Table 2. Constants of stability, relaxation efficiency, and paramagnetic double refraction for the complexes under investigation

Complex	lg _{βstab}	K_{e1} /L mol ⁻¹ s ⁻¹	${}_{m}^{P}{}_{\exp} \cdot 10^{15}$ /emu
Dy^{3+} , aq	<u> </u>	600	-21
$[DyAc]^{2+}$	2.10 ± 0.06	540 ± 27	63±5
[DvAc_] ⁺	$3.70 {\pm} 0.05$	375±18	67±7
DvBz ²⁺	$2.00 {\pm} 0.05$	520 ± 25	230 ± 15
[DyBz ₂] ⁺	3.90±0.07	375±19	280±25

stoichiometric theory, the coordination of Ac^- and Bz^- at the edges of a square antiprism (Fig. 2, b) should be preferred, which is consistent with X-ray diffraction data for a similar complex.¹²

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Synthesis and molecular and crystal structure of *trans*-{bis(4,6-diisopropyl-2,5-diphenyl-1,3,2,5dioxaboraphosphorinane)}dichloroplatinum(II)

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The *trans*-{bis(4,6-diisopropyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)}dichloroplatinum(II) complex was obtained by the interaction of 4,6-diisopropyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane with bis(benzonitrile)dichloroplatinum(II). In solution this complex occurs as a mixture of isomers. X-ray analysis revealed close contacts between the platinum atom and one oxygen atom of the ligands.

Key words: complex, (dioxaboraphosphorinane)dichloroplatinum(II), stereoisomers.

The use of conformationally labile cyclic ligands in metallocomplex synthesis allows one to study the influence of the conformational behavior of heterocycles on the properties and structural parameters of the complexes. In this case the free ligands are model compounds for the determination of the spatial structure of

Bond	d/Å	Angle	ω/deg	Angle	τ/deg
Pt-Cl	2.306(2)	Cl-Pt-Cl	180	O(1)-B(2)-O(3)-C(4)	2.7
Pt-P	2.320(1)	Cl-Pt-P(5)	88.25(5)	B(2) - O(3) - C(4) - P(5)	-47.7
P(5) - C(4)	1.861(6)	Cl-Pt-P(5)	88.25(5)	O(3) - C(4) - P(5) - C(6)	63.1
P(5) - C(6)	1.878(6)	Cl-Pt-P(5)	91.75(5)	C(4) - P(5) - C(6) - O(1)	-48.3
P(5) - C(7)	1.824(6)	P(5) - Pt - P(5)	180	P(5)-C(6)-O(1)-B(2)	12.9
O(1) - C(6)	1.431(7)	Pt-P(5)-C(4)	108.6(2)	C(6) - O(1) - B(2) - O(3)	18.5
O(1) - B(2)	1.354(9)	Pt-P(5)-C(6)	120.0(2)	Pt-P(5)-C(7)-C(8)	-169.4
O(3) - B(2)	1.361(9)	Pt-P(5)-C(7)	118.8(2)	Pt-P(5)-C(7)-C(12)	13.3
C(4)-C(19)	1.530(9)	C(4) - P(5) - C(6)	95.1(3)	C(4) - P(5) - C(7) - C(8)	-44.5
C(6)C(22)	1.529(9)	C(4) - P(5) - C(7)	108.9(3)	C(4) - P(5) - C(7) - C(12)	138.2
C(7) - C(8)	1.413(9)	C(6) - P(5) - C(7)	102.7(3)	C(6) - P(5) - C(7) - C(8)	55.4
C(7) - C(12)	1.388(9)	C(6) - O(1) - B(2)	125.2(5)	C(6) - P(5) - C(7) - C(12)	-121.8
C(8)-C(9)	1.364(10)	C(4) - O(3) - B(2)	123.1(6)	Cl-Pt-P(5)-C(4)	-80.9
C(9)-C(10)	1.412(14)	C(4) - O(3) - B(2)	123.1(6)	Cl-Pt-P(5)-C(6)	171.5
C(10) - C(11)	1.362(13)	P(5) - C(4) - O(3)	104.5(4)	Cl - Pt - P(5) - C(6)	-8.5
C(11) - C(12)	1.388(10)	P(5) - C(4) - C(19)	118.2(4)	CI - Pt - P(5) - C(7)	44.1
C(13)C(14)	1.391(10)	O(3) - C(4) - C(19)	108.4(5)	Pt-P(5)-C(4)-C(19)	59.7
C(13)-C(18)	1.394(10)	P(5) - C(6) - O(1)	110.3(4)	Pt-P(5)-C(4)-O(3)	-60.9
C(13)-B(2)	1.563(10)	P(5) - C(6) - C(22)	117.2(4)	C(6) - P(5) - C(4) - C(19)	-176.2
C(14) - C(15)	1.383(11)	O(1) - C(6) - C(22)	108.5(5)	C(7) - P(5) - C(4) - O(3)	-168.4
C(15)-C(16)	1.412(13)	O(1) - B(2) - O(3)	123.8(7)	C(7) - P(5) - C(4) - C(19)	-70.9
C(16)C(17)	1.354(13)	O(1) - B(2) - C(13)	119.0(6)	Pt-P(5)-C(6)-O(1)	66.6
C(17) - C(18)	1.393(11)	O(3) - B(2) - C(13)	117.1(7)	Pt-P(5)-C(6)-O(1)	-58.2
C(19) - C(20)	1.529(10)			C(14) - C(13) - B(2) - O(1)	175.5
C(19) - C(21)	1.514(9)			C(14) - C(13) - B(2) - O(3)	-4.5
C(22)C(23)	1.489(10)			C(18) - C(13) - B(2) - O(1)	-0.4
C(22)-C(24)	1.507(11)	······		C(18)-C(13)-B(2)-O(3)	178.5

