CHEMISTRY LETTERS, pp. 319-322, 1980.

STRUCTURE AND ABSOLUTE CONFIGURATION OF TRANS(O)-N,N'-ETHYLENEBIS-(S-METHYL-L-CYSTEINATO)COBALT(III) PERCHLORATE

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The crystal structure of trans(O)-N,N'-ethylenebis(S-methyl-L-cysteinato)cobalt(III) perchlorate was determined by X-ray diffraction study. The structure consists of two kinds of complex cations with asymmetric sulfur atoms of different absolute configuration (S(S)S(S) and R(S)S(S)). The differences between the configurations of the sulfur atoms in crystal and those in solution are discussed.

Trans(O)-N,N'-ethylenebis(S-methyl-L-cysteinato)cobalt(III) perchlorate, trans(O)-[Co(R,R-ebsmc)]ClO_4, was isolated in the course of our studies on stereochemistry of cobalt(III) complexes with sulfur-containing aminocarboxylates.[1,2] When the R,R-ebsmc containing two chiral centers, R(C)R(C), coordinates to cobalt(III) ion as a sexidentate ligand, two frameworks, trans(O)-R(N)R(N) and trans(S)-S(N)S(N), are possible and the former is dominant. The three isomers, S(S)S(S), R(S)S(S), and R(S)R(S), due to the two chiral sulfur atoms of the coordinated R,R-ebsmc are possible for both of the complexes. This letter is concerned with the X-ray diffraction studies of the trans(O)-R(N)R(N)-[Co(R,R-ebsmc)]ClO_4 and with the ^{13}C NMR spectrum in D_2O solution.

The sexidentate ligand, R,R-H_2ebsmc, was prepared from S-methyl-L-cysteine and 1,2-dibromoethane by the method analogous to that used in the preparation of S,S-ethylenediaminedisuccinic acid.[3] Seven tenths grams (2.35×10^{-3} mol) of R,R-H_2ebsmc was suspended in 50 cm^3 of hot water (70 °C). To the solution was added 0.55 g (2.35×10^{-3} mol) of $CoCl_2 \cdot 6H_2O$ and 1.5 g of PbO_2. The mixture was warmed at about 70 °C for about 20 min, whereupon the solution became orange-red. The reaction mixture was cooled, and filtered to remove excess of PbO_2. The orange-red filtrate was poured into an ion-exchange column (5 X 15 cm) containing SP-Sephadex

C-25 resin (Na$^+$ form). After sweeping the column with water, the adsorbed band was eluted with 0.2 mol dm^{-3} aqueous solution of NaClO$_4$. Only one orange-red band was eluted. The eluate was concentrated to 20 cm^3 using a rotary evaporator below 30 °C, and then kept in a refrigerator overnight. The dark-red crystals were collected, washed with ethanol and then ether, and dried in air. The dark-red crystal is orthorhombic with the space group $P2_12_12_1$: a = 9.055, b = 22.123, c = 17.111 Å, and Z = 8. The observed density is 1.77 g cm^{-3} and the calculated one 1.76 g cm^{-3}. The crystal structure determination was based on 2380 independent reflexions collected on an automated four-circle diffractometer (Philips PW 1100) by the θ-2θ scan technique, employing Mo-Kα radiation monochromatized by a graphite crystal. The structure was solved by the direct-methods program MULTAN,4) and the full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms gave an R value of 0.066.

