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CRYSTAL STRUCTURE OF (DIETHYLENETRIAMINE) (L-PENICILLAMINATO)COBALT(III) CHLORIDE

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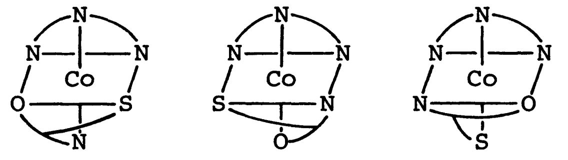
Three isomers of (diethylenetriamine)(L-penicillaminato)cobalt(III) complex were chromatographically isolated. The crystal structure of the first eluted isomer, trans(N_iN)-[Co(L-pen)(dien)]Cl·H_2O, was determined by X-ray diffraction study. Electronic absorption and circular dichroism spectra of the isomer are also reported.

Three isomers of (diethylenetriamine)(L-penicillaminato)cobalt(III) complex, $[Co(L\text{-}pen)(dien)]^+$, were chromatographically isolated as part of our studies on stereochemistry of cobalt(III) complexes with sulfur-containing aminocarboxylates, where these isomers are designated as trans(N_iN), trans(N_iO) and trans(N_iS) with respect to the coordinated atoms (Fig. 1). The coordinated sulfur atoms of these isomers react stereospecifically with dimethyl sulfate to give the thioether type sulfur with R(S) or S(S) configuration. However, the structural assignments of the present isomers are fairly difficult because of the close resemblance of their spectrochemical behavior. We attempted to determine the crystal structure of the first eluted isomer by the X-ray diffraction method, because electronic absorption and circular dichroism (CD) spectra of the isomer are available for the assignments of the remaining two isomers. This letter is concerned with the X-ray diffraction



trans(N_iN) trans(N_iO) trans(N_iS)

Fig. 1. Three possible isomers of [Co(L-pen)(dien)]Cl complex.

study of [Co(L-pen)(dien)]Cl·H_2O and with its electronic absorption and CD spectra.

The complex was prepared by a modified method in the literatures.[1,2] To a solution of 5.4 g of [$CoCl_3$(dien)][3] in 100 cm^3 of water was added a solution of 5.1 g of silver nitrate in 20 cm^3 of water, and the precipitated silver chloride was filtered off. After nitrogen gas was vigorously bubbled into the filtrate for 30 min, an aqueous solution containing 3.0 g of L-penicillamine was added to it. The nitrogen gas was constantly bubbled into the mixture at room temperature for about 20 hours. After the reaction mixture was poured into a column (30 X 1000 mm) containing strong-acid cation exchange resin (Dowex 50WX8), the column was swept with water. When the adsorbed band was eluted with 0.075 mol dm^{-3} aqueous solution of NaCl, the three brown bands were eluted. The first eluate was concentrated using a rotary evaporator below 15°C. The deposited NaCl was filtered off. To the filtrate was added a large amount of ethanol-acetone (1:3) mixture and then the solution kept in a refrigerator overnight. The dark-brown needle crystals appeared were collected by filtration. The remaining two isomers, trans(N_iO) and trans(N_iS), were also isolated by the same procedure as that for the isomer from the first eluate. It is found that each of three isomers gave a corresponding isomer of (diethylenetriamine)(S-methyl-L-penicillaminato)cobalt(III) chloride, [Co(L-smp)-

