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ISOLATION AND ABSOLUTE CONFIGURATION OF A NEW ISOMER OF (1,2-PROPYLENEDIAMINETETRAACETATO)COBALTATE(III) ION, $[Co(pdta)]^-$

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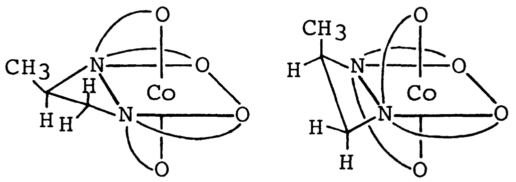
A new isomer of $[Co^{III}(pdta)]^-$, which has a methyl group in the axial orientation, was prepared and optically resolved. The complex was characterized by spectral behaviors. The absolute configuration was determined on the basis of the circular dichroism spectrum and the equilibrium experiment.



eq isomer(ΔΔΛ) *ax* isomer(ΔΛΛ)

Fig. 1. Possible isomers of $[Co\{(R)\text{-pdta}\}]^-$.

For the sexidentate 1,2-propylenediaminetetraacetato($pdta^{4-}$) complex of cobalt(III), $[Co(pdta)]^-$, two diastereomeric isomers are possible as shown for the (*R*)-pdta complex in Fig. 1. It is well known that one enantiomeric pair can exist with extremely high stereoselectivity, owing to a conformational preference for the equatorial orientation of methyl group.$^{1)}$ So far the second isomer has not been detected even in traces. The stable isomer is designated *eq* because it has a pseudoequatorial methyl group,$^{1)}$ while the unstable one is designated *ax* because it has a pseudoaxial methyl group as will be described below.

Im and Busch have pointed out that the *ax* isomer exists in relative concentrations of less than 1% of the *eq* isomer at equilibrium on the basis of a study of the electron-transfer rates, if it exists at all.$^{2)}$ For the $[Rh(pdta)]^-$ complex, the existence of the corresponding *ax* isomer has been reported by Blackmer *et al.* as a mixture with the *eq* isomer in a photolysis product in a solution.$^{3)}$ In the present work, we isolated the *ax* isomer of cobalt(III) complex as pure and stable crystals.

To a solution of *eq*-$K[Co(pdta)]\cdot H_2O$(100 g) in water(130 cm^3) was added active charcoal(6 g). The mixture was stirred at 100 °C for 2 h. After removal of the active charcoal, methanol(170 cm^3) was added to the filtrate and the *eq* isomer deposited was removed by filtration. To the filtrate was added an appropriate amount of ethanol to crystallize out most of the crystallizable complexes. The complex was collected by filtration and dissolved in water and an appropriate amount of methanol was added to it. The crystals deposited were removed by filtration and the filtrate was concentrated to syrup below 30 °C on a vacuum evaporator. The syrup was diluted with water and the solution was poured onto a column(ϕ3.5x80 cm) of Dowex 1X8(Cl^- form). By eluting the adsorbed band with 0.07 mol dm^{-3} potassium chloride, the *eq* and *ax*(new) isomers were separately eluted in this order. From the eluate containing the *ax* isomer, crystals of *ax* isomer were obtained after removal of the contaminant potassium chloride. Recrystallization was achieved from water by adding methanol. Found: C, 30.36; H, 4.17; N, 6.39%. Calcd for $K[Co(pdta)]\cdot 2H_2O = C_{11}H_{18}N_2O_{10}KCo$: C, 30.28; H, 4.16; N, 6.42%. The distribution of *ax* isomer in the reaction mixture on active charcoal was estimated to be approximately 0.1% of the *eq* isomer by measurement of the absorbance of the column eluate. In order to resolve into the enantiomers, the *ax* isomer was converted to the silver salt by using SP-Sephadex C-25(Ag^+ form). Found: C, 25.89; H, 3.69; N, 5.37%. Calcd for $Ag[Co(pdta)]\cdot 2.5H_2O = C_{11}H_{19}N_2O_{10.5}AgCo$: C, 25.70; H, 3.73; N, 5.45%. The silver salt was treated with a resolving agent, $(-)_D$-$[Co(ox)(en)_2]I$, and the resulting less-soluble diastereomer was purified by recrystallization from water by adding methanol. Found: C, 29.08; H, 5.43; N, 11.89%. Calcd for $[Co(ox)(en)_2]\cdot[Co\{(R)\text{-}pdta\}]\cdot 4H_2O = C_{17}H_{38}N_6O_{16}Co_2$: C, 29.15; H, 5.47; N, 12.00%. The optically pure *ax* isomer of potassium salt, $(+)_D$-*ax*-$K[Co\{(R)\text{-}pdta\}]\cdot 2H_2O$, was obtained from the diastereomer by using SP-Sephadex C-25(K^+ form). Found: C, 30.27; H, 4.18; N, 6.32%. Calcd for $K[Co\{(R)\text{-}pdta\}]\cdot 2H_2O = C_{11}H_{18}N_2O_{10}KCo$: C, 30.28; H, 4.16; N, 6.42%. $[\alpha]_{589}$ +240°.

