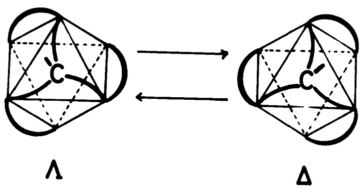
CHEMISTRY LETTERS, pp. 1047 - 1050, 1984.

STRUCTURE AND THERMAL RACEMIZATION OF 1,1,1-TRIS(5-AMINO-2-AZA-PENTYL)ETHANECOBALT(III) COMPLEX

Kanji TOMIOKA, Takaki KASHIHARA, Ushio SAKAGUCHI, and Hayami YONEDA*
Department of Chemistry, Faculty of Science, Hiroshima University,
Hiroshima 730

The chiral form of the title complex ion, $[Co(stn)]^{3+}$, has been found to racemize thermally both in the solid state and in solution, and the racemization rates have been measured. The structure of $[Co(stn)]Cl_3 \cdot 3.5H_2O$ has been determined and used to discuss the origin of this facile racemization.

It is generally believed that optically active $[Co(N)_6]^{3+}$ complexes are not subject to thermal racemization with few exceptions.1) We here report that the chiral form of 1,1,1-tris(5-amino-2-aza-pentyl)-ethanecobalt(III), $[Co(stn)]^{3+}$, racemizes thermally both in the solid state and in solution. Based on kinetic studies, a novel racemization mechanism is proposed. In addition, we have determined the structure of $[Co(stn)]Cl_3 \cdot 3.5H_2O$ by X-ray techniques [stn = $(NH_2CH_2CH_2CH_2NHCH_2)_3C-CH_3$].



Hermer and Douglas2) reported previously the synthesis and optical resolution of $[Co(stn)]^{3+}$, but their methods are tedious and inefficient for large-scale synthesis, as noted recently by Geue and Searle3) and us.4) Thus, the ligand stn was prepared in this work by a method similar to that used for sen (sen = 1,1,1-tris(4-amino-2-aza-butyl)ethane).4) The method employed here is essentially similar to the method of Geue and Searle,3) and involved the tosylation of 1,1,1-tris(hydroxymethyl)ethane in pyridine (py), refluxing the tritosylate in a large excess of 1,3-propanediamine (tn), and extraction of crude stn with pyridine. The crude stn was mixed with a warm methanol solution of trans-$[CoCl_2(py)_4]Cl$5) and the resulting rose-pink precipitate of $[Co(stn)]Cl_3 \cdot 3.5H_2O$ was suction-filtered and recrystallized from warm water. The overall yield based on 1,1,1-tris-(hydroxymethyl)ethane was about 60%.

Optical resolution was effected by the use of the optically active

Table 1. Crystallographic Data

Formula	$C_{14}H_{43}N_6Cl_3CoO_{3.5}$
Crystal system	monoclinic
Space group	C2/c (No. 15)
a/Å	29.038(10)
b/Å	10.975(5)
c/Å	14.763(3)
β/deg.	99.861(23)
V/Å^3	4633.83(269)
d_{calcd}/g cm^{-3}	1.267
d_{obsd}/g cm^{-3}	1.27
z	8
Color	orange red
Dimensions/mm	0.5.x0.13x0.25
Diffractometer	Syntex R3
Radiation	Mo K_α(λ0.71069 Å)
Monochromator	graphite
Mode	ω-scan
2θ range/deg.	2 -55
Reflections(measd.)	5412
(used)	4503
R	0.0585
R_W	0.0746

$[Co(ox)_3]^{3-}$ (ox = oxalate),$^{6)}$ yielding the less-soluble distereomer of Λ-Δ combination of the cation and anion. Both enantiomers were isolated as perchlorate salts with $\Delta\varepsilon_{522}$ = ±0.514(lit.$^{2)}$ $\Delta\varepsilon_{521}$ = ±0.50).