Table 1. Bonds lengths (d), bond (ω), and torsion angles (τ) in 2

metallocomplexes both in the crystalline state and in solutions. It has been shown previously¹ that 1,3,2,5dioxaboraphosphorinanes form square-planar complexes of the composition L_2PtCl_2 with $PtCl_2$. When substituents are at the positions 4 and 6, uncommon *trans*-complexes with phosphines are formed. In the case of *cis*-{bis(2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)}dichloro-platinum(II) the heterocycle exists in the twist conformation. It was assumed that the latter is stable due to attraction between the O and P atoms.¹

Results and Discussion

It is known that bulky substituents may have a pronounced effect upon the conformation of heterocycles and the structure of complexes. We have carried out the reaction of 4,6-diisopropyl-2,5-diphenyl-1,3,2,5-dioxaborophosphorinane (1) with bis(benzonitrile)dichloroplatinum(II) in acetonitrile. Within hours after mixing, large yellow crystals of the *trans*-{bis(4,6-diisopropyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)dichloroplatinum(II) complex (2) were formed.

As in the case of 2,4,5,6-tetraphenyl-1,3,2,5dioxaboraphosphorinane,¹ the coordination of the metal in complex 2 is accomplished by phosphorus atoms in both symmetrical ligands. *i*-Pr substituents result in *trans*-configuration of the central ion as evidenced by the ³¹P NMR spectra of the DMF solution of this complex. The spectrum contains a signal at -14.9 ppm with a spin-spin coupling constant ${}^{1}J_{P-Pt} = 2722$ Hz. The IR spectrum of **2** contains absorption bands that are characteristic for the initial P,B-containing ligand; chemical analysis is in agreement with the proposed structure. Unlike the initial ligand, complex **2** has a high melting point (216-219 °C).

The structure of the symmetric *trans*-complex is supported by X-ray analysis. The bond lengths, bond and torsion angles are listed in Table 1. The structure of the complex is shown in Figure 1. The P,B-containing ligands in 2 are completely symmetric relative to each other; they are in the *trans*-position relative to the central Pt atom. The coordination of the metal is accomplished by phosphorus atoms. The heterocyclic fragments of the ligands in complex 2 are in a distorted chair onformation. The C(4)O(3)B(2)O(1)C(6) fragment





Fig. 1. Molecular structure of *trans*-{bis(4,6-d6i-*i*-Pr-2,5-di-Ph-1,3,2,5-dioxaboraphosphorinane)}dichloroplatinum(II).

is non-planar; the deviations of the O(1), C(6), and P(5)atoms from the plane are -0.130(4), 0.100(6), and 1.025(1) Å. The C(4)O(3)B(2)O(1) fragment is planar within 0.010(5) Å; the deviations of the P(5) and C(6)atoms from the plane are 1.29(1) and 0.414(5) Å. In the previously studied molecule 2,5-diphenyl-1,3,2,5dioxaborophosphorinane² the heterocycle exhibited a regular chair conformation with the phenyl fragment at the phosphorus atom being in an axial position. The phenyl substituent at the phosphorus atom is essentially in the same plane as the heterocycle. The boron atom exhibits plane-trigonal coordination. Within the limits of experimental error, the O-B and B-C(Ph) bond lengths in 2 are the same as those found previously.² Of the three possible stereoisomers, the one realized is that in which the ligands in the crystalline complex have equatorial substituents both at the C and at the P atoms. The presence of three rather bulky substituents at positions 4, 5, and 6 of the heterocycle corresponds to a sterically overloaded conformation. In addition, the heterocyclic fragment of the complex in the crystalline state is turned in such a way that the Pt-Cl and P-C(6) bonds in each of the ligands are shielded (the torsion angle C1-Pt-P(5)-C(6) is 8.5°), while the Cl and O(1) atoms are brought close together, within 3.242(6) Å, which is the sum of van der Waals radii (3.2 Å). This spatial structure of the ligands is attributable to some additional stabilizing interactions in the complex, for example, between the Pt and O atoms.¹ Indeed, the bond angles Pt-P(5)-C(4) (108.6°) and P(5)-C(4)-O(3) (104.5°) in one of the PtPCO fragments in each ligand are considerably smaller than the related angles in the other fragment, namely, Pt-P(5)-C(6) (120.0°), Pt-P(5)-C(7) (118.8°), and P(5)-C(6)-C(6)O(1) (110.3°) in the crystal. Likewise, the Pt...O(3) distance (3.451(2) Å) is less than both the Pt...O(1) (4.025(2) Å) distance and the sum of van der Waals radii for Pt-O (3.8 Å). The obtained results can be interpreted in terms of attractive interactions between the Pt and O atoms, which cause a distortion of the chair conformation of the heterocyclic ligand.

