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Preparation and Properties of Cobalt(III) Complexes Containing *meso*-1,2-Diphenyl-1,2-ethanediamine

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Synopsis. Two new complexes, [Co(*meso*-dpen)$_3$]$^{3+}$ and [Co(NH$_3$)$_4$ (*meso*-dpen)]$^{3+}$ have been obtained, where *meso*-dpen denotes *meso*(*R*,*S*)-1,2-diphenyl-1,2-ethanediamine. The former is stable in the solid state, but decomposes slowly in solution at room temperature, while the latter is stable in solution.

Williams and Bailar[1] reported that *meso*(*R*,*S*)-1,2-diphenyl-1,2-ethanediamine (dpen) did not form a tris-chelate complex with a cobalt(III) ion, although the corresponding optically active (*R*,*R* or *S*,*S*) dpen complex was easily obtained. A *meso*-dpen chelate ring in the gauche conformation has one axially disposed phenyl group. Such an axial group may cause steric interactions with other ligands in an octahedral complex, and hence the tris-*meso*-dpen complex will be unstable compared with the tris-(*R*,*R* or *S*,*S*)-dpen complex in which both phenyl groups of the ligand can take the equatorial disposition. This note reports the preparation of [Co(*meso*-dpen)$_3$]$^{3+}$ together with *trans*-[CoCl$_2$(*meso*-dpen)$_2$]$^+$ and [Co(NH$_3$)$_4$(*meso*-dpen)]$^{3+}$ and compares their properties with those of the corresponding *S*,*S*-dpen complexes.

Experimental

Ligand. *meso*-1,2-Diphenyl-1,2-ethanediamine (*meso*-dpen) was prepared by the method of Irving and Parkins.[2]

trans-[CoCl$_2$(meso-dpen)$_2$]Cl·3H$_2$O. To a solution of CoCl$_2$·6H$_2$O (0.29 g, 1.2 mmol) in methanol (10 cm^3) was added a solution of *meso*-dpen (0.51 g, 2.4 mmol) in methanol (15 cm^3). The solution was aerated for 4 h at room temperature and then mixed with concd hydrochloric acid (1 cm^3) to yield green crystals. After standing the mixture overnight in a refrigerator, the crystals were filtered and recrystallized from methanol. Yield: 45%. Found: C, 51.81; H, 6.17; N, 8.90%. Calcd for $CoC_{28}H_{38}N_4Cl_3O_3$=*trans*-[CoCl$_2$(*meso*-dpen)$_2$]Cl·3H$_2$O: C, 52.22; H, 5.95; N, 8.70%.

[Co(meso-dpen)$_3$]Cl$_3$·6H$_2$O. To a solution of *trans*-[CoCl$_2$(*meso*-dpen)$_2$]Cl·3H$_2$O(0.25 g, 0.39 mmol) in methanol (10 cm^3) was added a solution of *meso*-dpen (0.10 g, 0.47 mmol) in methanol (20 cm^3). Orange crystals which formed on standing the resulting solution for 2 days at room temperature were filtered and washed with methanol. Recrystallization was not carried out because of decomposition of the complex. Yield: 31%. Found: C, 55.92; H, 6.15; N, 9.45%. Calcd for $CoC_{42}H_{60}N_6Cl_3O_6$=[Co(*meso*-dpen)$_3$]Cl$_3$·6H$_2$O: C, 55.97; H, 6.71; N, 9.32%.

[Co(NH$_3$)$_4$(meso-dpen)]Cl$_3$·2.5H$_2$O. This complex was prepared from [Co(NH$_3$)$_5$(H$_2$O)](ClO$_4$)$_3$ and *meso*-dpen in dimethyl sulfoxide (DMSO) by a method similar to that for the corresponding (*R*,*R*)-2,4-pentanediamine complex.[3] Yield: 30%. Found: C, 34.34; H, 6.81; N, 17.05%. Calcd for $CoC_{14}H_{33}N_6Cl_3O_{2.5}$=[Co(NH$_3$)$_4$(*meso*-dpen)]Cl$_3$·2.5H$_2$O: C, 34.26; H, 6.78; N, 17.13%.

