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A Surprising Example of Crystal Structure Retention for 3,5-Di-(*tert*-butyl)-2-hydroxyazobenzene Ligand during the Formation of Ni(II) and Pd(II) Complexes

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Abstract—The structures of 3,5-di-(*tert*-butyl)-2-hydroxyazobenzene (L) in the free state and in complexes with Ni^{2+} (**I**) and Pd^{2+} (**II**) cations are studied by X-ray diffraction (XRD). The same space group $R\bar{3}c$ with close unit cell parameters, the same crystal structure motif, and unusual conformations of the cupola-shaped coordination polyhedra of complexes **I** and **II** are revealed by XRD for ligand L. In complexes **I** and **II** based on this compound as the ligand, the coordinating atoms form *trans*-planar coordination nodes.

Keywords: XRD, azo compounds, isomerism, conformation, quantum chemical calculations

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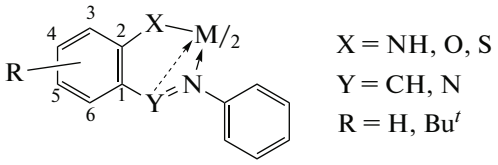
INTRODUCTION

Unusual isomers can be formed for the complexes based on the azobenzene derivatives of type **1** (Y = N), which is a consequence of the ambidentate character of the azo group. Both nitrogen atoms were shown [1] to exhibit approximately equal donor activities and, hence, both of them can be involved in coordination with the metal atom.



Chelate complex of type **1**

Thus, the formation of both five- and six-membered cycles can be expected for the chelate complexes of type **1**, resulting in the situation where the azo group would be either exocyclic, or endocyclic. The complexes containing simultaneously five- and six-membered cycles in one molecule were also synthesized [2–5]. The synthesis and physicochemical properties of the metallochelates prepared for the first time and based on 3,5-di-(*tert*-butyl)-2-oxyazobenzene were described [6]. A possibility of existing in a solution of four alternative structures and possible isomeric transformations between them were assumed on the basis of the NMR spectra, electrical magnetic moments, and quantum chemical analysis. The XRD study of the structure of the Ni(II) complex showed that the introduction of *tert*-butyl substituents can result in the formation of a cupola-type coordination polyhedron unusual for metallochelates with the MN_2O_2 coordination node, where the ligands are arranged at one side of the planar coordination node due to inflections of the metallochelate cycles to one side and form the unusual cupola-shaped conformation. It is revealed that in the Ni(II) complexes the 3,5-di-(*tert*-butyl)-2-oxyazobenzene molecules are randomly arranged in two equiprobable positions and linked by the crystallographic 2-fold axis [7]. The structure of the later synthesized 3,5-di-(*tert*-butyl)-2-oxyazobenzene complex with Pd^{2+} was studied by XRD and quantum chemistry [8]. Both complexes have similar cupola structures.

The number of the described chelate complexes with the PdN_2O_2 coordination node are fairly low, and all of them are characterized by the planar-square structure with the inflection of the metallocycles to different sides [9, 10], which is characteristic of the palladium complexes with other ligands [10]. The purpose of this work is to study the structure of the initial ligand L and a possible influence of its structure on the structures of the Ni(II) (**I**) and Pd(II) (**II**) complexes.

EXPERIMENTAL

The syntheses of 3,5-di-(*tert*-butyl)-2-hydroxyazobenzene and its complexes with Ni^{2+} and Pd^{2+} were described [6].

XRD of ligand L was carried out on an XCalibur automated diffractometer (Agilent) with an EOS coordinate CCD detector (Agilent Technologies UK

Table 1. Crystallographic and structure refinement parameters for compound L

Parameter	Value
Empirical formula	$C_{20}H_{26}N_2O$
FW	310.43
Crystal system	Hexagonal
Space group	$P\bar{3}c$
a, Å	23.626(3)
b, Å	23.626(3)
c, Å	17.561(4)
α, deg	90
β, deg	90
γ, deg	120
Cell volume, Å^3	8489(2)
Z	18
ρ, g/cm^3	1.093
μ, mm^{-1}	0.067
F(000)	3024
θ_{max}, deg	1.72–26.06
Ranges of *h, k, l*	$-29 \le h \le 25$, $0 \le k \le 29$, $0 \le l \le 19$
Number of measured/independent reflections (R_{int})	5441/1807 (0.0487)
Refinement method	Full-matrix least squares for F^2
Number of parameters	172
S	0.864
R_1, wR_2 for N_1	$R_1 = 0.0482$, $wR_2 = 0.1135$
R_1, wR_2 for N_2	$R_1 = 0.1200$, $wR_2 = 0.1402$
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	0.125/–0.142

