SHORT COMMUNICATIONS

Stereochemical Study of *N,N'*-Dimethylethylenediamine Cobalt(III) Complex *trans*-Dinitrobis(*N,N'*-dimethylethylenediamine)cobalt(III) Ion

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(Received May 29, 1971)

Recently Buckingham *et al.*[1] prepared *trans,trans*-$[CoX_2(N\text{-Meen})_2]^+$ ($X=Cl^-$, NO_2^-; *N*-Meen=*N*-methylethylenediamine) ion whose *N*-methyl groups are *trans* to each other. They obtained three isomers of the meso (R,S) and the optically active (R,R and S,S) forms, where R and S refer to the chirality of the coordinated nitrogen centers. In these complexes, the nonbonding interactions between the N–CH_3 groups and the N–H groups do not seem to be so large as to exclude their sterically crowded meso isomer. However, in the case of *trans*-$[CoX_2(N,N'\text{-Me}_2\text{en})_2]^+$, where *N,N'*-$Me_2$en denotes *N,N'*-dimethylethylenediamine, strong nonbonding interactions can be expected to be present between the N–CH_3 groups on neighboring ligand molecules. On the other hand, seven isomers are theoretically possible for *trans*-$[CoX_2(N,N'\text{-Me}_2\text{en})_2]^+$ complex owing to the asymmetry of coordinated nitrogen centers, three meso {(RR,SS), (RS,RS), and (RS,SR)} and four optically active {(RR,SR) and (SS,SR), and (RR,RR) and (SS,SS)} forms. Of these, the last two forms in which all four *N*-methyl groups have an equatorial arrangement are likely to be the most favorable sterically.

In order to see the presence of isomerism in the complexes of such type, we investigated *trans*-$[Co(NO_2)_2(N,N'\text{-Me}_2\text{en})_2]I$ as follows.

$Na_3[Co(NO_2)_6]$ (22 g) was allowed to react with a refluxing solution of *N,N'*-Me_2en (10 g) and water for 2 hr. Addition of sodium iodide, then, gave brown crystals of the pure compound. Found: C, 21.06; H, 5.14; N, 18.58%. Calcd for $C_8H_{24}N_6O_4CoI$: C, 21.16; H, 5.33; N, 18.51%. The PMR spectrum of the product in D_2O showed one *N*-methyl singlet (2.2 ppm) and a methylene multiplet (2.4—3.2 ppm) which was regarded to be of AA'BB' pattern by means of iterative analysis.[2] It was shown by PMR study[2] that in aqueous solution *N,N'*-Me_2en chelate rings have a similar *gauche* conformation (Fig. 1). The fact that only one PMR signal of the *N*-methyl group is observed suggests that this complex is assigned to *trans*-$[Co(NO_2)_2(N,N'\text{-Me}_2\text{en})_2]^+$ composed of the most preferred isomers in optically active form. To examine whether it was the unique product under the given conditions, the reaction product of $Na_3[Co(NO_2)_6]$ and *N,N'*-Me_2en was evaporated to dryness and its PMR spectrum was measured in D_2O. An *N*-methyl singlet (2.2 ppm) and a methylene multiplet (2.4—3.2 ppm) were observed. The iodide was successfuly resolved into its optical forms with silver α-bromo-π-camphorsulfonate. It is very likely that all four asymmetric nitrogen atoms in $(-)_{589}$-*trans*-$[Co(NO_2)_2(N,N'\text{-Me}_2\text{-en})_2]^+$ are of *S*-configuration in view of their CD spectrum as compared with those of some *trans*-dinitrobis(*N*-methylated diamine)cobalt(III) ions which have asymmetric nitrogen atoms with a known configuration.[3]

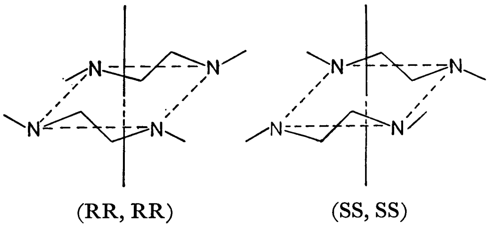

Fig. 1

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[1] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 3428 (1967).

[2] S. Yano, M. Saburi, and Y. Koike, unpublished.

[3] M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).