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The Crystal Structure, Absolute Configuration and Circular Dichroism of $(-)^{CD}_{630}$- and $(+)^{CD}_{630}$-cis-Bis[2-(2-benzoxazolyl)-phenol-N]dichloroplatinum(II)·ethanol

Akiko FURUHASHI,* Kunihiko ENDO, Akira OUCHI,† and Yoshihiko SAITO††

Department of Chemistry, Aoyama Gakuin University, Morinosato-Aoyama, Atsugi, Kanagawa 243-01

† Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

†† Department of Chemistry, Facalty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223

The crystals of the title complex resolve spontaneously. The enantiomeric crystals were separated under a microscope. They are orthorhombic, space group $P2_12_12_1$. This is a square planar complex with 2Cl in cis-positions. The ligand acts as a unidentate with its N atom. The absolute configuration was correlated with the CD spectrum in microcrystalline state.

Recently the structures of platinum complexes were intensively studied concerning their catalytic and/or antitumour effects.$^{1-3)}$ The authors have obtained the crystals of the title complex. They resolve spontaneously and the enantiomeric crystals can be easily identified under a microscope, which could be separated by hand. The CD spectra were measured in microcrystalline state. The crystal structure and absolute configuration were determined by single crystal X-ray diffraction method.

The crystals were grown as follows: The solution of platinum(IV) chloride pentahydrate ($\underset{\sim}{1}$) (1 g, 2 mmol, in 15 cm^3 of ethanol) or hydrogen hexachloroplatinate(IV) hexahydrate ($\underset{\sim}{2}$) (1.5 g, 2 mmol, in 15 cm^3 of ethanol) and 2-(2-benzoxazolyl)phenol (Hbxp) (1.5 g, 7 mmol, in 300 cm^3 of ethanol) were mixed, stirred, and the mixture was left standing at room temperature for one month or longer, and the yellow crystals precipitated. The product was separated, washed with a small amount of ethanol, and dried in vacuo over silica gel for one night. Yield: 0.38 g (22%) from $\underset{\sim}{1}$, and 0.57 g (40%) from $\underset{\sim}{2}$. Anal. Found; C, 45.77; H, 3.26; N, 3.76; Cl, 9.67%. Calcd for $PtC_{28}H_{24}N_2O_5Cl_2$: C, 45.75; H, 3.00; N, 3.81; Cl, 9.67%.

Figure 1 illustrates well-formed crystal shapes. The hemihedral facets are only found on alternate corners of the crystal. They belong to class 222. The enantiomorphous forms can be easily identified under a microscope from the arrangement of the facets. The two forms are tentatively called r and l, respectively. They were separated by hand. The CD spectra were measured by JASCO J-600 spectropolarimeter in microcrystalline state, because the complex is insoluble in any solvent except being decomposed. The KBr disks were prepared as described earlier.4) The CD spectra over the region 400-700 nm are shown in Fig. 2.

The pale yellow r and l crystals were shaped into spheres of diameter, ca. 0.40 mm. Accurate cell dimensions were determined on a Rigaku AFC-6A diffractometer on the basis of 25 independent reflections ($20<2\theta<27°$). They are orthorhombic, space group $P2_12_12_1$, F.W.=734.50, a=10.346(4), b=31.20(6), c=8.353(4) Å, U=2695(6) $Å^3$, Z=4, D_m= 1.81(3), D_x=1.81 g cm^{-3}, μ(Mo Kα)=57.20 cm^{-1}. The intensity data of the r- and l-crystals were collected with graphite monochromatized Mo Kα radiation(λ= 0.71073 Å). The ω-scan technique was employed over the scan range 3—60° (2θ), scan rate and scan width being 4° min^{-1} and 1.15°(in θ), respectively. The intensities were corrected for Lorentz and polarization factors as well as adsorption. Of the 3246(r), and 4496(l) independent unique reflections observed, 2873(r) and 3622(l) reflections with $|F_o|>3\sigma(|F_o|)$ were used for structure refinement, respectively. The structure r was solved by the heavy atom method. The positional and thermal parameters were refined by means of block-diagonal least-squares method. At the final stage, all the non-hydrogen atoms were refined anisotropically, the final R and R_w values became 0.036 and 0.043, respectively, while those of the enantiomeric structure converged to 0.057 and 0.071, respectively. To make sure, the structure of l was also refined. The enantiomeric set of the final coordinates for the r-crystal was used as a starting set. The final R and R_w were reduced to 0.047 and 0.051, respectively. The enantiomeric structure gave R and R_w of 0.063 and 0.074, respectively. It was also confirmed that the intensity relations between 12 selected Bijvoet pairs of r and l

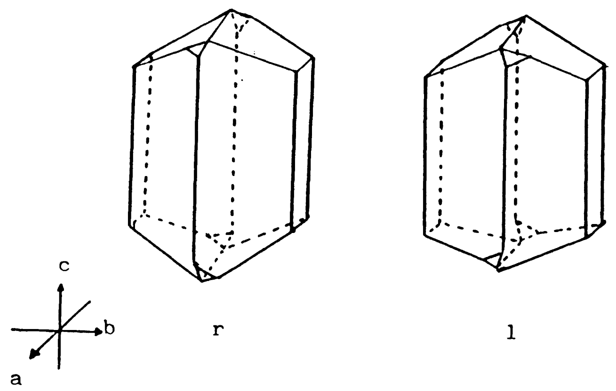

Fig. 1. Crystal shapes of (1) r and (2) l.

