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AN OPTICALLY ACTIVE COBALT(III)-SELENIDE COMPLEX. INVERSION AT SELENIUM IN TWO ISOMERS OF THE [2-(METHYLSELENO)ETHYLAMINE][TRIS(2-AMINOETHYL)AMINE]COBALT(III) ION

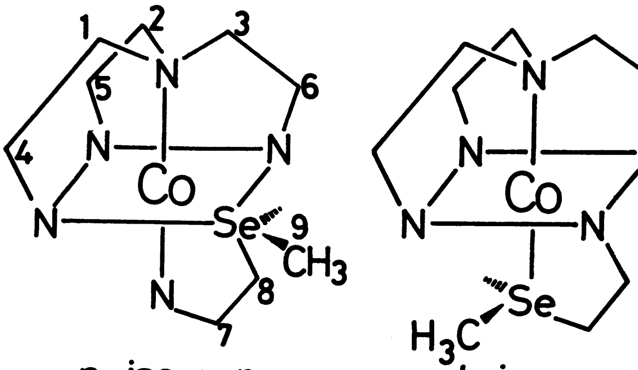
Kiyohiko NAKAJIMA, Masaaki KOJIMA, and Junnosuke FUJITA*
Department of Chemistry, Faculty of Science,
Nagoya University, Chikusa-ku, Nagoya 464

The optically active selenide complex, trans(tertiary amine nitrogen, Se)-$[Co(CH_3SeCH_2CH_2NH_2)\{N(CH_2CH_2NH_2)_3\}]^{3+}$, has been obtained for the first time by SP-Sephadex column chromatography. It loses ca. 50% of optical activity in 1 h at 22°C in 1 mol/dm^3 $NaClO_4$.

The selenium atom of a SeR'R"-type selenide ligand becomes chiral on coordination to a metal ion. It has been reported, however, that inversion at a coordinated selenide site is too rapid for the resolution in such complexes as Pt(II), Pt(IV), and Pd(II), although it is generally slower than that at an analogous sulfide site.1) On the other hand, a few isomeric pairs arising from a pair of chiral sulfur atoms have been isolated for $[Co^{III}(terdentate)(L\text{-}methioninate)]^+$ complexes.2) The configurational stability of selenium in some cobalt(III)-selenide complexes might be sufficient to support optical activity.

In this study we have chosen the $[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ complex (tren: tris(2-aminoethyl)amine), in which the configuration of the selenium atom is the sole source of chirality. Jackson and Sargeson3) reported that the inversion rate at sulfur in $[Co(CH_3SCH_2CH_2NH_2)(tren)]^{3+}$ and related complexes is slow ($K_i < 10\ s^{-1}$) on the NMR time scale at 25°C, but exceeds 0.1 s^{-1}.

The $[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$ complex was prepared by a method similar to that for the corresponding thiolato complex3) using the diselenide.4) Two geometrical isomers of the complex (Fig. 1) were separated by SP-Sephadex column chromatography, 0.15 mol/dm^3 Na_2SO_4 being used as an eluent. The formation ratio of p-isomer to t-isomer5) was ca. 3:1. The isomers were assigned on the basis of the elution order in column chromatography. The p-isomer has a set of three N-H bonds suitable for



p-isomer t-isomer

Fig. 1. Two geometrical isomers of $[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$.

hydrogen bonding with a sulfate ion and should be eluted faster than the t-isomer which lacks such a set.[6,7] The characteristics in absorption spectra of the isomers thus assigned quite resemble those of respective isomers of the thiolato complex.[3] The p- and t-isomers were isolated as perchlorate and tetrachlorozincate salts, respectively. Found for the p-isomer: C, 18.38; H, 4.66; N, 13.55%. Calcd for $[Co(SeCH_2CH_2NH_2)(tren)](ClO_4)_2$ = $C_8H_{24}N_5Cl_2O_8SeCo$: C, 18.23; H, 4.60; N, 13.30%. Found for the t-isomer: C, 17.07; H, 4.82; N, 12.24%. Calcd for $[Co(SeCH_2CH_2NH_2)$-$(tren)]ZnCl_4 \cdot 2H_2O$ = $C_8H_{28}N_5Cl_4O_2SeCoZn$: C, 16.82; H, 4.94; N, 12.26%.

