CHEMISTRY LETTERS, pp. 1941-1942, 1982.

SPONTANEOUS RESOLUTION AND CRYSTAL STRUCTURE OF BIS(ETHYLENEDIAMINE)(2-SELENINATOETHYLAMINE)COBALT(III) NITRATE

Ken-ichi OKAMOTO,* Takumi KONNO, Masayo NOMOTO,
Hisahiko EINAGA,** and Jinsai HIDAKA
Department of Chemistry, University of Tsukuba, Ibaraki 305
** Institute of Materials Science, University of Tsukuba, Ibaraki 305

The absolute configuration of the spontaneously resolved title compound was determined by X-ray diffraction study. The employed crystal which showed a negative CD value at 500 nm has Δ configuration. The 2-seleninatoethylamine is bound to the cobalt atom by the N and O atoms and the asymmetric selenium atom takes S configuration. The six-membered chelate ring formed takes a chair conformation.

2-Seleninatoethylamine (siea) in the title complex cation, which was derived from the cobalt(III) complex of the selenium-bonded 2-selenolatoethylamine (sea),1) acts as a bidentate and it is possible to take either of the two coordination modes, siea-N,Se and siea-N,O. However, there has been no real evidence for the coordination mode of the seleninato complex except for the anticipation on the basis of the absorption spectra of the related sulfinato complexes.2-4) This letter deals with the preparation and spontaneous resolution of $[Co(siea)(en)_2](NO_3)_2$, and also with the absolute configuration of the $(-)^{CD}_{500}$ isomer determined by X-ray diffraction. This is the first example of the seleninato(N,O) coordinated to cobalt(III) ion.

The nitrate salt of $[Co(siea)(en)_2]^{2+}$ was prepared by a similar procedure to that used for $(+)^{CD}_{500}$-$[Co(siea)(en)_2]^{2+}$,2) using the nitrate salt instead of the perchlorate one. The spontaneous resolution of the nitrate salt was observed for the needle crystals prepared as follows; the racemic nitrate was dissolved in a small amount of water at room temperature and when the solution was kept in a refrigerator for a day, the spontaneously resolved red complex was obtained as fairly large needle crystals.

The red needle crystals are monoclinic with space group $P2_1$; a = 9.572(4), b = 10.410(3), c = 8.838(5) Å, β = 115.35(3)°, V = 795.9(6) $Å^3$, and Z = 2. The observed density is 1.90 g cm^{-3} and the calculated one 1.91 g cm^{-3}. The crystal structure determination was based on independent 2358 reflections with $|Fo| > 3\sigma(|Fo|)$ collected on a Rigaku-denki four circle diffractometer (AFC-5) by the ω-2θ scan technique up to 2θ = 60°, employing graphite-monochromated Mo Kα radiation. The structure was solved with the heavy atom method and refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms (program RFINE by L. W. Finger, which was modified by H. Horiuchi (1979), was used). The final residual values were R = 0.036 and Rw = 0.049, respectively.

The absolute configuration was determined by anomalous scattering technique.

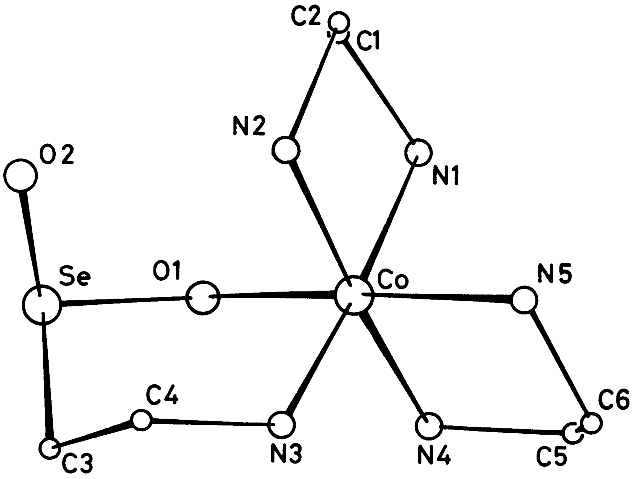

Fig. 1. Perspective view of $(-)^{CD}_{500}$-$[Co(siea)(en)_2]^{2+}$ ion.

The atomic scattering factors for all the non-hydrogen atoms were taken from literature.5) When the refinements were carried out by use of a set of the atomic parameters containing the Δ configuration of the complex cation, the residual values converged to R = 0.035 and Rw = 0.046, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the Λ configuration) resulted in the residual values of R = 0.041 and Rw = 0.055, respectively. These facts indicate that the former is probably the correct choice, namely, the complex cation has the Δ configuration. The crystal, which was used for the X-ray intensity measurement, showed the enantiomeric CD curve for that of $(+)^{CD}_{500}$-$[Co(siea)(en)_2]^{2+}$ derived from $(+)^{CD}_{500}$-$[Co(sea)(en)_2]^{2+}$.2) This is in line with the result that the $(+)^{CD}_{500}$ isomer of the siea complex has been assigned to the Λ configuration from a comparison with the CD spectrum of Λ-$[Co(mea)(en)_2]^{3+}$ (mea = 2-(methylthio)ethylamine).2,6)

A perspective drawing of the present complex cation is shown in Fig. 1. The 2-seleninatoethylamine coordinates to cobalt atom with the nitrogen and oxygen atoms instead of the nitrogen and selenium ones in the starting complex, $[Co(sea)(en)_2]^{2+}$.1) The six-membered chelate ring of the coordinated siea ligand takes a chair conformation. The asymmetric selenium atom in Δ-$(-)^{CD}_{500}$-$[Co(siea)(en)_2]^{2+}$ takes the S configuration as shown in Fig. 1. Both of the ethylenediamine chelate rings take reasonable conformations, that is, an asymmetric gauche form with the λ conformation. The bond lengths and angles are similar to those for the cobalt(III) complexes with ethylenediamine and/or selenium-containing ligand.1,3) The selenium-oxygen bond lengths, Se-O1 and Se-O2, are 1.698 and 1.680 Å, respectively. They are longer than those of the sulfur-oxygen ones (1.456 and 1.476 Å) in the bis(ethylenediamine)(2-sulfinatoethylamine-N,S)cobalt(III) perchlorate nitrate.3)

References

1) C. A. Stein, P. E. Ellis, Jr., R. C. Elder, and E. Deutsch, Inorg. Chem., 15, 1618 (1976).

2) T. Konno, K. Okamoto, and J. Hidaka, Chem. Lett., 1982, 535.

3) B. A. Lange, K. Libson, E. Deutsch, and R. C. Elder, Inorg. Chem., 15, 2985 (1976).

4) H. Mäche, V. Houlding, and A. W. Adamson, J. Am. Chem. Soc., 102, 6888 (1980).

5) "International Tables for X-ray Crystallography". The Kynoch Press, Birmingham (1974), Vol. IV.

6) K. Yamanari, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Jpn., 50, 2299 (1977).

(Received October 16, 1982)