Figure 2 shows the absorption spectrum(ε_{max}=315 at 18660 cm^{-1} and ε_{max}=214 at 26250 cm^{-1}) of the isomer newly isolated in the d←d absorption band region. This is quite similar to that of the *eq* isomer.[4] The ^{13}C NMR spectral data and the primary assignments of the new isomer are shown with those of the *eq* isomer in Table 1. The new isomer shows eleven peaks expected for the $[Co(pdta)]^-$ as in the *eq* isomer. The spectra of the two isomers are similar on the whole to each other, but are clearly different in chemical shift values. The chemical shift values of the carboxylate carbons indicate that all the acetate groups are coordinated, because it has been

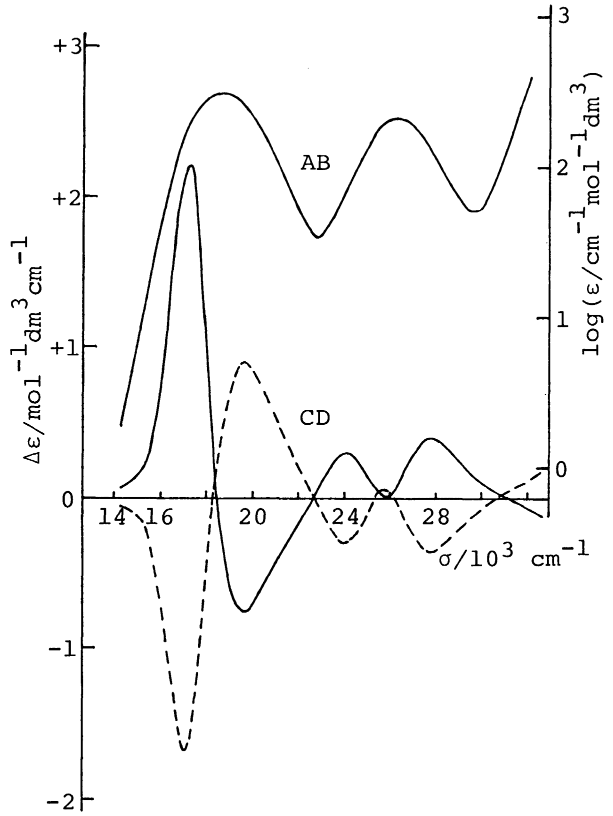


Fig. 2. Absorption(AB) spectrum of *ax*-$[Co(pdta)]^-$, and CD spectra of $(+)_D$-*ax* isomer$\{(+)_D$-ΔΛΛ-$[Co\{(R)\text{-}pdta\}]^-\}$: —— and $(-)_D$-*eq* isomer$\{(-)_D$-ΔΔΛ-$[Co\{(R)\text{-}pdta\}]^-$: ---.