Ltd., Yarnton, Oxfordshire, England). Reflections were collected and unit cell parameters were determined and refined using the CrysAlis PRO software (Agilent (2011), CrysAlis PRO version 171.35.19, Agilent Technologies UK Ltd., Yarnton, Oxfordshire, England). The XRD data were obtained at a sample temperature of 100(2) K using MoK_α (λ = 0.71073 Å) radiation. The structure was solved by direct methods. The full-matrix refinement of positions and thermal parameters of non-hydrogen atoms was performed isotropically and then anisotropically by least squares. The key crystallographic parameters and structure refinement parameters for compound L are given in Table 1. All calculations were performed using the SHELXTL software [11].

The crystal structure of compound L was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2034471; www.ccdc.cam.ac.uk/data_request/cif).

Quantum chemical calculations. In order to understand how the structures of complex **II** and ligand L depend on the crystalline environment, we performed quantum chemical calculations of two types: using the GAUSSIAN-09 program [12] and VASP program [13]. The full geometry optimization of ligand L' isolated from complex **II** was performed using the GAUSSIAN-09 program in the TPSSh/6-311+G*(C, N, O, H) approximation.

The VASP 5.3.3 software (Vienna ab-initio simulation program) used for nonempirical calculations of the total energy and molecular dynamics was developed at the Institute of Physics of Materials at the University of Vienna (Austria) [13]. The exchange and correlations components of the total energy of complex **II** were described by the PBE functional. The starting geometry of complex **II** was taken from the XRD data presented above and then optimized. Residual forces on the atoms were lower than 10^{-2} mdyne, which corresponds to a good final

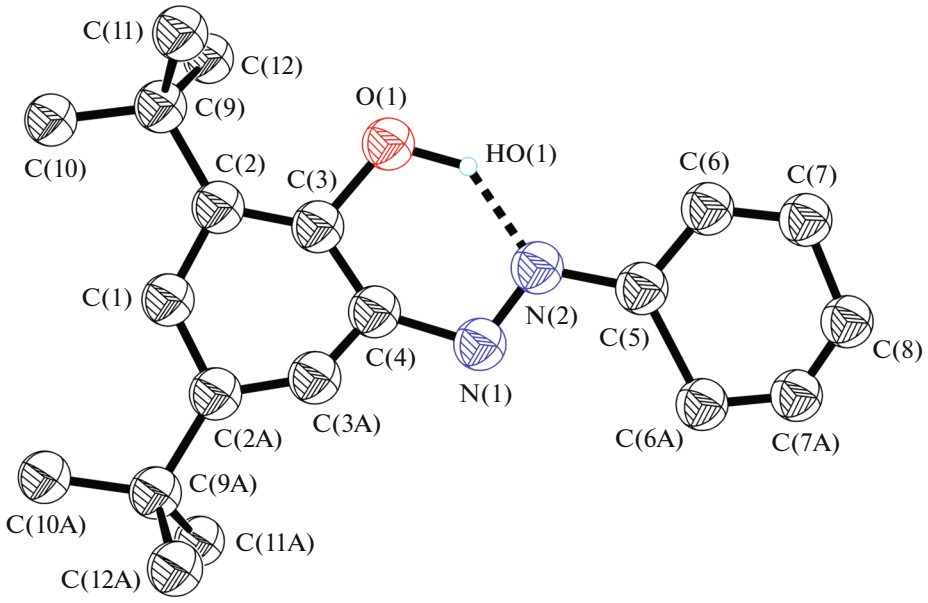


Fig. 1. General view of ligand L (only one hydrogen atom is shown, other hydrogen atoms are omitted).

geometry with an error in energy of 10^{-3} eV. The PAW potentials were used to take into account core electrons [14]. The component of the wave function corresponding to the valence electrons was expanded over the basis of planar waves with a kinetic energy limit of 950 eV. The optimized structure of complex **II** was obtained by its optimization as an isolated object in a box 22 × 21 × 16 Å in size. The calculated structure was tested to stability by the calculation of imaginary frequencies. No negative frequencies were obtained.