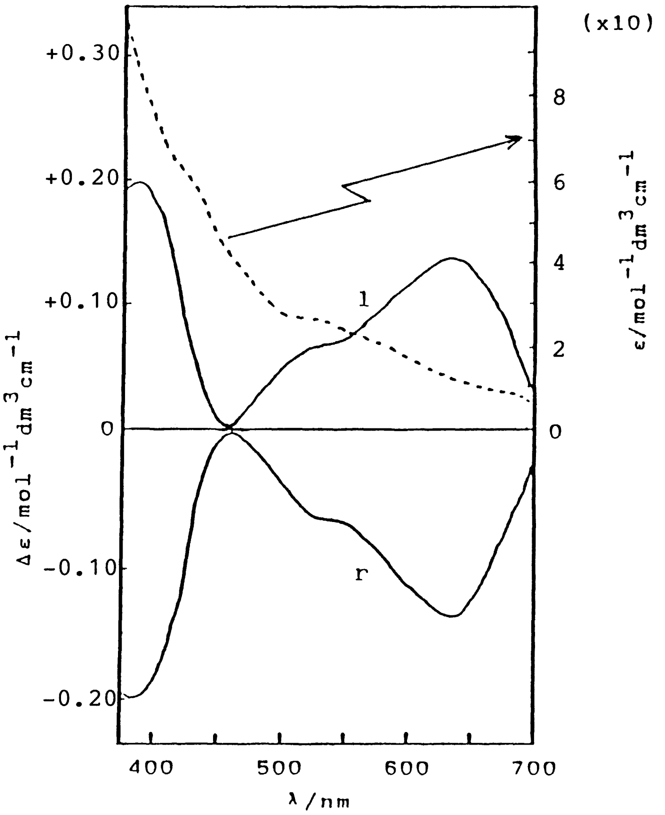

Fig. 2. The CD and KBr disk absorption spectra(broken line) of the complex.

crystals are inverted. All the calculations were carried out on a HITAC M-682H computer at the Computer Center of the University of Tokyo.

Figure 3 represnts exactly the absolute configuration of the r complex viewed on the coordination plane.

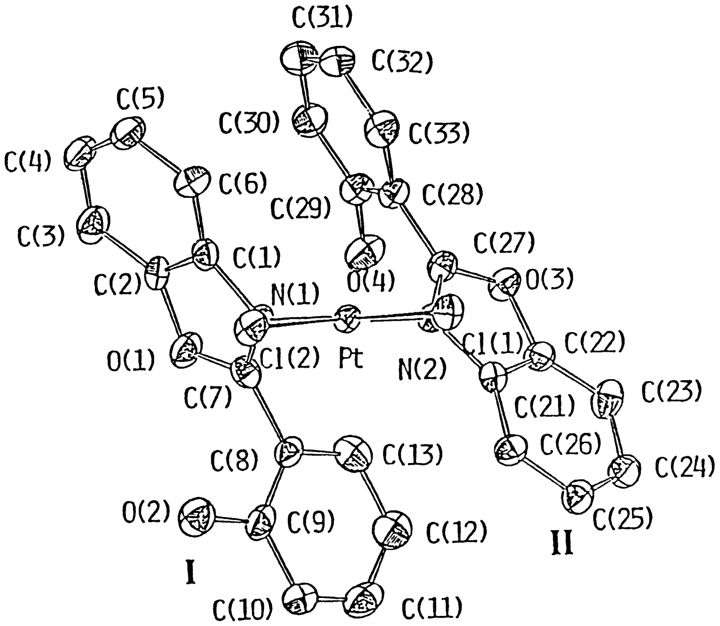

Fig. 3. The r complex viewed on the coordination plane.