Table 1. The 25 MHz $^{13}C\{^1H\}$ NMR data of $[Co(pdta)]^-$ in D_2O(at 21 °C)[a]

	$-CH_3$	$-CH_2-$	>CH-	-COO
ax isomer	17.2	61.7	73.2	182.3
		68.2		182.9
		68.5		183.1
		68.9		183.7
		70.4		
eq isomer	10.9	57.8	68.6	182.4
		64.8		182.5
		65.8		183.1
		66.7		183.2
		68.5		

a) Values in ppm from TMS: dioxane(67.4 ppm) was used as an internal standard.

found that the signal of uncoordinated groups is situated near at 170 ppm.[5)] The new isomer of potassium salt was converted to that of the hydrogen salt by using SP-Sephadex C-25(H^+ form). The IR spectrum of the hydrogen salt does not exhibit a band which is characteristic of protonated carboxylate groups(1700–1750 cm^{-1}).[6)] Furthermore, the ^1H and ^{13}C NMR spectra of the hydrogen salt in D_2O is almost unchanged from those of the potassium salt. These facts confirm that the new complex contains $pdta^{4-}$ functioning as a sexidentate ligand, that is, it is the desired complex.

Figure 2 shows also the circular dichroism(CD) spectrum($\Delta\varepsilon_{ext}$=+2.24 at 17180 cm^{-1} and $\Delta\varepsilon_{ext}$=-0.77 at 19570 cm^{-1}) of $(+)_D$-*ax* isomer and that($\Delta\varepsilon_{ext}$=-1.69 at 17120 cm^{-1} and $\Delta\varepsilon_{ext}$=+0.89 at 19530 cm^{-1}) of the $(-)_D$-*eq* isomer, $(-)_D$-ΔΔΛ-$[Co\{(R)\text{-}pdta\}]^-$, which is of known absolute configuration.[1)] The CD spectra of the isomers are similar to each other with opposite signs for each CD component except for the lack of a negative component near at 26000 cm^{-1} for the $(+)_D$-*ax* isomer. This observation indicates that the absolute configuration of the $(+)_D$-*ax* isomer is opposite to that of the $(-)_D$-*eq* one, because the CD of a chiral complex is predominantly contributed by the configurational effect due to the chiral arrangement of chelate rings around the metal ion.[7)] Thus, we conclude that the $(+)_D$-*ax* isomer is ΔΛΛ-$[Co\{(R)\text{-}pdta\}]^-$. This conclusion is undoubtedly confirmed by the following observation. The $(+)_D$-*ax* isomer isomerizes to the $(-)_D$-*eq* isomer on active charcoal in aqueous solution. After 10 min at 60 °C, the CD of the resulting solution coincided with that of the $(-)_D$-*eq* isomer within the experimental error.