Further, the geometric structure of complex **II** with the removed Pd^{2+} ion was optimized.

RESULTS AND DISCUSSION

The general view of a molecule of ligand L is shown in Fig. 1. The intramolecular hydrogen bond of the O–H...N type with the parameters HO(1)...N(2) (1.621 Å), N(2)...O(1) (2.558(3) Å), and O(1)HO(1)N(2) (140.1°) takes place in ligand L.

Molecule L in the crystal is disordered over the 2-fold axis. The character of this disordering is shown in Fig. 2a. Surprisingly, this disordering of the ligand is retained in the crystal structures of complexes **I** and **II**. The character of ligand disordering in the Ni(II) and Pd(II) complexes is shown for comparison in Fig. 2b. To compare the configurations of the discussed fragment in the free state and in the complex, the superposition of the independent part of ligand L over the positions of the atoms of the chelate cycle in the Pd(II) complex is shown in Fig. 2c.

The molecule of ligand L crystallizes in the space group $R\bar{3}c$ as in the Ni(II) and Pd(II) complexes with close unit cell parameters (Table 2).

The general view of the Ni(II) complex without atomic disordering in the ligand is shown in Fig. 3a. The disordered Pd(II) complex with the ligands disordered over two positions and bound by symmetry elements in the space group $R\bar{3}c$ is shown in Fig. 3b. The disordering of the metal-coordinating O and N atoms over two positions O(10), O(10A) and N(5), N(5A) results in the situation where each position of the metal atom is occupied by 50% only. The disordering of the azo group induces the disordering of the phenyl ring bound to this group. The main crystallographic parameters for crystals of compounds L, **I**, and **II** are given in Table 2.

The character of packing of ligand L and complex **II** in the projection along parameter b is shown in Fig. 4.

In crystals, the molecules of ligand L form a loose packing with a density of 1.093 g/cm^3. A cavity is formed between the adjacent ligand molecules and is occupied by metal ions in the structures of complexes **I** and **II**. The distance between the oxygen atoms of the nearest molecules in the crystal of L (O(1)...O(1A) $^{\#}$ $0.6 - x$, $0.3 - x + y$, $-0.17 - z$) is 4.15 Å, the N(2)...N(2A) distance is 5.08 Å, and the angle between these two molecules of ligand L (the angle between the mean planes passed through the atoms of each molecule) is 89.9°. The similar O(1B)...O(1D) distance in complex **II** is 4.04 Å, the N(2B)–N(2D) distance is 4.05 Å, and the angle between the coordinated ligands is 99.1°. The ligand molecule in complex **II** differs from free molecule L by the turn of the phenyl ring at an angle of 12.4°. Approximately the same values of the indicated distances are observed in the earlier studied square palla-

