

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

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The crystals of the title complex resolve spontaneously. They are orthorhombic, space group $P2_12_12_1$, $a = 1034.6(4)$, $b = 3120(6)$, $c = 835.3(4)$ pm and $Z = 4$. The final R values of the enantiomers are 0.036 and 0.047 for 2873 and 3622 unique reflections, respectively. This is a square-planar complex with 2 Cl atoms in *cis*-positions. The ligand molecule acts as a unidentate and is coordinated to the Pt atom with its N atom. The average Pt—Cl and Pt—N distances are 228.9(3) and 200.9(8) pm, respectively. The two benzoxazolyl moieties are approximately related by a twofold rotation axis through the central Pt atom and the midpoint of the two N atoms. The optical activity arises from the dissymmetric disposition of the two ligand molecules with respect to the coordination plane. The CD spectra in the range 13,000—40,000 cm^{-1} were measured in KBr matrix. The CD patterns were correlated with the absolute configuration as well as the crystal habit.

INTRODUCTION

Recently, the structures of platinum(II) complexes have been intensively studied concerning their catalytic as well as anticancer effects.¹⁻³ The structures of several square-planar platinum(II) complexes with two halogen atoms in *cis*-positions have been reported.⁴⁻¹⁴ The title ligand, 2-(2-benzoxazolyl)phenol (Hbxp), involves two planar ring systems linked by a single bond. In its cadmium(II)¹⁵, copper(II)¹⁵, and iron(III)¹⁶ complexes, the ligand acts as a bidentate, bxp^- , and both ring systems are almost coplanar. In the course of preparation of the Pt complex, it was accidentally found that excellent crystals exhibiting well defined 222 symmetry were obtained on depositing the mother liquor for a month or more. Figure 1 illustrates well-formed crystal

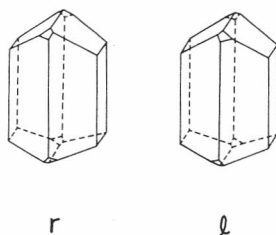


Figure 1. The crystal habits of *cis*-bis[2-(2-benzoxazolyl)-phenol-*N*]dichloroplatinum(II)-ethanol.

shapes. The hemihedral facets are only found on alternate corners of the crystal. The two enantiomorphous forms can be easily identified under a microscope. They are tentatively called *r* and *l*, respectively. X-Ray crystal structure analysis revealed that the organic ligand acts as a unidentate, Hbxp, and the optical activity arises from the dissymmetric arrangement of the two ligands. Moreover, the benzoxazolyl ring and the phenol ring are not coplanar and thus the two ligands are chiral. The absolute configurations of the *r* and *l* forms were determined and the CD spectra were measured in KBr matrix. In this paper, the crystal structure, absolute configuration and the CD spectra of the complex will be reported. A preliminary report has already been published.¹⁷

EXPERIMENTAL

Synthesis of cis-Bis[2-(2-benzoxazolyl)phenol-N]platinum(II) · ethanol

The solution of platinum(IV) chloride pentahydrate (1) (1 g, 2 mmol, in 15 cm³ ethanol) or hydrogen hexachloroplatinate(IV) (2) (1.5 g, 2 mmol, in 15 cm³ ethanol) and 2-(2-benzoxazolyl)phenol (Hbxp) (1.5 g, 7 mmol, in 300 cm³ ethanol) were mixed, stirred, and the mixture was left standing at room temperature for one month or longer. Well-formed tiny crystals of the complex, lemon yellow in colour, grew at the bottom of the beaker containing the mixture. They were ca. 1 ~1.5 mm in each dimension. The crystals were separated, washed with a small amount of ethanol, and dried *in vacuo* over silica gel for one night.

Yield: 0.38 g (22%) from 1, and 0.57 g (40%) from 2. *Anal.* Calcd. for PtC₂₈H₂₄N₂O₅Cl₂ (*M_r* = 734.47) C 45.75, H 3.00, N 3.81, Cl 9.67%; found: C 45.77, H 3.26, N 3.81, Cl 9.67%.