The 400 MHz ^1H NMR spectrum of the *ax* isomer is shown in Fig. 3. The four AB quartets due to the methylene protons of four acetate rings can be easily assigned, and were distinguished between the G and R rings according to the magnitude of the J_{AB} value as indicated under the spectrum.[8)] The signals due to the methyne(H_C) and methylene(H_A and H_B) protons on the diamine backbone consist of approximately a first-order pattern, AMX-spin system, with the coupling of H_C to the methyl protons. Their resonance centers are at 3.36, 3.66, and 3.83 ppm. The signal at 3.66 ppm is undoubtedly assigned to the H_C proton because it couples to the methyl protons(H_X) with J_{C-X}=7.6 Hz(the methyl doublet at 1.36 ppm is not shown) as seen in the double-resonance measurement in Fig. 3. By the first-order analysis of the AMX pattern, the J values were determined to be 14.0, 6.1, and less than 0.3 Hz(Fig. 3). The value of 14.0 Hz is reasonable for the coupling(J_{A-B}) between the geminal protons H_A and H_B,[9,10)] and therefore the other J values are of the couplings(J_{vic}) between the vicinal protons, J_{A-C} and J_{B-C}. The J_{vic} values are apparently different from those of the *eq* isomer(12.6 and 3.3 Hz)[11)] and of many complexes containing *C*-alkyl substituted ethylenediamines[9,12)] and 1,2-propylenediaminetriacetate.[10)] On the other hand, similar J_{vic} values to the present case were found for the nickel(II) complex containing a macrocyclic amine with 1,2-propylenediamine fragment and the axial orientation of methyl group has been pointed out from the J_{vic} values.[13)] From the same argument as for the macrocyclic amine complex, it is concluded that the diamine fragment of the *ax* isomer adopts a *gauche* conformation which has the methyl group of a pseudoaxial orientation. Namely, the Karplus-like relation[14)] determines that J_{A-C}<0.3 Hz and J_{B-C}=6.1 Hz and, consequently, the signals of the H_A and H_B protons are assigned as indicated in Fig. 3. From the value of J_{A-C}, the dihedral angle of H_A–C–C–H_C fragment is estimated to be about 90° and also the value of J_{B-C} is consistent with such a conformation of diamine backbone. In brief, the *ax* complex with (*R*)-pdta, ΔΛΛ-[Co{(*R*)-pdta}]$^-$, adopts the *δ-gauche* conformation, which is simply drawn in Fig. 3.

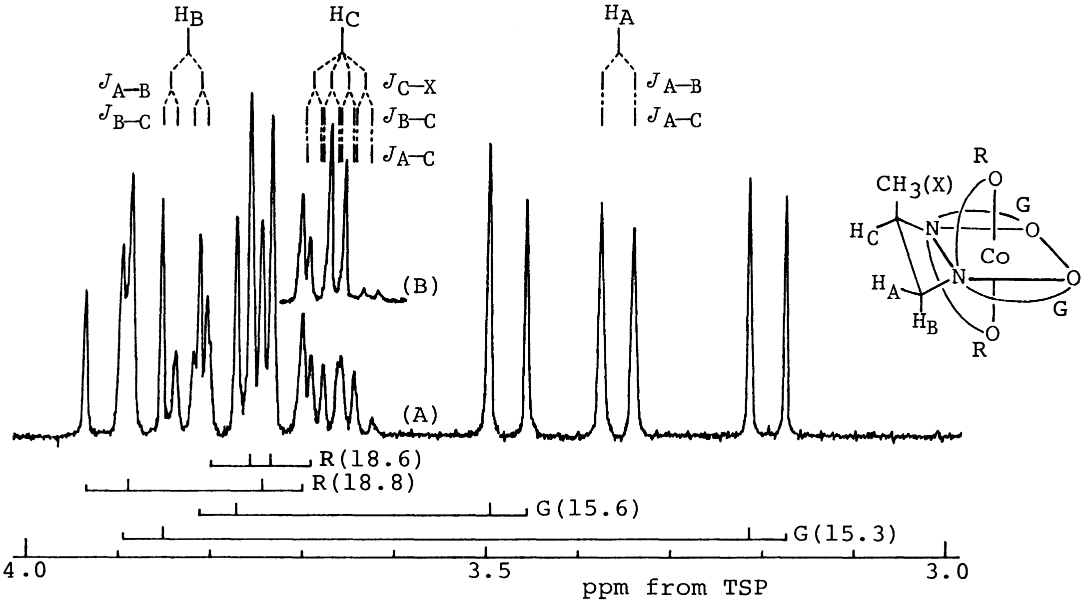


Fig. 3. The 400 MHz ^{1}H NMR spectrum of *ax*-[Co(pdta)]$^-$(A) and the double-resonance spectrum irradiated on the methyl signal(B) in D_2O(at 24 °C). TSP{sodium 3-(trimethylsilyl)propionate-d_4} was used as an external standard. The numerals in parentheses indicate the J_{AB} values in Hz for the AB quartet due to the R or G acetate ring.

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