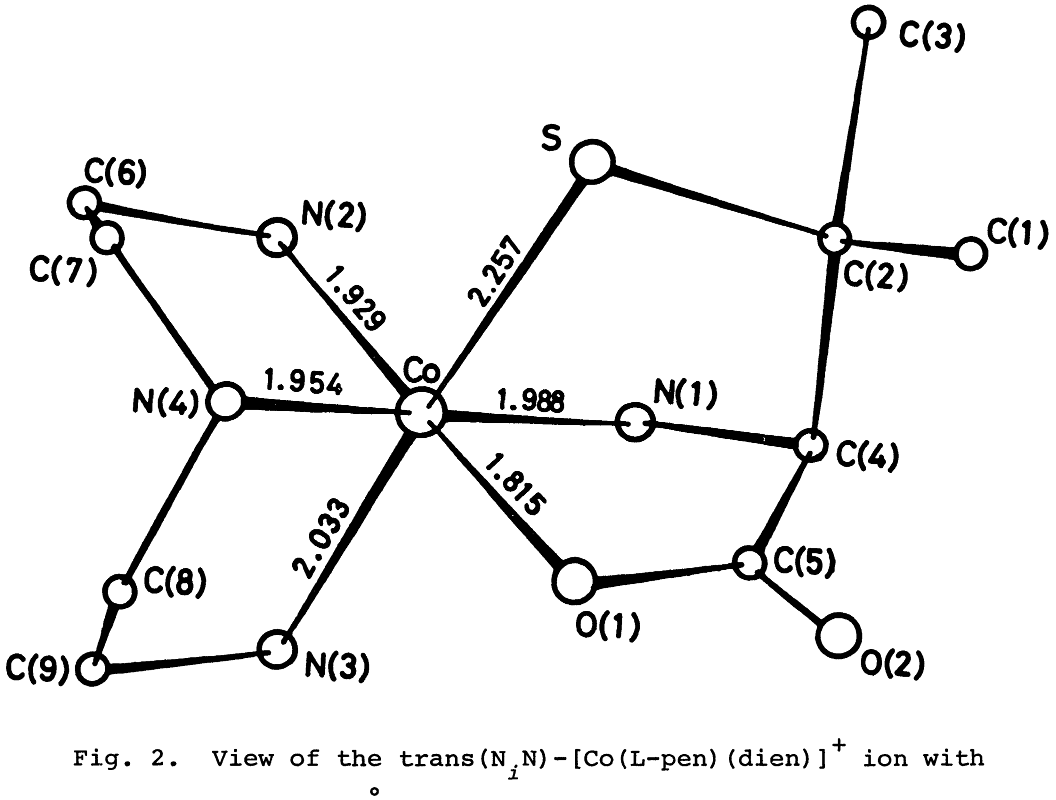


Fig. 2. View of the trans(N_iN)-[Co(L-pen)(dien)]$^+$ ion with distances (Å) around the metal.

(dien)]Cl_2, by methylation in aqueous solution of dimethyl sulfate.[4)] The dark-brown crystal from the first eluate is hexagonal with the space group $P6_1$; a = 21.035 (5), c = 6.459 (3) Å, and Z = 6. The observed density is 1.49 g cm^{-3} and the calculated one 1.46 g cm^{-3}. The crystal structure determination was based on 707 independent non-zero reflections collected on a Rigaku-Denki automatic four circle diffractometer (AFC-5) by the ω-2θ scan technique, employing Mo-Kα radiation monochromatized by a graphite crystal. The structure was solved with the heavy atom method, 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 0.094.

A perspective drawing of the present complex cation is shown in Fig. 2. The L-penicillaminate and diethylenetriamine coordinate facially to the cobalt atom as terdentate ligands and the nitrogen atom of the L-penicillaminate occupies the trans position of the imino nitrogen of the diethylenetriamine. The absolute configuration of the isomer in crystal was confirmed on the basis of the configuration of the asymmetric carbon atom in the L-penicillaminate ligand. The diamine chelate rings in the diethylenetriamine took reasonable conformations[5)], δ form for N(3)-C(9)-C(8)-N(4) and λ one for N(2)-C(6)-C(7)-N(4). The bond lengths and angles are similar to those for the cobalt(III) complexes with diethylenetriamine and/or sulfur-containing aminocarboxylates.[5-9)] The averages of the cobalt-ligand bond lengths are 2.26 Å for Co-S, 1.82 Å for Co-O and 1.98 Å for Co-N. Of the bond lengths 2.033 Å for Co-N(3), which occupies the trans position to the sulfur atom, is the longest of all the Co-N bonds. This fact suggests the trans effect due to the coordinated sulfur atom.[10)]

The electronic absorption and CD spectra of the trans(N_iN)-[Co(L-pen)(dien)]$^+$ are shown in Fig. 3, in which the absorption and CD curves of the corresponding trans(N_iN)-[Co(L-smp)(dien)]$^{2+}$ is also plotted for comparison. The spectral behavior of the L-pen complex in the first absorption band region is considerably different from that of the L-smp complex. However, these complexes show the similar CD pattern in the corresponding region. It seems to suggest, therefore, that the L-smp complex has also trans(N_iN) configuration. The sulfur-to-metal charge transfer band in these complexes as well as the cobalt(III) complexes with the aminocarboxylates containing the thioether[11)] and thiolate[4)] are observed at about 34.5 X 10^3 cm^{-1}. On the basis of the assignment for the first eluted isomer, the configurations of the remaining two isomers will be elucidated from their electronic absorption and CD spectra.