NMR spectra provide a means for determining the spatial structure of the complex in solution. However, we failed to obtain well-resolved NMR spectra in solvents with low polarity and weak basicity due to low solubility of the complex. Well-resolved NMR spectra were obtained for DMF solutions of 2 prepared with heating. It was shown¹ that weak Pt-O interactions disappear in DMF, which is likely due to competitive solvation processes. In addition, the fast interconversion of stereoisomers was shown³ to take place for 1,3,2,5dioxaboraphosphorinane in solution. Some time after dissolution, the ${}^{31}P$ NMR spectrum of complex 2 in DMFA exhibited three signals at -13.7, -14.1, and -4.9 ppm in the ratio of 1:2:20 with spin-spin coupling constants ${}^{1}J_{P,Pt} = 2722$ Hz for all of the signals. This is indicative of the presence of Pt-P bonds in the complex. It also suggests that the central ions possess the trans-configuration in solution. The ¹H NMR spectrum of complex 2 in DMF-d₆ contained an intense set of lines that corresponded to the dominant signal in the ³¹P NMR spectrum. The distinguishing features of the signals for the methine protons of the cycle, the *i*-Pr protons, and the methyl groups suggest a symmetric structure for the heterocyclic ligand, which differs from that of the crystalline state. This observation correlates well with the assumption that weak attractive interactions disappear in solution. When the ¹H NMR spectrum of the complex with initial ligand 1 are compared with those of the three individual stereoisomers of 4,6-diisopropyl-2.5-diphenyl-5-thio-1.3.2.5-dioxaboraphosphorinane (3) (see ref. 3) it is apparent that complex 2 and stereoisomer 3 are very much alike. The latter compound possesses a chair conformation with equatorial substituents at positions 4 and 6 and P=S bond. Like the ³¹P NMR spectra, the ¹H NMR spectra contain signals for the other isomer. A comparison of the spectral features of complexes 2 and 3 allows one to assign the structure of a stereoisomer with equatorial *i*-Pr groups and an axial P-Pt bond to the ligand. The obtained data on the spatial structure of complex 2 in solution suggest the possibility of ligand isomerization in the complex on dissolving. This is in keeping with the smooth interconversions of stereoisomers 1 and 3 on heating or in the presence of an acidic catalyst (a Pt(II) ion in our case).

Experimental

 1 H and 31 P NMR spectra were recorded with a Bruker WM-250 instrument (operating frequencies: 250 MHz for protons; 101 MHz for 31 P). IR spectra were recorded with a Specord M-80 instrument.

Crystals of **2**: $C_{40}H_{52}O_4B_2Cl_2P_2Pt$, m.p. 216–219 °C, monoclinic. At 20 °C a = 10.792(3), b = 11.329(4), c = 17.390(7) Å, $\beta = 99.40(3)^\circ$, Z = 2, $d_{calc} = 1.50$ g · cm⁻³, space group $P2_1/n$. Cell parameters and intensities of 2841 independent reflections were measured with an Enraf-Nonius CAD-4 four-circle diffractometer (Mo-K_{α}, graphite monochromator, $\omega/2\theta$ scan, $\theta < 30^\circ$). An empirical absorption correction was applied ($\mu M_0 = 36.2 \text{ cm}^{-1}$). The structure was solved by the standard heavy atom technique; the Pt atom was located at the origin since the molecule occupied a special position. Nonhydrogen atoms were refined by a full-matrix least-squares procedure, first in the isotropic and then in the anisotropic approximation. All hydrogen atoms were revealed by the difference Fourrier syntheses. Contributions from electron density series were taken into account in the subsequent refinement cycles with fixed positional and isotropic thermal parameters, $B_{iso} = 4$ Å². Least-squares refinement converged at R =0.029 and $R_{\rm W} = 0.040$. All calculations were made with a PDP 11/23 computer using a SPD software package. The coordinates of non-hydrogen atoms are listed in Table 2.