The methyl derivatives were obtained from the selenolato isomers by methylation with CH_3I in dimethyl sulfoxide (DMSO). To a DMSO solution (50 cm^3) of each isomer (5 mmol) was added CH_3I (50 mmol). The color of the solution changed almost immediately from dark brown to orange. The reaction mixture was diluted with 10^{-3} mol/dm^3 HCl (500 cm^3), and the excess CH_3I was extracted with $CHCl_3$(150 cm^3 x 2). The orange aqueous layer was poured onto a small SP-Sephadex column (ϕ1.5 x 2 cm), and the product adsorbed was eluted with an appropriate eluent. The p- and t-isomers of the selenide complex were isolated as chloride and bromide, respectively. Found for the p-isomer: C, 21.84; H, 6.69; N, 14.36%. Calcd for $[Co(CH_3SeCH_2CH_2NH_2)(tren)]Cl_3$-$2.5H_2O$ = $C_9H_{32}N_5Cl_3O_{2.5}SeCo$: C, 21.85; H, 6.52; N, 14.16%. Found for the t-isomer: C, 17.95; H, 5.04; N, 11.99%. Calcd for $[Co(CH_3SeCH_2CH_2NH_2)(tren)]Br_3 \cdot H_2O$ = C_9H_{29}-N_5Br_3OSeCo: C, 17.98; H, 4.86; N, 11.65%.

The t-$[Co(CH_3SeCH_2CH_2NH_2)(tren)]Br_3 \cdot H_2O$ (ca. 70 mg) was charged on the top of an SP-Sephadex column (ϕ2 x 30 cm). By elution with 0.15 mol/dm^3 $Na_2[Sb_2(d\text{-tartrate})_2]$, the band showed an indication of optical resolution. Each of the first and last fractions was diluted with water, poured again onto a small SP-Sephadex column (ϕ1.5 x 2 cm), and the complex adsorbed was eluted with 1 mol/dm^3 $NaClO_4$. The two eluates showed enantiomeric CD patterns to each other as shown in Fig. 2. To the

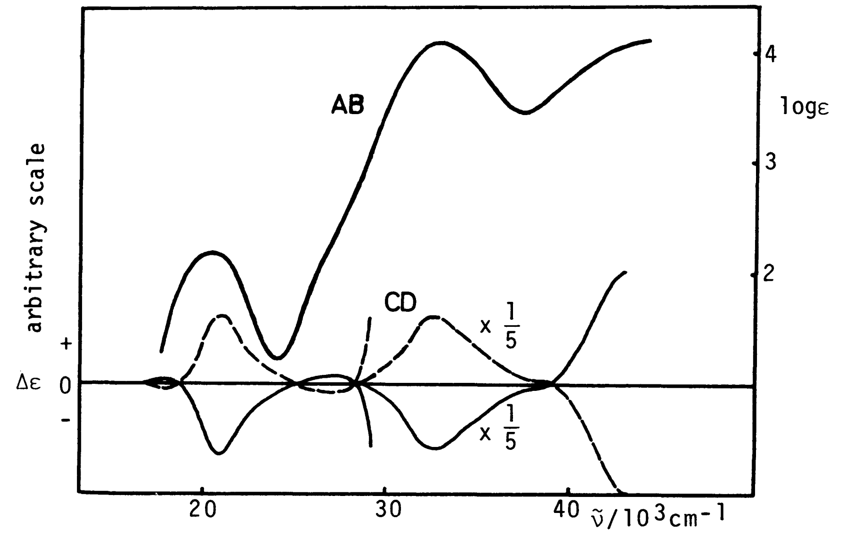


Fig. 2. The absorption spectrum of t-$[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ in water, and CD spectra of the enantiomers (in 1 mol/dm^3 $NaClO_4$) obtained from the first (———) and the last (-----) fractions in SP-Sephadex column chromatography (eluent: 0.15 mol/dm^3 $Na_2[Sb_2(d\text{-tartrate})_2]$).