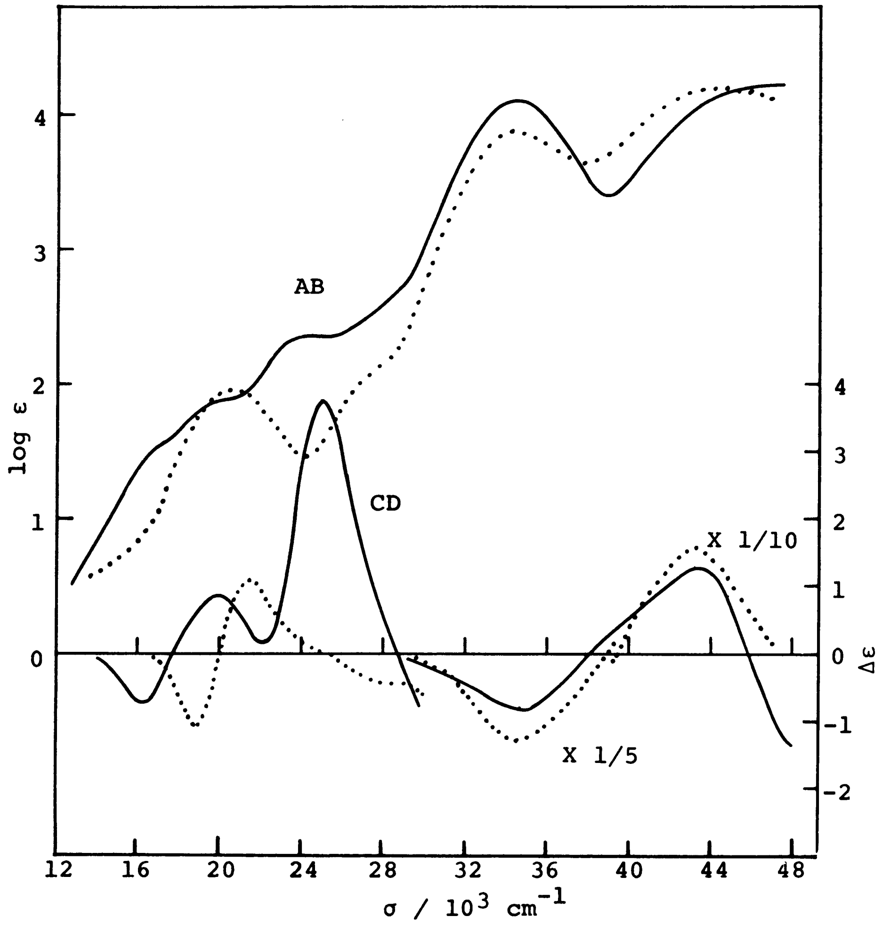


Fig. 3. Absorption and CD spectra of trans(N$_i$N)-[Co(L-pen)(dien)]$^+$ (————) and trans(N$_i$N)-[Co(L-smp)(dien)]$^{2+}$ (-------).

REFERENCES

1) J. L. Legg and D. W. Cooke, Inorg. Chem., 5, 594 (1966).
2) K. Okamoto, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Jpn., 48, 2456 (1975).
3) P. H. Crayton, Inorg. Synth., 7, 207 (1963).
4) K. Wakayama, K. Okamoto, and J. Hidaka, Presented at the 30th Symposium on the Coordination Chemistry, Tokyo, Japan, 1980, Abstracts No 1a14.
5) M. Konno, F. Marumo, and Y. Saito, Acta Cryst., B29, 739 (1973).
6) T. Isago, K. Okamoto, M. Ohmasa, and J. Hidaka, Chem. Lett., 1980, 319.
7) P. de Meester and D. J. Hodgson, J. Chem. Soc. Dalton Trans., 1976, 618.
8) R. C. Elder, G. J. Kennard, M. D. Payne, and E. Deutsch, Inorg. Chem., 17, 1296 (1978).
9) R. J. Magee, W. Mazurek, M. J. O'Connor, and A. T. Phillip, Aust. J. Chem., 27, 1629 (1974).
10) R. C. Elder, M. J. Heeg, M. D. Payne, M. Trkula, and E. Deutsch, Inorg. Chem., 17, 431 (1978).
11) T. Isago, K. Igi, and J. Hidaka, Bull. Chem. Soc. Jpn., 52, 407 (1979).

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