Measurements. Absorption spectra were recorded on a Hitachi 323 spectrophotometer. FT ^{13}C-NMR spectra were obtained in DMSO at 15.04 MHz on a JEOL FX-60 spectrometer using dioxane as an external reference, the chemical shift of which is at 67.6 ppm downfield from TMS sealed in an external capillary.

Results and Discussion

Williams and Bailar[1] prepared *trans*-[CoCl$_2$(dpen)$_2$]$^+$ by oxidizing a mixture of the diamine and CoCl$_2$·6H$_2$O (molar ratio of 2: 1) in ethanol with H$_2$O$_2$. They found that the *S*,*S*-dpen complex was prepared easily in good yield (62%), while the *meso*-dpen one was formed in very poor yield (*ca.* 1%). They also attempted to prepare [Co(dpen)$_3$]$^{3+}$ from the diamine and CoCl$_2$·6H$_2$O (molar ratio of 4: 1) by a similar method. The [Co(*S*,*S*-dpen)$_3$]$^{3+}$ complex was obtained in good yield (81%), but the products from the *meso*-dpen were *trans*-[CoCl$_2$(*meso*-dpen)$_2$]$^+$ and *trans*-[CoCl(H$_2$O)(*meso*-dpen)$_2$]$^{2+}$. As stated previously, one of the phenyl groups of the *meso*-dpen ligand is forced to take the axial position upon coordination, regardless of the conformation assumed by the chelate ring, δ- or λ-gauche, while the *S*,*S*-dpen ligand should adopt the δ-gauche conformation with both phenyl groups in the equatorial disposition. The axial phenyl group may cause steric interactions with other ligands in a complex, and hence the *meso*-dpen complexes will be less stable than the *S*,*S*-dpen ones.

In the present study, we have obtained *trans*-[CoCl$_2$(*meso*-dpen)$_2$]$^+$ in fairly good yield (45%) by oxidizing the cobalt(II) ions in methanol with air in place of ethanol and H$_2$O$_2$, respectively. By the reaction between this complex and *meso*-dpen in methanol, we have succeeded in preparing [Co(*meso*-dpen)$_3$]$^{3+}$ in 31% yield. It is known that a reaction of a *trans*-dichloro-bis(diamine) complex with a diamine in organic solvents is very useful for obtaining an unstable tris(diamine) complex.[4] The [Co(*meso*-dpen)$_3$]Cl$_3$·6H$_2$O complex isolated is highly soluble in *N*,*N*-dimethylformamide (DMF) and DMSO, but hardly soluble in water, methanol, and ethanol. In the former solvents, the complex decomposes gradually to give unknown brown precipitate.

The [Co(NH$_3$)$_4$(*meso*-dpen)]$^{3+}$ complex was prepared by the reaction between [Co(NH$_3$)$_5$(H$_2$O)]$^{3+}$ and *meso*-dpen in DMSO. Such a reaction is also known to be very useful for obtaining tetraammine complexes containing a diamine.[3] The complex is stable in water, methanol, ethanol, DMF, and DMSO.

Yano *et al.*[5] suggested by PMR study of [Pt(en)(*meso*-dpen)]Cl$_2$ (en=ethylenediamine) that the *meso*-dpen chelate ring changes its conformation ($\delta \rightleftharpoons \lambda$-gauche) rapidly on the NMR time scale in solution at room