The crystal structure consists of two crystallographically independent complex

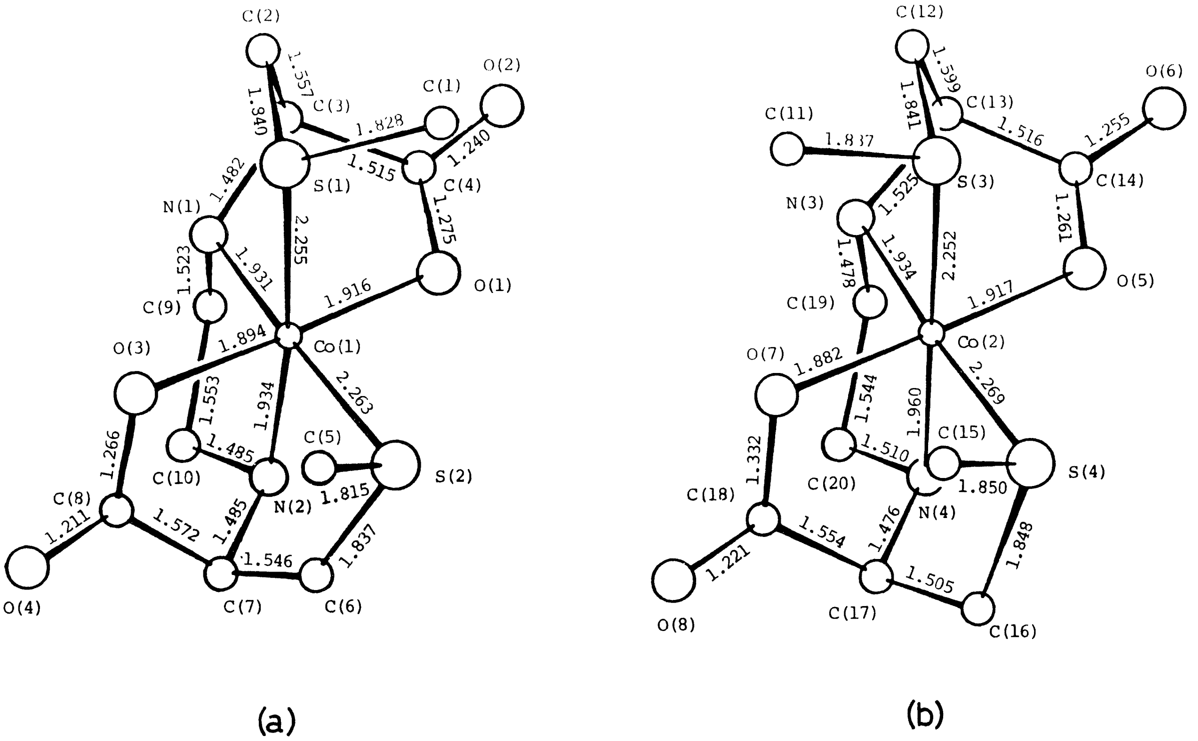

Figure 1. Configuration and bond lengths of trans(O)-[Co(R,R-ebsmc)]$^+$ ion; (a) S(S)S(S) and (b) R(S)S(S) isomers.

cations. Their perspective drawings are shown in Figure 1. The coordinations around cobalt(III) of the two complex cations are approximately octahedral, the R,R-ebsmc ligands being sexidentate. The cobalt atoms are surrounded by two cis sulfur, two cis nitrogen, and two trans oxygen atoms. The absolute configurations of these complex cations were determined from the known configurations of the asymmetric carbon atoms of the ligands. One (a) of the complex cations takes an S(S)S(S) configuration with respect to two sulfur atoms, the other (b) an R(S)S(S) configuration (Figure 1). In the both complex cations, the absolute configurations of the two nitrogen atoms are also determined to be R(N)R(N). The backbone diamine rings of the both complex cations have λ conformation. The S(S)S(S) complex has a pseudo-twofold axis through the Co(1) which bisects the S(1)-S(2) edge of the octahedron, whereas the R(S)S(S) complex does not. The cobalt-ligand bond lengths are all similar to those of recently determined values for a variety of cobalt(III) complexes.5-7) The average Co-S, Co-O, and Co-N bond lengths are 2.26, 1.90, and 1.94 Å, respectively. The bond angles at the cobalt atoms of the both complexes are slightly distorted from their idealized values, that is, cis angles are in the range 82.6-98.5° and trans angles 171.8-177.4°. The angles S(1)-Co(1)-S(2) and S(3)-Co(2)-S(4) are 98.5° and 96.6°, respectively. The values are significantly larger than the normal values, and these deviations may be attributed to the repulsion between methyl groups on the sulfur atoms.

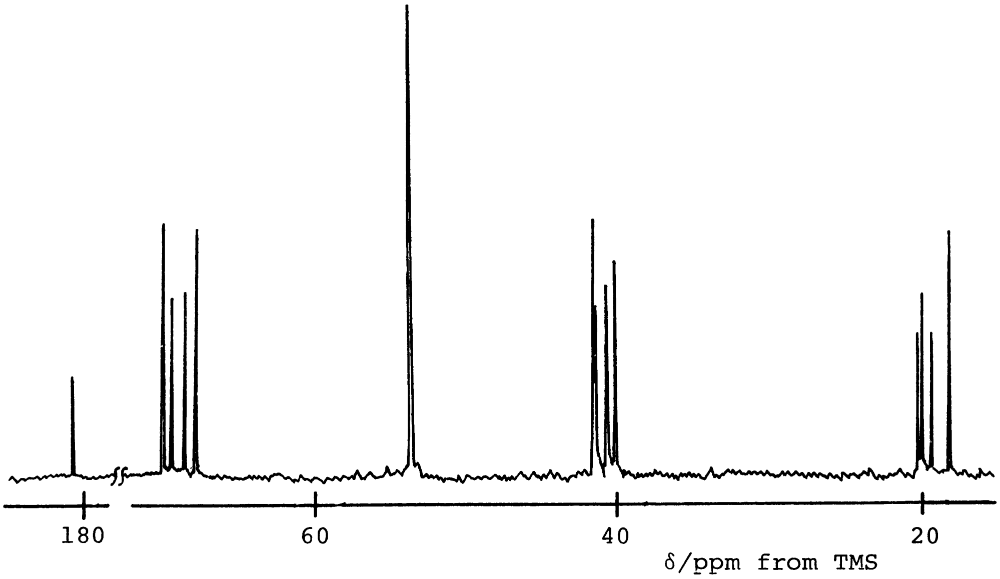

Figure 2. ^{13}C NMR spectrum of trans(O)-[Co(R,R-ebsmc)]$^+$ in D_2O

^{13}C NMR spectrum of trans(O)-[Co(R,R-ebsmc)]ClO_4 was measured in D_2O and is shown in Figure 2. The spectrum shows four peaks due to the S-methyl (18.3-20.3 ppm from TMS), methylene (40.3-41.8 ppm), and methine (68.1-70.3 ppm) carbons, respectively. Benzene (δ = 128.50 ppm downfield from TMS) was used as an external standard. Taking the sulfur atoms into considerations, ^{13}C NMR spectrum of the S(S)S(S) or R(S)R(S) isomer having a twofold axis should show a single peak due to the S-methyl, methylene, and methine carbons, respectively. On the other hand, the spectrum of the R(S)S(S) isomer should show two peaks. This result indicates that the chiral sulfur atoms in D_2O solution have different configurations from those in crystals and take the S(S)S(S), R(S)S(S), and R(S)R(S). Recently, Jackson and Sargeson reported that the sulfur inversion in the S-bonded thioether-cobalt(III) complexes occurs in aqueous solution.8) The present results also suggest the sulfur inversion in aqueous solution.

The authors thank to Prof. Y. Iitaka, the University of Tokyo, for his help in collection of X-ray data.

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(Received January 11, 1980)