X-ray Crystal Structure Analysis

The lemon yellow *r* and *l* crystals were shaped into spheres of ca. 0.4 mm in diameter. Accurate cell dimensions were determined on a Rigaku AFC-6A diffractometer on the basis of 25 independent reflections ($20^\circ < 2\theta < 27^\circ$). The crystallographic data and the refinement details are presented in Table I. The intensity data were collected on the same diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 71.073$ pm). The structure of *r* was solved by using Patterson and Fourier syntheses. The positional and thermal parameters were refined by a block-diagonal least squares procedure. At the final stage, all the non-hydrogen atoms were refined anisotropically. The final *R* and *R_w* values were reduced to 0.036 and 0.043, respectively. The enantiomeric structure gave *R* and *R_w* of 0.057 and 0.071, respectively. To be sure, the structure of *l* was also refined. The inverted set of the final coordinates for the *r* crystal was employed as the 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. The final positional parameters thus obtained agreed with the inverted set of the coordinates of the *r* crystal within three times of the corresponding standard deviations. It was

also confirmed that the intensity relations between 11 selected Bijvoet pairs of *r* and *l* crystals are inverted. All the calculations were carried out on a HITAC M-682H computer at the Computer Centre of the University of Tokyo with the local version of the UNICS program.¹⁸ The scattering factors were taken from ref. 19.

TABLE I
Crystal data and refinement details

Chemical Formula: PtC ₂₈ H ₂₄ N ₂ O ₅ Cl ₂		Formula Weight: 734.47	
Orthorhombic	Space Group: P2 ₁ 2 ₁ 2 ₁	Z = 4	
<i>a</i> (l/pm)	1034.6(4)	<i>D_x</i> (d/Mg m ⁻³)	1.81
<i>b</i> (l/pm)	3120(6)	<i>D_m</i> (d/Mg m ⁻³)	1.81(3)
<i>c</i> (l/pm)	835.3(4)	μ (Mo K α) (n/mm ⁻¹)	5.72
<i>U</i> (v/10 ⁶ · pm ³)	2695(6)		
		<i>r</i>	<i>l</i>
Number of reflections measured		3246	4496
Reflections used for the calculation: [<i>F_o</i> > 3 σ (<i>F_o</i>)]		2873	3622
Scan range (2 θ /°)		3—53	3—60
Scan width (θ /°) (ω -scan)		1.14	1.15
Size of used crystal (in sphere) (\varnothing in mm)		0.42	0.40
Number of parameters refined		343	343
(Δ/σ) _{max}		0.005	0.006
<i>R</i> (<i>R_w</i>) ^a		0.036(0.043)	0.047(0.051)
<i>S</i> ^a		1.33	1.37

^a $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, and $S = [\sum (|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$, where $w = 1/[\sigma(|F_o|)^2 + \{F_w \times F_o\}^2]$, $F_w = 0.020$, N_o = Number of reflections, N_p = Number of parameters.

Lists of structure factors, anisotropic temperature factors of *r* and *l* crystals, positional atomic coordinates of *l* crystals, the intensity relations between the selected Bijvoet pairs and the equations of the least squares planes have been deposited at the Editorial Office. (These matters will be available on request from the Office at a price covering only postal and administration costs.)

Preparation of KBr Disk and Measurement of Absorption and Circular Dichroism Spectra in Microcrystalline State

Electronic absorption and circular dichroism spectra were measured in KBr matrix, because the complex is insoluble in any solvent and decomposes in contact with them.

A required amount of the sample and about 100 mg of dried KBr were weighed and shaped into a disk as described earlier.^{20,21} The electronic spectra were recorded with a Shimadzu UV-240 spectrometer. The CD spectra were measured by JASCO J-600 spectropolarimeter. Absorption and circular dichroism measurements were made for disks of different concentrations: 1, 2 and 4% in the visible region and 0.06 and 0.2% in the ultraviolet region. It was established that there is a linear relationship between the spectrometer deflection and sample concentration. Accordingly, ϵ and $\Delta\epsilon$ values were calculated in the usual way. To check exchange of Cl in the complex with KBr matrix, the CD spectra were measured in KCl matrix, too. The result was quite the same as before, indicating no exchange of Cl and Br.

RESULTS AND DISCUSSION

Spontaneous resolution of coordination compounds is rather uncommon. Only about fifty examples are known. Especially, neutral (molecular) complexes that resolve spontaneously are very rare: for example: bis- α -hydroxy- α -phenylbutyramidine-copper(II),²² *cis*-dichloroethylenediamineplatinum(II) and palladium(II),⁴ *cis*-dichlorobis(methyldiphenylphosphine)platinum(II).¹⁰ In these papers, however, no relevant characterizing data for the enantiomeric crystals are given.