Table. Data of the first absorption bands

Complex	$\tilde{\nu}$/cm^{-1} (log ε)	Solvent	Reference
trans-[CoCl$_2$(*meso*-dpen)$_2$]$^+$	16180 (1.67) 21690 (1.68)	b	This work
trans-[CoCl$_2$(*S,S*-dpen)$_2$]$^+$	16500 (1.70) 22980 (1.78)	b	7)
[Co(NH$_3$)$_4$(*meso*-dpen)]$^{3+}$	21100 (1.87)	a	This work
[Co(NH$_3$)$_4$(*S,S*-dpen)]$^{3+}$	21280 (1.92)	a	8)
[Co(*meso*-dpen)$_3$]$^{3+}$	20900 (2.20)	c	This work
Λ(*lel*$_3$)-[Co(*S,S*-dpen)$_3$]$^{3+}$	21300 (2.13)$^{a)}$	b	9)
trans-[CoCl$_2$(*meso*-2,3-bn)$_2$]$^+$	16180 (1.60) 21900 (1.49)	b	6)
trans-[CoCl$_2$(*S,S*-2,3-bn)$_2$]$^+$	16370 (1.62) 22520 (1.52)	b	6)
[Co(NH$_3$)$_4$(*meso*-2,3-bn)]$^{3+}$	21100 (1.86)	a	6)
[Co(NH$_3$)$_4$(*S,S*-2,3-bn)]$^{3+}$	21230 (1.84)	a	6)
fac-[Co(*meso*-2,3-bn)$_3$]$^{3+}$	21100 (2.03)	a	10)
Λ(*lel*$_3$)-[Co(*S,S*-2,3-bn)$_3$]$^{3+}$	21500 (2.00)	a	6)

a) Taken from the figure in the text. Solvent, a: water, b: methanol c: DMSO.

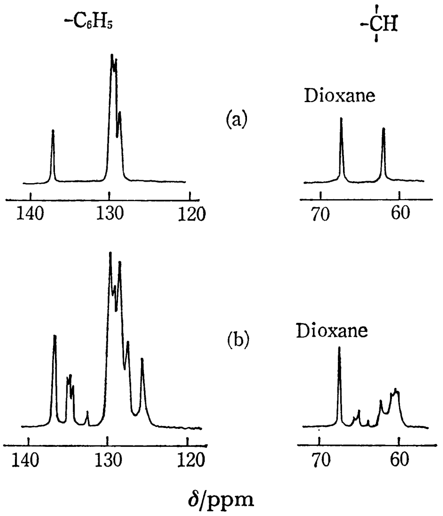

Fig. Proton-decoupled ^{13}C-NMR(15.04 MHz) spectra of (a) [Co(NH$_3$)$_4$(*meso*-dpen)]Cl$_3$·2.5H$_2$O and (b) [Co-*meso*-dpen)$_3$]Cl$_3$·6H$_2$O in DMSO.

temperature. In the present study, we have utilized ^{13}C-NMR spectroscopy. The spectrum of [Co(NH$_3$)$_4$-(*meso*-dpen)]Cl$_3$·2.5H$_2$O gives one and four resonances for the methine and the phenyl carbons, respectively, indicating rapid inversion of the chelate ring (Fig. a).

The [Co(*meso*-dpen)$_3$]$^{3+}$ complex ion can give two geometric isomers, *mer* and *fac*, by the alignment of asymmetric carbons (*R* and *S*). If the conformational change were also rapid in this complex, the *mer*(C$_1$ symmetry) isomer would show six and twenty-four signals for the methine and the phenyl carbons, respectively, while the *fac*(C$_3$ symmetry) isomer two and eight signals for the corresponding carbons, respectively. The appearance of the multiplet due to the methine carbons indicates the presence of the *mer* isomer (Fig. b). Although the presence of the *fac* isomer is not clear, the complex seems to be a mixture of the *mer* and *fac* isomers, since the less crowded *fac* isomer should be formed to a greater extent than the more crowded *mer* one. Attempts to separate the geometric isomers by column chromatography were unsuccessful because of decomposition of the complex.

The absorption spectral data for the dpen complexes are listed in the Table. The first absorption maxima of the *meso*-dpen complexes shift to longer wavelengths compared with those of the corresponding *S,S*-dpen complexes. The shift may be caused by the crowded and strained structure due to the axial phenyl group of the *meso*-dpen ligand. A similar shift is observed for the 2,3-butanediamine (2,3-bn) complexes, as shown in the Table. The *meso*- and *S,S*-2,3-bn chelate rings have similar structures to those of the *meso*- and *S,S*-dpen ligands, respectively. The differences in the first absorption maxima between the *meso*- and *S,S*-dpen complexes are larger than those between the corresponding 2,3-bn complexes. This result may be correlated with larger steric interactions caused by the more bulky phenyl group than the methyl one.

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