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Stereoisomers of *trans*-Dichlorocobalt(III) Complex with 1,7-Bis[(*S*)-2-pyrrolidinyl]-2,6-diazaheptane

Masahiko SABURI,* Shusei OBATA, Motowo YAMAGUCHI, and Sadao YOSHIKAWA*
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Synopsis. The complex *trans*-$[CoCl_2(SS\text{-pyht})]^+$ (SS-pyht=1,7-bis[(*S*)-2-pyrrolidinyl]-2,6-diazaheptane), prepared *via* the HCl treatment of Λ-β-$[CoCO_3(SS\text{-pyht})]^+$, was found to take the (*R,R*) configuration with regard to the secondary nitrogen centers involving the central chelate. The isomer ratio of two diastereomers (trans(*R,S*) and trans(*R,R*)) was estimated at the equilibrium in methanol; (*R,S*)/(*R,R*)= 10.4±2.6.

The *trans*-dichlorocobalt(III) complex of 1,7-bis[(*S*)-2-pyrrolidinyl]-2,6-diazaheptane (SS-pyht), an optically active 2,3,2-tet derivatives having the pyrrolidine rings at the both side arms, was first reported by Jun and Liu[1] (2,3,2-tet=3,7-diazanonane-1,9-diamine). They supposed that the *trans*-$[CoCl_2(SS\text{-pyht})]^+$ produced by the standard air-oxidation method takes the (*R,R*)[2] configuration with respect to the secondary nitrogen centers connecting the central six-membered chelate and the five membered chelates (Fig. 1a).[1] However, the true structure of the complex ion determined by an X-ray crystallographic study[3] was found to assume the trans(*R,S*) configuration (Fig. 1b).

In our previous report,[4] an alternative method, *i.e.*, the treatment of $[CoCO_3(SS\text{-pyht})]^+$ with hydrochloric acid, was applied for preparing *trans*-$[CoCl_2(SS\text{-pyht})]ClO_4$. This Note describes that the above mentioned dichloro complex adopts the trans(*R,R*) configuration, as is expected from the observations that the HCl treatment of β-carbonatocobalt(III) with 2,3,2-tet[5] or its chiral derivatives[6] yields trans-dichloro complex having the C_2 symmetry (trans(*R,R*) and/or (*S,S*)).

Experimental

Materials. The ligand, 1,7-bis[(*S*)-2-pyrrolidinyl]-2,6-diazaheptane (SS-pyht), was synthesized by the reported method.[1,4] The complex *trans*(*R,S*)-$[CoCl_2(SS\text{-pyht})]ClO_4$ was obtained by the air-oxidation method.[1] The *trans*(*R,R*)-$[CoCl_2(SS\text{-pyht})]ClO_4$ was prepared by the reported method *via* the carbonato complex.[4]

Measurements. Visible absorption and circular dichroism (CD) spectra were obtained on a Shimadzu UV-210 spectrophotometer and JASCO J-500 spectropolarimeter, respectively. ^{13}C NMR spectra at 100 MHz were obtained on a JEOL GX-400 spectrometer in the standard manner, employing methanol-*d* as a solvent and tetramethylsilane as an external reference.

Results and Discussion

It has been demonstrated that ^{13}C NMR spectrometry is a convenient tool to determine the molecular symmetry of cobalt(III) complexes with polyamine ligand(s) which has no probe signal appropriate for ^1H NMR spectral examination.[6,7,8] As for the *trans*-$[CoCl_2(SS\text{-pyht})]^+$ ion, the (*R,S*) isomer, which has no symmetry element (Fig. 1b), is expected to show, in principle, thirteen resonances on the spectrum, while the (*R,R*) isomer with the C_2 symmetry (Fig. 1a), should exhibit maximally seven resonances.

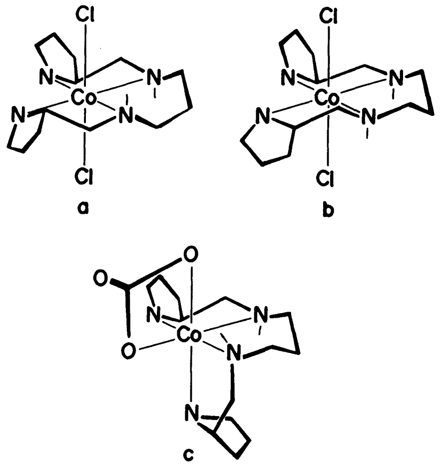
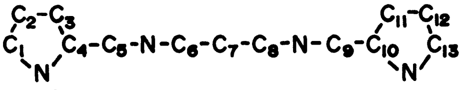


Fig. 1. Structures of *trans*(*R,R*)-$[CoCl_2(SS\text{-pyht})]^+$ ion, (a), *trans*(*R,S*)-$[CoCl_2(SS\text{-pyht})]^+$ ion, (b), and Λ-β-$[CoCO_3(SS\text{-pyht})]^+$ ion, (c).