The crystal structure is composed of discrete [$PtCl_2(bxp)_2$] and C_2H_5OH molecules, the latter being held by hydrogen bonds. The title complex exhibits a square-planar geometry with the two Cl atoms in cis-positions. The coordination plane is quite planar, the average positional deviation being 0.043 Å. The Pt-Cl distances are 2.298(3) and 2.279(3) Å. The two organic ligands, bxp I and II (see Fig. 3) act as a unidentate and are coordinated to the Pt atom with their N atoms of the oxazol ring (Pt-N: 2.024(8) and 1.993(8) Å). These values are not much different from the corresponding bond lengths of other square-planar complexes.[5-8] As seen from Fig. 3, the two benzoxazolyl moieties are approximately related by a twofold axis through the Pt atom and the center of the two ligating N atoms. However, the dihedral angles between the benzoxazolyl ring and the phenol ring are different. In bxp I, the dihedral angle is 87.7°, while it is 59.0° in bxp II.

Projection of the unit cell along the a-axis is presented in Fig. 4. The ethanol oxygen atom, O(5), is hydrogen bonded to the phenol oxygen atom O(4), and with the Cl atom of the complex shifted by a unit translation along the a-axis, where O(5)$\cdots$O(4)=2.615(13), O(5)$\cdots$Cl(2^{i})=3.307(12) Å (i; 1+x, y, z), and O(4)$\cdots$O(5)$\cdots$Cl(2^{i})=118.1(4)°. There exists another hydrogen bond between Cl(1) and the phenol oxygen atom of the complex next to the c-axis direction, O(2^{ii}) (ii; x, y, 1+z), where Cl(1)$\cdots$O(2^{ii})=3.142(9) Å, and Cl(1)$\cdots$O(2^{ii})$\cdots$C(9^{ii})=119.5(6)°. These hydrogen bonds are shown by broken lines in Fig. 4.

The CD curves of the r and l crystals are mirror images to each other. The CD of the r crystals show negative peaks at 390, 510, and 630 nm. The optical activity of this complex arises from the dissymmetric special arrangement of the two organic ligands. The interpretation appears to be difficult, unless the CD in the shorter wavelength region is more clarified.

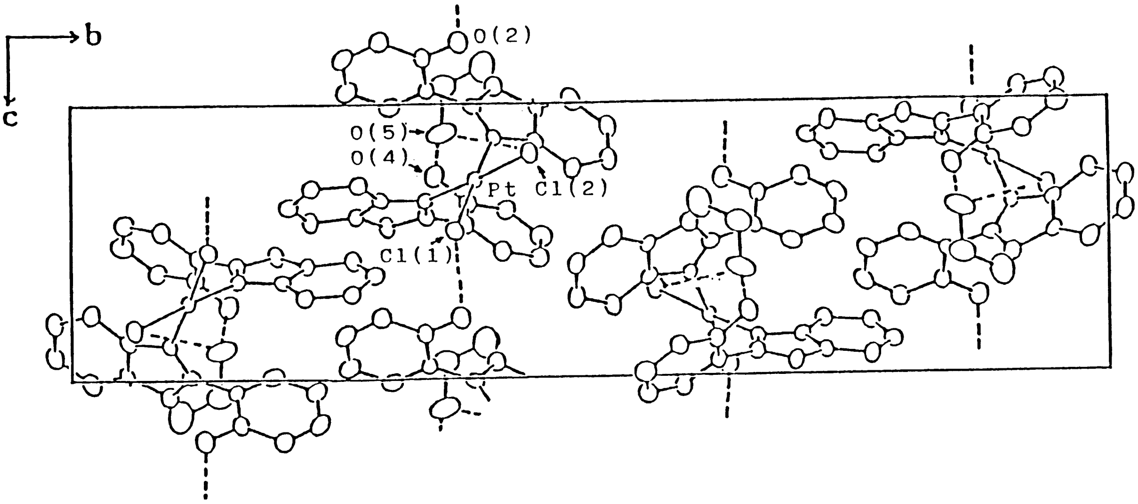

Fig. 4. Projection of the unit cell along the a-axis. Positive a-axis is taken downward.

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References

1) H. E. Howard-Lock and C. J. L. Lock, "Comprehensive Coordination Chemistry," ed by G. Willkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford (1987), Vol. 6, p. 756.
2) A. Spencer, "Comprehensive Coordination Chemistry," ed by G. Willkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford (1987), Vol. 6, pp. 263, 291, 295.
3) A. F. Wells, "Structural Inorganic Chemistry," Clarendon, Oxford (1984), 5 th ed, p. 1232.
4) R. Kuroda and Y. Saito, Bull. Chem. Soc. Jpn., 49, 433 (1976).
5) C. A. L. Filgueras, Acta Crystallogr., Sect. B, 38, 954 (1982).
6) W. N. Hunter, K. W. Muir, and D. W. A. Sharp, Acta Crystallogr., Sect. C, 40, 37 (1980).
7) G. R. Champion and L. G. Marzilli, Acta Crystallogr., Sect. C, 40, 639 (1984).
8) C. J. L. Lock, R. A. Speranzili, and M. Zvagulis, Acta Crystallogr., Sect. B, 36, 1789 (1980).

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