trans-Bis(4,6-diisopropyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)dichloroplatinum(II) (2). A solution of 0.25 g (0.74 mmole) of 4,6-diisopropyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (1) in 10 mL of MeCN was added to a solution of 0.17 g (0.36 mmole) of bis(benzonitrile)dichloroplatinum(II) in 10 mL of MeCN. Large light-yellow crystals were filtered after 4 h and washed with MeCN. The yield of 2 was 0.26 g (76 %); m.p. 216–219°C. ³¹P NMR, δ : -13.72 (¹ $J_{\text{Pt,P}}$ = 2720 Hz); -14.10, (¹ $J_{\text{Pt,P}}$ = 2720 Hz); -14.85, $({}^{1}J_{Pt P} = 2720 \text{ Hz})$; (a mixture of stereoisomers, DMF), the integral intensities were in the ratio 1:2:20. ¹H NMR of the dominant isomer, δ : 8.15–7.28 (10 H, Ar–H); 5.15 (d, ${}^{3}J_{H,H}$ = 7.9 Hz, 2 H, P-CH-O); 2.82 (m, 2 H, CHMe₂); 1.37 (d, ${}^{3}J_{\text{H,H}} = 6.6 \text{ Hz}, 6 \text{ H}, \text{ CH}_{3}$; 0.75 (d, ${}^{3}J_{\text{H,H}} = 6.7 \text{ Hz}, 6 \text{ H},$ CH₃); the spectrum of the other isomer: 4.7 (t, ${}^{3}J_{H,H} = 7.9$ Hz, ${}^{2}J_{PH} = 4.6$ Hz, 2 H, P–CH–O); 1.04 (d, ${}^{3}J_{H,H} = 6.8$ Hz, 6 H, CH_3); 1.01 (d, ${}^{3}J_{H,H} = 6.7$ Hz, 6 H, CH_3). From integral intensities of the NMR it was derived that the stereoisomers are in the ratio of 10:1. Found (%): C, 50.14; H, 6.04; P, 6.41. C₄₀H₅₂P₂B₂O₄PtCl₂. Calculated (%): C, 50.15; H, 5.91; P, 6.55.

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3	3
$B_{ini}^{equiv} = 4 / 3 \Sigma$	$\sum (\bar{a}_i \bar{a}_j) B(i_j) A^2$
/=1]	/=[

Atom	x	у	z	В
Pt	0	0	0	2.392(4)
Cl	0.0863(1)	0.0620(2)	0.12346(9)	3.81(3)
P(5)	-0.1754(1)	0.1137(1)	0.01029(8)	2.42(2)
O(1)	-0.3631(4)	0.0261(3)	-0.0990(3)	3.37(9)
O(3)	-0.3105(4)	-0.0744(3)	0.0231(2)	3.38(8)
C(4)	-0.2773(5)	0.0299(4)	0.0676(3)	2.7(1)
C(6)	-0.3009(5)	0.1355(5)	-0.0770(3)	2.9(1)
C(7)	-0.1525(5)	0.2626(5)	0.0500(3)	3.2(1)
C(8)	-0.2556(6)	0.3266(5)	0.0629(4)	3.8(1)
C(9)	-0.2387(8)	0.4400(7)	0.0950(4)	5.3(2)
C(10)	-0.118(1)	0.49223(6)	0.1047(5)	5.8(2)
C(11)	-0.0198(7)	0.4302(6)	0.0854(5)	5.4(2)
C(12)	-0.0348(6)	0.3150(6)	0.0584(4)	3.9(1)
C(13)	-0.3935(5)	-0.1938(5)	-0.0948(4)	3.5(1)
C(14)	-0.3789(7)	-0.2994(6)	-0.0535(5)	5.1(2)
C(15)	-0.4029(8)	-0.4075(7)	-0.0899(6)	6.6(2)
C(16)	-0.4477(7)	-0.4094(7)	-0.1708(6)	6.0(2)
C(17)	-0.4775(7)	-0.3072(7)	-0.2114(5)	5.5(2)
C(18)	-0.4405(6)	-0.1991(6)	-0.1743(4)	4.4(1)
C(19)	-0.2223(5)	-0.0063(5)	0.1510(3)	3.3(1)
C(20)	-0.2002(6)	0.1012(6)	0.2047(3)	4.2(1)
C(21)	-0.3070(7)	-0.0948(7)	0.1819(4)	4.8(2)
C(22)	-0.2612(5)	0.1910(6)	-0.1493(4)	3.5(1)
C(23)	-0.203(1)	0.3101(7)	-0.1361(4)	7.5(2)
C(24)	-0.3713(9)	0.198(1)	-0.2148(5)	11.1(3)
B(2)	-0.3528(6)	-0.0731(6)	-0.0550(4)	3.3(1)

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