best of our knowledge, this is the first optically active selenide metal complex whose optical activity originates from only chiral selenium atom. The absolute configuration was tentatively assigned from a comparison of the CD spectrum with those of cobalt(III)-sulfide complexes. The Λ-$[Co(CH_3SCH_2CH_2NH_2)(en)_2]^{3+}$ 8) and Δ-$[Co(CH_3SCH_2CH_2CH_2NH_2)(en)_2]^{3+}$ 9) (en: ethylenediamine) complexes show a positive CD band in the region of the Co(III)-S charge-transfer band (ca. 35000 cm^{-1}), while the CD patterns in the other region are almost enantiomeric to each other. The sulfide ligands in these isomers are considered to have the same R configuration stereoselectively, reducing nonbonded interactions between the methyl group and the en chelate ring. Thus the fast-moving isomer of the selenide complex in column chromatography can be assigned to have S configuration on the basis of the negative CD sign in the region of the Co(III)-Se charge-transfer band (ca. 33000 cm^{-1}, see Fig. 2). The complex loses the optical activity at a moderate rate (ca. 50% in 1 h) in 1 mol/dm^3 $NaClO_4$ solution at 22°C.

On the other hand, attempts to resolve p-$[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ by the chemical method with several resolving agents and by SP-Sephadex column chromatography were all unsuccessful. However, the complex exhibits nine signals in the ^{13}C NMR spectrum as shown in Fig. 3. The diastereotopic carbon resonances of the tren ligand arising from the presence of the chiral selenide group are clearly resolved,

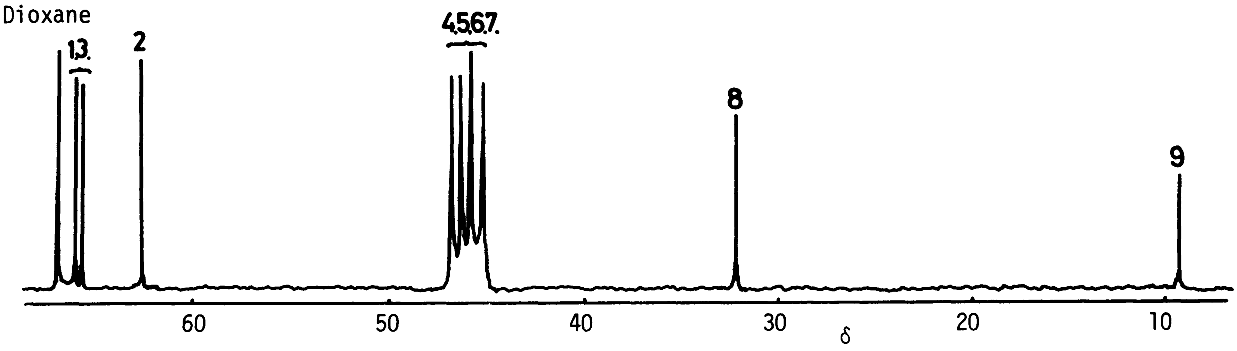


Fig. 3. The ^{13}C NMR spectrum (15.04 MHz) of p-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]$^{3+}$ in D_2O with internal dioxane (67.69 ppm) (See Fig. 1 for signal numbers).

demonstrating the stability toward inversion on the NMR time scale. Thus it can be concluded that the inversion at selenium in the p-isomer is slow on the NMR time scale, but not so slow as to be resolved by conventional techniques.

For the analogous sulfenato complex, [Co{S(O)$CH_2CH_2NH_2$}(tren)]$^{2+}$, the p-isomer also racemizes much faster than the t-isomer does by a factor of at least 50.$^{9)}$ The rate of inversion at Se(S) in a tren complex seems to be governed by a steric factor, if the inversion would proceed via trigonal planar Se(S).$^{10)}$ In the p-isomer, the two hydrogen atoms on 1,3 carbons of the tren ligand are close to the Se-CH_3 or S=O group. Such proximity would make the formation of trigonal planar, intermediate Se(S) easier to accelerate the inversion.

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