Crystallographic data for the racemic chloride salt, $[Co(stn)]Cl_3$ $3.5H_2O$, are summarized in Table 1, and the structure of the cation with atom labels is given in Fig. 1 as a stereopair. The cation has a pseudo-threefold axis of rotation. The geometry of the trimethyleneethane capping group is very close to that in Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)$ $6H_2O$.$^{7)}$ The three six-membered chelate rings are all in a flattened chair form. This flattening can be seen on the dihedral angle between the NCoN and NCCN planes of 159.4(2)°. This value may be compared with 150.6(36)° and 150.5(62)° of $[Co(tn)_3]^{3+}$ and Λ-fac-$[Co(R,S\text{-}ptn)_3]^{3+}$ (ptn = 2,4-pentanediamine), respectively.$^{8,9)}$ Further, the flattening seems to be more significant at secondary nitrogens, because the Co-N-C-C torsional angles are 45.0(8)° near the cap and 51.1(24)° for the other. The N-Co-N angle of 94.5(4)° of $[Co(stn)]^{3+}$ appears to be larger than the angles of other six-membered chelates. For

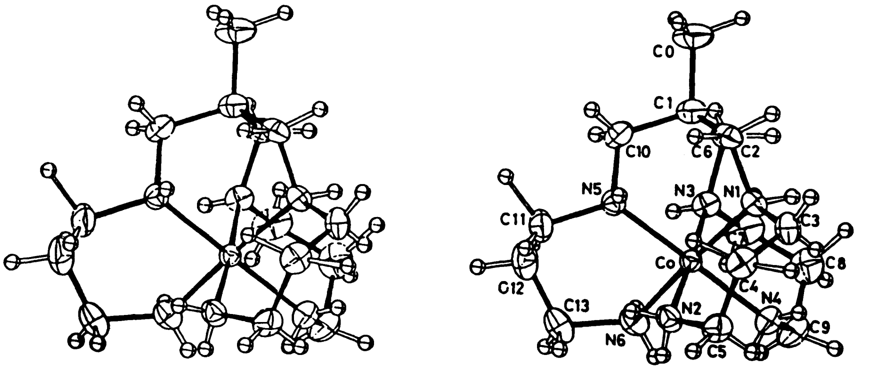


Fig. 1. Stereoscopic drawing of the cation.

comparison, the N-Co-N angles in $[Co(tn)_3]^{3+}$, Λ-ob_3-$[Co(R,R\text{-}ptn)_3]^{3+}$, Λ-fac-$[Co(R,S\text{-}ptn)_3]^{3+}$, and Δ-$lel_3$-$[Co(R,R\text{-}ptn)_3]^{3+}$ are 90.4(1)°, 88.3(15)°, 89.9(25)°, and 89.1(3)°, respectively.[8-10] These features suggest that the $[Co(stn)]^{3+}$ cation is more strained than the parent $[Co(tn)_3]^{3+}$ owing to the trimethyleneethane capping. In the crystal, amine hydrogens are bonded weakly to mostly chloride ions, and it is only one of the two N6 hydrogens that apparently bonds to oxygen atoms.

Racemization studies were performed both in the solid state and in solution. In solution, rate constants were collected for 5×10^{-2} mol dm^{-3} 2,4,6-collidine buffered solutions (ph 6.73-7.96) between 55.0 °C and 70.0 °C. The racemization in these buffers accompanied no decomposition[11] and followed a rate law of the form $k_{obsd} = k[OH^-]$, where k_{obsd} is the observed pseudo-first-order rate constant and k the second-order rate constant. The k values were $(2.87\pm0.14)\times10^2$, $(7.24\pm0.52)\times10^2$, $(1.27\pm0.08)\times10^3$, and $(2.63\pm0.04)\times10^3$ $dm^3\ mol^{-1}s^{-1}$ at 55.0, 60.0, 65.0, and 70.0 °C, respectively. From these values, the enthalpy and entropy of activation for racemization were determined at $+132\pm6$ kJ mol^{-1} and $+204\pm18$ J $K^{-1}mol^{-1}$, respectively. The racemization of the chloride salt in the solid state accompanied some decomposition, but that of the perchlorate salt did not. For the solid perchlorate salt, the racemization proceeded in two stages. The second, slower process could be described by a simple exponential law, but the first, rapid process could not. The enthalpy and entropy of activation for the slower process were $+58\pm17$ kJ mol^{-1} and -206 ± 48 J $K^{-1}mol^{-1}$, respectively.