TABLE. ^{13}C NMR SPECTRAL DATA OF *trans*-$[CoCl_2(SS\text{-pyht})]^+$ ION[a)]

Chemical Shift (ppm)[b)]		Assignments[c)]
trans(*R,S*)	*trans*(*R,R*)	
25.44	23.35 (1)[d)]	C_7
26.95	27.18 (2)	C_2, C_3, C_{11}, C_{12}
27.65	27.83 (2)	
28.39		
29.41		
48.73	44.65 (2)	C_1, C_6, C_8, C_{13}
49.93	49.57 (2)	
50.22		
50.85		
56.17	59.96 (2)	C_4, C_5, C_9, C_{10}
60.80	62.44 (2)	
61.42		
63.82		

a) Taken at 100 MHz in methanol-d solution. b) From external TMS. c) The order of each carbon atom is as



shown. d) The values in parentheses are the relative intensities of resonances.

The *trans*(*R,S*)-$[CoCl_2(SS\text{-pyht})]^+$ ion, the structure of which has been clarified by the X-ray analysis study,[3] exhibits, in fact, thirteen resonances in the ^{13}C NMR spectrum (see Table). The ligand SS-pyht has thirteen carbon atoms so that the above spectral feature is in accord with that the tetramine in this complex ion adopts a rigid conformation without symmetry, which is anticipated for the trans(*R,S*) configuration. The carbon resonances can be classified into four subgroups as in Table, though it is difficult to assign every reso-

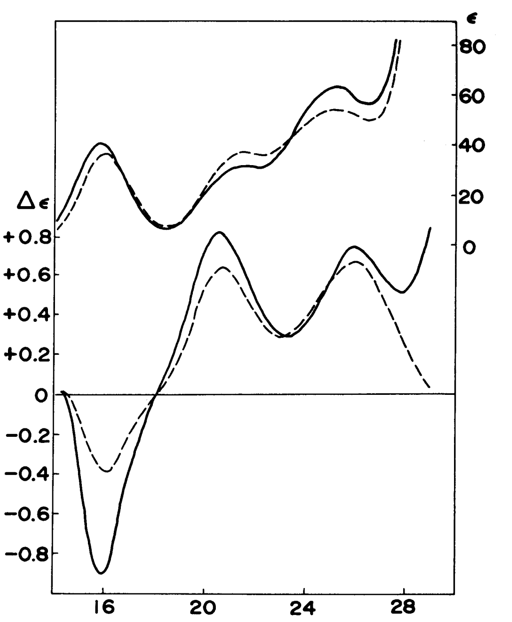


Fig. 2. Visible absorption and CD spectra of *trans*-$[CoCl_2\text{-(SS-pyht)}]^+$ ion; trans(R,S) isomer, (——), and trans(R,R) isomer (----).

nance to the individual carbon of SS-pyht.

We have prepared the *trans*-dichlorocobalt(III) complex of SS-pyht *via* the carbonato complex.⁴⁾ The carbonato complex $[CoCO_3\text{(SS-pyht)}]^+$, which was produced *in situ* by a reaction of SS-pyht with $[Co(CO_3)_3]^{3-}$, showed a dominant positive CD peak in the ${}^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ transition region. It has been indicated that the oxalato complex $[Co(C_2O_4)\text{(SS-pyht)}]^+$ adopts specifically the Λ-β(R,R) configuration,³⁾ and that the CD curve of this complex exhibits a positive Cotton effect in the ${}^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ transition. Thus, it is probable that the carbonato complex of SS-pyht also assumes the Λ-β(R,R) configuration (Fig. 1c).