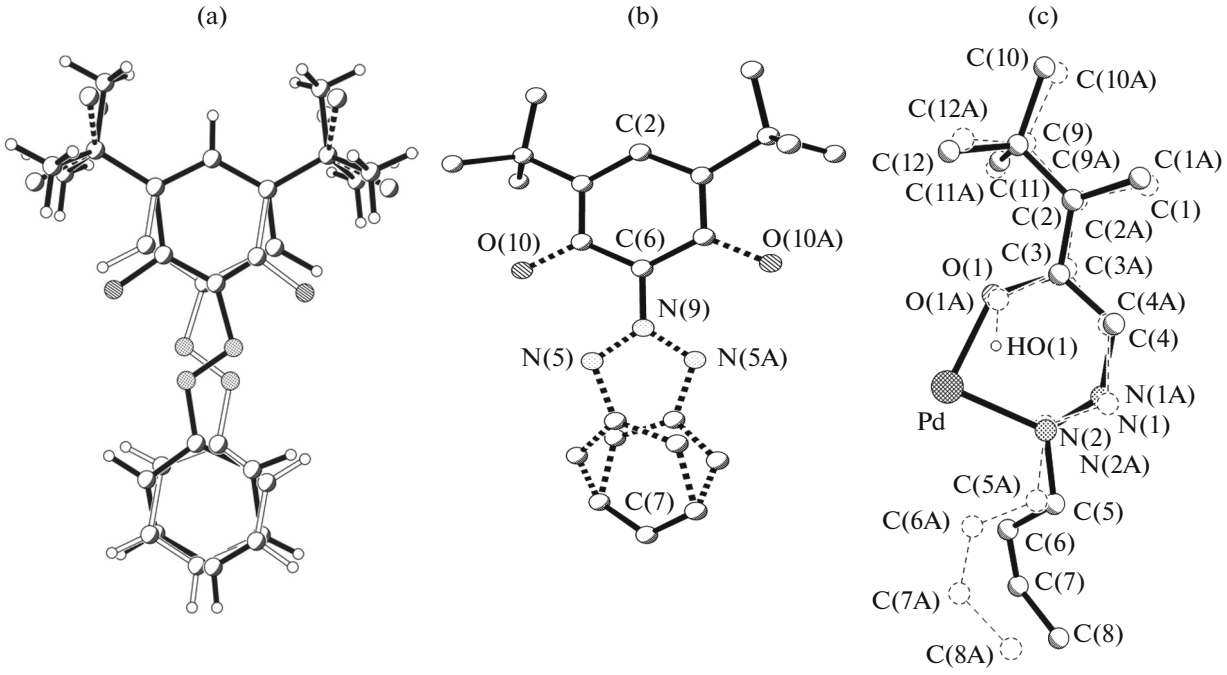


Fig. 2. (a) Character of structure disordering in ligand L and the superposition of the independent part of ligand L over the positions of the atoms of the chelate cycles in complexes (b) **I** and (c) **II**.

dium complexes with the PdO_2N_2 coordination: 4.008–4.014 and 4.060–4.110 Å [6, 10]. Similar distances for complex **I** are 4.00 and 4.04 Å, respectively. The elongation of the Ni–O and Ni–N bonds is observed in complexes **I** and **II**. For instance, the Ni–O and Ni–N bond lengths in complex **I** are 2.00 and 2.02 Å, respectively. In a series of the square complexes with the MO_2N_2 coordination node, similar bond lengths lie in ranges of 1.816–1.845 and 1.882–1.904 Å [15, 16].

From the formal point of view, an insignificant rearrangement of the fragment of the ligand is sufficient for complex formation: the distance between the nitrogen atoms in the ligand equal to 5.08 Å should reach its value in the complex (4.04 Å). This means that a molecule of the future complex is virtually specified by the mutual arrangement of the ligand molecules, which is shown in Fig. 5.

The calculations gave the structure in which both ligands nearly retain their arrangements as in the initial crystal of L. In this case, the molecules become planar (the phenyl rings turned at an angle of 12.4°).

Selected bond lengths calculated for ligand L' isolated from the palladium complex are compared with the bond lengths of ligand L in the crystal, which were determined by XRD (Table 3). As can be seen from that data in Table 3, the differences in bond lengths do not exceed 0.1 Å.

Table 2. Main crystallographic parameters for crystals of compounds L, **I**, and **II**

Parameter	Value		
	L	**I**	**II**
Empirical formula	$C_{20}H_{26}N_2O$	$C_{40}H_{50}N_4O_2Ni$	$C_{40}H_{50}N_4O_2Pd$
FW	310.43	677.55	725.27
Crystal system, space group	Hexagonal, $R\bar{3}c$		
Cell parameters	a = 23.626(3) Å, α = 90° b = 23.626(3) Å, β = 90° c = 17.561(4) Å, γ = 120°	a = 23.770(3) Å, α = 90° b = 23.770(3) Å, β = 90° c = 17.224(4) Å, γ = 120°	a = 23.806(6) Å, α = 90° b = 23.806(6) Å, β = 90° c = 17.330(3) Å, γ = 120°
Cell volume, Å^3	8489(2)	8428(3)	8506(3)
Z; density, g/cm^3	18; 1.093	18; 1.221	18; 1.271