TABLE II

Final positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters (r complex)

TABLE III
Selected interatomic distances (l/pm) and angles ($\Phi/^\circ$)

Bond length	(l/pm)	Bond length	(l/pm)
Pt—Cl(1)	229.8(3)	Pt—Cl(2)	227.9(3)
Pt—N(1)	202.4(8)	Pt—N(2)	199.3(8)
N(1)—C(1)	139.7(12)	N(2)—C(21)	138.6(12)
N(1)—C(7)	126.9(13)	N(2)—C(27)	130.8(12)
O(1)—C(2)	141.9(12)	O(3)—C(22)	138.6(12)
O(1)—C(7)	132.8(12)	O(3)—C(27)	132.3(12)
O(2)—C(9)	132.4(13)	O(4)—C(29)	133.7(13)
C(1)—C(2)	138.2(15)	C(21)—C(22)	138.0(14)
C(6)—C(1)	140.7(15)	C(21)—C(26)	138.7(13)
C(2)—C(3)	140.1(16)	C(22)—C(23)	138.5(14)
C(3)—C(4)	136.7(13)	C(23)—C(24)	140.1(18)
C(4)—C(5)	139.5(18)	C(24)—C(25)	139.6(17)
C(5)—C(6)	142.4(15)	C(25)—C(26)	141.3(14)
C(7)—C(8)	148.2(14)	C(27)—C(28)	148.5(13)
C(8)—C(9)	138.9(16)	C(28)—C(29)	140.9(14)
C(8)—C(13)	140.4(16)	C(28)—C(33)	143.1(15)
C(9)—C(10)	143.1(15)	C(29)—C(30)	141.0(15)
C(10)—C(11)	136.9(17)	C(30)—C(31)	140.0(17)
C(11)—C(12)	141(2)	C(31)—C(32)	140.2(18)
C(12)—C(13)	140.5(17)	C(32)—C(33)	136.9(16)
O(5)—C(41)	141(2)	C(41)—C(42)	142(3)
O(4)···O(5)	261.5(13)	O(5)···Cl(2 ¹)	330.7(12)

Bond angle	($\Phi/^\circ$)	Bond angle	($\Phi/^\circ$)
Cl(1)···O(2 ¹¹)	314.2(9)	Cl(1)—Pt—N(1)	177.4(2)
Cl(1)—Pt—Cl(2)	90.9(1)	Cl(2)—Pt—N(1)	90.1(2)
Cl(1)—Pt—N(2)	89.2(2)	N(1)—Pt—N(2)	90.0(3)
Cl(2)—Pt—N(2)	176.8(2)	Pt—N(2)—C(21)	125.6(6)
Pt—N(1)—C(1)	122.2(6)	Pt—N(2)—C(27)	129.5(6)
Pt—N(1)—C(7)	130.1(7)	C(21)—N(2)—C(27)	104.9(8)
C(1)—N(1)—C(7)	107.7(8)	C(22)—O(3)—C(27)	105.1(8)
C(2)—O(1)—C(7)	105.0(8)	N(2)—C(21)—C(22)	108.1(8)
N(1)—C(1)—C(2)	106.7(9)	N(2)—C(21)—C(26)	131.3(9)
N(1)—C(1)—C(6)	133.0(10)	C(22)—C(21)—C(26)	120.5(9)
C(2)—C(1)—C(6)	120.3(9)	O(3)—C(22)—C(21)	107.1(8)
O(1)—C(2)—C(1)	106.4(8)	O(3)—C(22)—C(23)	127.3(9)
O(1)—C(2)—C(3)	128.4(10)	C(21)—C(22)—C(23)	125.6(10)
C(1)—C(2)—C(3)	125.3(10)	C(22)—C(23)—C(24)	113.3(10)
C(2)—C(3)—C(4)	115.2(11)	C(23)—C(24)—C(25)	123.1(10)
C(3)—C(4)—C(5)	121.1(11)	C(24)—C(25)—C(26)	121.2(10)
C(4)—C(5)—C(6)	124.3(11)	C(21)—C(26)—C(25)	116.2(9)
C(1)—C(6)—C(5)	113.9(10)	N(2)—C(27)—O(3)	114.8(8)
N(1)—C(7)—O(1)	114.3(9)	N(2)—C(27)—C(28)	128.3(9)
N(1)—C(7)—C(8)	127.6(9)	O(3)—C(27)—C(28)	116.9(8)
O(1)—C(7)—C(8)	118.0(9)	C(27)—C(28)—C(29)	118.6(9)
C(7)—C(8)—C(9)	117.3(9)	C(27)—C(28)—C(33)	121.4(9)
C(7)—C(8)—C(13)	120.4(10)	C(29)—C(28)—C(33)	120.0(9)
C(9)—C(8)—C(13)	122.2(10)	O(4)—C(29)—C(28)	118.0(9)
O(2)—C(9)—C(8)	119.6(9)	O(4)—C(29)—C(30)	123.5(9)
O(2)—C(9)—C(10)	120.9(10)	C(28)—C(29)—C(30)	118.4(9)
C(8)—C(9)—C(10)	119.5(10)	C(29)—C(30)—C(31)	120.0(11)
C(9)—C(10)—C(11)	117.4(11)	C(30)—C(31)—C(32)	121.7(11)
C(10)—C(11)—C(12)	123.8(12)		