The transformation from Λ-β(R,R)-$[CoCO_3\text{(SS-pyht)}]^+$ to trans-dichloro complex in acidic medium should proceed with retention of the configuration with regards to the secondary N centers at the central chelate ring. Thus, it was expected that the *trans*-$[CoCl_2\text{(SS-pyht)}]ClO_4$ obtained via the carbonato complex has the (R,R) configuration with C_2 symmetry (Fig. 1a). The ^{13}C NMR spectrum of the present complex actually showed seven resonances (Table), demonstrating that the complex ion has the C_2 symmetry and, therefore, is assigned to the trans(R,R) geometry. Thus, *trans*-$[CoCl_2\text{(SS-pyht)}]^+$ produced by two independent methods clearly differs from each other.

The CD curve of *trans*(R,S)- and *trans*(R,R)-$[CoCl_2\text{(SS-pyht)}]^+$, measured in methanol solution, were apparently dissimilar to each other as shown in Fig. 2. Further, it was noticed that the CD curve of trans(R,S) isomer obtained here is not identical with that reported by Jun and Liu,¹⁾ though the complex employed are considered to have the same structure. The reason for such difference is uncertain.

It has been shown⁹⁾ that both of *trans*(R,S)- and *trans*(R,R)-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ (2,10-Me_2-2,3,2-tet=(2S,10S)-2,10-diamino-4,8-diazaundecane) give rise to an equilibrium mixture of these diastereomers by the base treatment in methanol solution, and that the isomer ratio at the equilibrium is readily determined by CD measurements when both of the chiral diastereomers are available. Thus, the CD changes of *trans*(R,S)-and *trans*(R,R)-$[CoCl_2\text{(SS-pyht)}]ClO_4$ were followed in basic methanol solution, in a similar manner to that employed for the 2,10-Me_2-2,3,2-tet complexes.⁹⁾ The curve of the trans(R,R) isomer changed remarkably, while that of the trans(R,S) varied slightly. After 2 h standing, however, the CD curves of two diastereomers became identical with each other within experimental error. The wavenumbers and intensities of the CD intersections for the two species (at 23200 and 24900 cm^{-1}) did not change during the base treatment, indicating that any isomer other than the trans(R,R) and (R,S) was not formed during the above conversion. It was determined, therefore, that the equilibrium mixture contains only two diastereomers of *trans*-$[CoCl_2\text{(SS-pyht)}]^+$.

Based on the CD intensities (at 625 and 351 nm) before and after the base treatment, the isomer ratio at the equilibrium is estimated to be $(R,S)/(R,R)=10.4\pm2.6$, which corresponds to $-\Delta G=5.85\pm0.71$ kJ·mol⁻¹ (or 1.40 ± 0.17 kcal·mol⁻¹) at 300 K. The energy difference between the diastereomers obtained here is large enough for the more stable (R,S) isomer to occupy more than 90% of the equilibrium mixture, and is the largest one observed so far between the possible diastereomers of trans-dichloro complexes with chiral 2,3,2-tet derivatives.⁶,⁹⁾

The preference of the (R,S) isomer over the (R,R) has been postulated for *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ ion, supposing a significant conformation energy difference between the chair and skew conformation of the central six-membered chelate ring adopted, respectively, by the (R,S) and (R,R) isomer, though the exact value has not been determined yet.⁵⁾ In line with this assumption, the (R,S) isomer is more stable than the (R,R) isomer for most trans-dichloro complexes with chiral 2,3,2-tet derivatives in spite of the destabilizing factors caused by the axially oriented substituent involved in the (R,S) isomers.⁶⁾ The present observation on the SS-pyht complex also supports a general tendency that metal complexes with six-membered chelate ring in the chair conformation is more favourable than those with the chelate in the skew conformation.

References

1) M. J. Jun and C. F. Liu, *J. Coord. Chem.*, **5**, 1 (1975).

2) The absolute configuration of the coordinated secondary nitrogen centers is indicated with R or S in parentheses.

3) W. A. Freeman, *Inorg. Chem.*, **17**, 2982 (1978).

4) M. Yamaguchi, S. Yamamatsu, T. Furusawa, S. Yano, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **19**, 2010 (1980).

5) H. G. Hamilton and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).

6) M. Saburi, Y. Ishii, S. Obata, M. Yamaguchi, and S. Yoshikawa, *Inorg. Chem.*, in press.

7) G. R. Brubaker and D. W. Johnson, *Inorg. Chem.*, **21**, 2223 (1982).

8) M. Saburi, Y. Yokowo, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **57**, 1235 (1984).

9) M. Goto, T, Makino, M, Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1879 (1976).