jpn., 48, 1653 (1975).
3) Y.Hosokawa, J.Hidaka, and Y.Shimura, Bull, Chem. Soc. Jpn., 48, 3175 (1975).
4) J.E.Richman and T.J.Atkins, J. Am. Chem. Soc., 96, 2268 (1974).
5) H.Siebert, Z. Anorg. Chem., 327, 63 (1964).

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