Bond angle	($\Phi/^\circ$)	Bond angle	($\Phi/^\circ$)
C(11)—C(12)—C(13)	118.7(12)	C(31)—C(32)—C(33)	118.6(11)
C(8)—C(13)—C(12)	118.3(11)	C(28)—C(33)—C(32)	121.1(11)
O(5)—C(41)—C(42)	115.0(15)		
O(4)···O(5)···Cl(2 ⁱ)	118.1(4)		
Cl(1)···O(2 ⁱⁱ)···C(9 ⁱⁱ)	119.5(6)		

Key to the symmetry operations: i, $1 + x, y, z$; ii, $x, y, 1 + z$.

The final positional coordinates with their equivalent temperature factors for non-hydrogen atoms are listed in Table II. Figure 2 illustrates exactly the absolute configuration of the *r* complex viewed on the coordination plane. Relevant interatomic distances and bond angles are given in Table III. The crystal structure is composed of discrete $[\text{PtCl}_2(\text{Hbxp})_2]$ and $\text{C}_2\text{H}_5\text{OH}$ molecules, the latter being held by hydrogen bonds to the former.

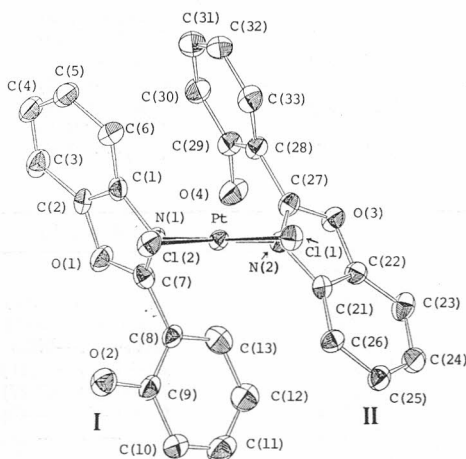


Figure 2. The *r* complex viewed on the coordination plane: 30% probability thermal ellipsoids are shown for the nonhydrogen atoms.

The complex molecule exhibits a square-planar geometry with the two Cl atoms in *cis*-positions. The coordination plane is quite planar, the average positional deviation being 4.3 pm. The Pt—Cl distances are 229.8(3) and 227.9(3) pm. The two organic ligands, Hbxp I and II (See Figure 2) act as a unidentate and are coordinated to the Pt atom with their N atoms of the oxazolyl ring (Pt—N: 202.4(8) and 199.3(8) pm). These values are not very different from the corresponding bond lengths of other related complexes.^{6,7,9,11} As seen from Figure 2, the two benzoxazolyl moieties are approximately related by a twofold axis through the Pt atom and the centre of the two ligating N atoms. The dihedral angles between the benzoxazolyl ring and the phenol ring are different: in Hbxp I, the dihedral angle is 87.7°, while it is 58.8° in Hbxp II. The OH group of the phenol ring is disposed on opposite sides of the benzoxazolyl ring. The long axis of Hbxp I is inclined at an angle of 60.9° with respect to the coordination plane. The corresponding angle of Hbxp II is

55.4°. The shape and size of the ligand do not differ much from those observed for the Cd(II), Cu(II) and Fe(III) complexes, in spite of the fact that the ligand acts as a bidentate, bxp^- , in these complexes.^{15,16}