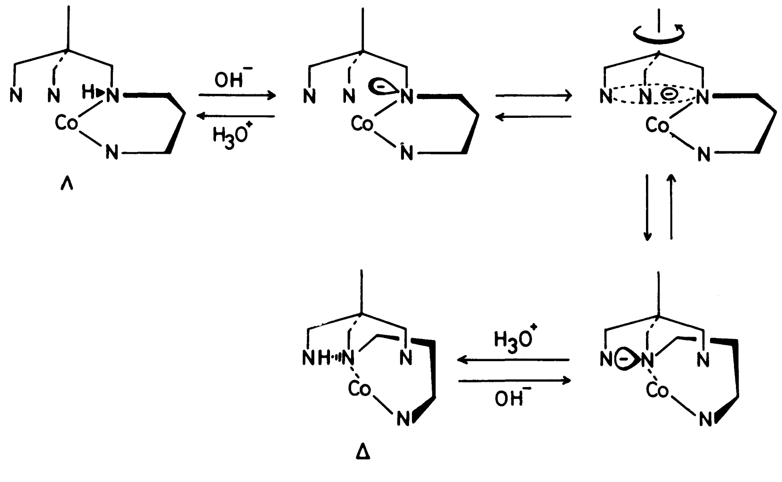


Fig. 2. A possible mechanism of racemization.

As mentioned above, the racemization of $[Co(stn)]^{3+}$ in solution is catalyzed by OH^-. This indicates that the first step of racemization is the deprotonation at a secondary nitrogen, because secondary amine groups are usually more acidic than primary amine groups. One possible mechamism leading to racemization is depicted in Fig. 2. The second step of racemization may be a trigonal twist about the threefold axis of the deprotonated intermediate. Note here (i) that the inversion of the ablolute configuration about the metal ion by trigonal twist should take place synchronously with the inversion of the absolute configuration of secondary amine groups, because the chirality of the amine guoups are predetermined by the chirality about the metal ion. (ii) Further, due to the presence of the interlinkage of chelate rings, it is necessary to invert the absolrte configuration of all three asymmetric nitrogens simultaneously, i.e., Δ(R,R,R) to Λ(S,S,S) or vice versa. In other words, the second step may be described as a hopping of two hydrogens over three secondary nitrogens. Concurrently with this hopping, the inversion of the absolute configuration of both nitrogen and metal centers take place. A similar hopping of hydrogen over six nitrogens was reported for the deprotonated form of $[Co(sep)]^{3+}$ (sep = 1,3,6,8,10-13,16,19-octaazabicyclo[6.6.6]eicosane).$^{12)}$ Most possibly, the trigonal twist would be facilitated by the steric strain noted above.

The authors are grateful to Dr. Yoshimasa Fukazawa for many helpful suggestions and to Mr. Masayuki Yoneda for experimental assistance.

References

1) D. J. Royer, G. J. Grant, D. G. Van Derveer, and M. J. Castillo, Inorg. Chem., 21, 1902(1982).
2) R. E. Hermer and B. E. Douglas, J. Coord. Chem., 7, 43(1977).
3) R. J. Geue and G. H. Searle, Aust. J. Chem., 36, 927(1983).
4) U. Sakaguchi, K. Tomioka, and H. Yoneda, Chem. Lett., 1984, 349; K. Tomioka, U. Sakaguchi, and H. Yoneda, Inorg. Chem., in press.
5) A. Werner and R. Feenstra, Ber., 39, 1538(1906).
6) J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, Inorg. Chem., 8, 1201(1969); K. R. Butler and M. R. Snow, J. Chem. Soc., Dalton Trans., 1976, 251.
7) H. Okazaki, U. Sakaguchi, and H. Yoneda, Inorg. Chem., 22, 1539(1983).
8) R. Nagao, F. Marumo, and Y. Saito, Acta Crystallogr., Sect.B, 29, 2438(1973).
9) S. Sato and Y. saito, Acta Crystallogr., Sect.B, 34, 420(1978).
10) A. Kobayashi, F. Marumo, and Y. Saito, Acta Crystallogr., Sect.B, 28, 3591 (1972); A. Kobayashi, F. Marumo, and Y. Saito, ibid., 29, 2443(1973).
11) Confirmed by absorption, ^{1}H NMR, and circular dichroism spectra, ion-exchange chromatography on SP-Sephadex C-25, and the pH dependence of rate constants.
12) H. Sugimoto, H. Hataoka, and M. Mori, J. Chem. Soc., Chem. Commun., 1982, 1301.

(Received March 10, 1984)