A projection of the unit cell along the a -axis is shown in Figure 3. The complexes form two dimensional network parallel to (010) by hydrogen bonds in the following way. The ethanol oxygen atom, O(5), is hydrogen bonded to the phenol oxygen atom, O(4) and with the Cl(2) atom of the complex shifted by a unit translation along the a -axis, where $\text{O}(5) \dots \text{O}(4) = 261.5(3)$, $\text{O}(5) \dots \text{Cl}(2^i) = 330.7(1.2)$ pm ($i: 1 + x, y, z$) and $\text{O}(4) \dots \text{O}(5) \dots \text{Cl}(2^i) = 118.1(4)^\circ$. There is another hydrogen bond between Cl(1) and the phenol oxygen atom of the complex next to the c -axis direction, $\text{O}(2^{ii})$ ($ii: x, y, 1 + z$). The $\text{Cl}(1) \dots \text{O}(2^{ii})$ distance is 314.2(9) pm and the $\text{Cl}(1) \dots \text{O}(2^{ii}) \dots \text{C}(9^{ii})$ angle is $119.5(6)^\circ$. These hydrogen bonds are drawn in broken lines in Figure 3.

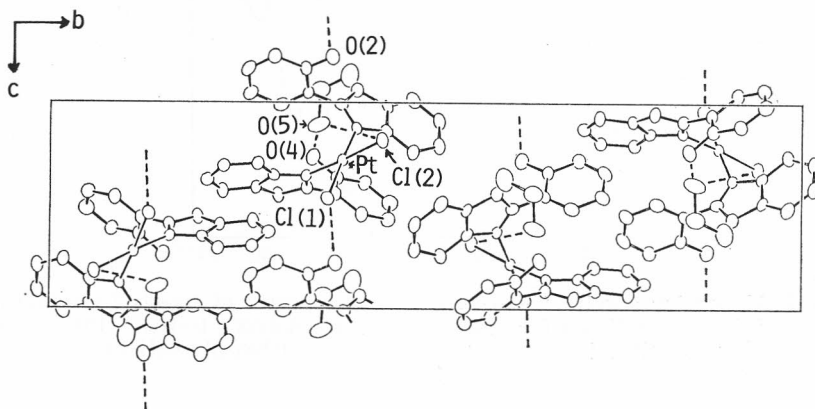


Figure 3. The packing of the r molecules in the unit cell projected along the a -axis. Hydrogen bonds are drawn in broken lines. Positive a -axis direction is taken downwards.

The CD spectra for the r and l crystals are given in Figure 4, together with the visible and ultraviolet absorption spectra. The CD curves of the r and l crystals are mirror images of one another, indicating that the spontaneous resolution is complete. The r complex of which the absolute stereochemical configuration is shown in Figure 2 corresponds to $(-)\text{CD}_{630}^{\text{CD}}\text{-}[\text{PtCl}_2(\text{Hbxp})_2]$. The r crystal can be easily identified under a microscope by its crystal habit (Figure 1). The observed CD spectra are weak in intensity. Generally, the CD spectra of the complexes involving only unidentate ligands are known to be much weaker than those with chelate rings.²³ The CD spectra of the r enantiomer exhibit two weak negative peaks with shoulders in the range $13,000 \sim 30,000 \text{ cm}^{-1}$ and a bisignate circular dichroism in the range from $30,000 \sim 40,000 \text{ cm}^{-1}$. The latter appears to exhibit a characteristic feature of exciton coupling. The weak CD in the low energy $d-d$ region from $13,000 \sim 30,000 \text{ cm}^{-1}$ does not seem to be understood systematically, because the effects of the bulky organic ligands on the energies of different d -orbitals may be more complicated than other related complexes with $[\text{PtCl}_2\text{N}_2]$ chromophore,^{24,25,26} and stronger spin-orbit coupling for Pt than the first transition

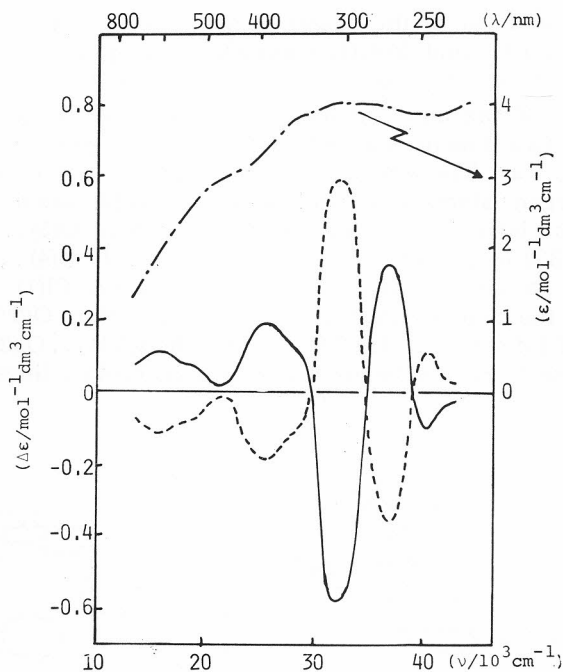


Figure 4. Absorption spectra (---) and CD spectra of *cis*-bis[2-(2-benzoxazolyl)phenol-N]dichloroplatinum(II)·ethanol in KBr matrix: (—) $_{630}^{CD}$ -[PtCl₂(Hbxp)₂]-C₂H₅OH (*r* complex) (— · — · —) (+) $_{630}^{CD}$ -[PtCl₂(Hbxp)₂]-C₂H₅OH (*l* complex) (— · — · —)

series metals would make the intensity of the singlet-triplet transition approach that for the spin-allowed transitions.²⁴ The CD spectra in the range 30,000 ~ 40,000 cm⁻¹ may be accounted for on the basis of two-group electric-dipole mechanism. Single crystal studies of aromatic substances indicated that over the quartz ultraviolet region the lowest-energy absorption band with a high intensity of benzene derivatives arises from a $\pi-\pi^*$ transition with the moment directed along the shorter inplane axis of the molecule.²⁷ Accordingly, the lowest energy absorption band with a higher intensity in the electronic spectra near 33,000 cm⁻¹ of the complex is considered to arise from a $\pi-\pi^*$ transition in the benzoxazolyl group whose moment is directed parallel to the C₁-C₂ and the C₂₁-C₂₂ bonds. The two benzoxazolyl groups are approximately related by a twofold axis and the two moments form a skew pair λ (IUPAC, 1970).²⁸ Thus, they give a bisignate circular dichroism couplet, positive at the lower frequency and negative at a higher frequency in agreement with the observation.²⁹ Though the CD curve exhibits a characteristic exciton form, the intensities are weak. This may be due to minor rotational strength produced, and in part small frequency separation between these rotational strengths. The band areas of the two components of the bisignate CD couplet are unequal in magnitude, because the CD contribution of the Pt d-electrons in this wavelength region (probably positive) may be responsible for such unequal magnitude.

It is to be noted here that the current IUPAC rules for nomenclatures of optically active metal complexes cannot be applied to the present complex.²⁸

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SAŽETAK

Kristalna struktura, apsolutna konfiguracija i cirkularni dikroizam (–) i (+) *cis*-bis[2-(2-benzoksazolil)fenol-*N*]dikloroplatinium(II)-etanola

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Kristali naslovnih kompleksa podliježu spontanom razdvajanju (enantiomorfa). Oni su ortorombski, prostorna skupina $P2_12_12_1$, $a = 1034.6(4)$, $b = 3120(6)$, $c = 835.3(4)$ pm i $Z = 4$. Konačne R-vrijednosti iznose za enantiomere 0,036, odn. 0,047, za 2873, odn. 3622 jedinične refleksije. Kompleks je kvadratno-planaran, s dva atoma klora u *cis*-položaju. Molekula liganda djeluje kao monodentat i koordinirana je na atom Pt preko svog N-atoma. Prosječne udaljenosti Pt—Cl i Pt—N iznose 228.9(3), odn. 200.9(8) pm. Dvije benzoksazolilne jedinice približno su u (simetrijskom) odnosu preko dvostruke rotacijske osi koja prolazi kroz središnji atom Pt i središnjom udaljenošću između dva N atoma. Optička aktivnost javlja se uslijed disimetričnog položaja dvije molekule liganda s obzirom na koordinacijsku ravninu. CD spektri u području 13000–40000 cm^{-1} mjereni su KBr-matrici. Oblik CD krivulje koreliran je s apsolutnom konfiguracijom i kristalnim habitusom.