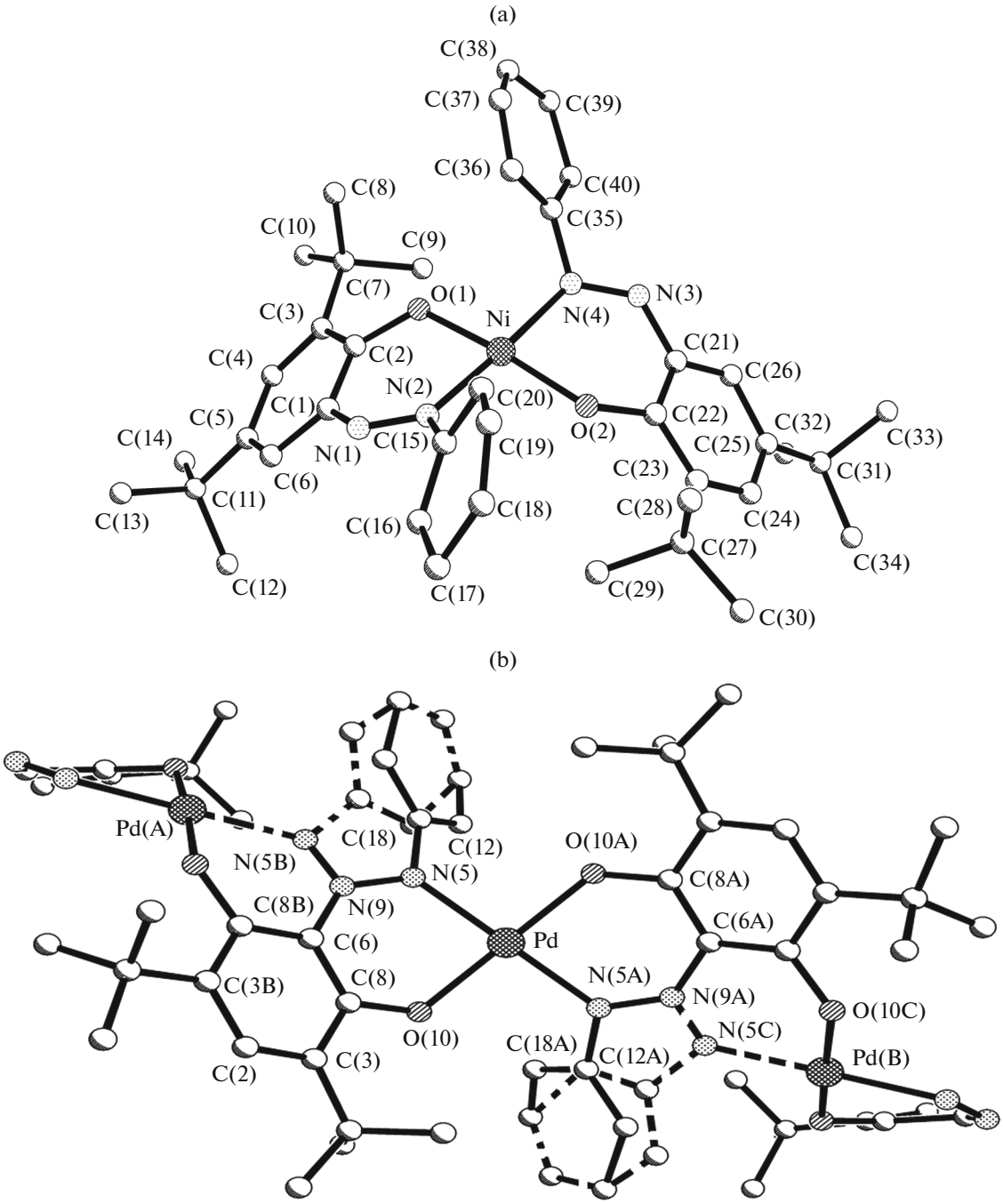


Fig. 3. General views of complexes (a) **I** and **II** (b).

Upon complex formation, the ligand insignificantly changes its configuration due to the turn of the phenyl ring around the N(3)–C(18) bond by 12.4°. The energy of the phenyl fragment turning is only 6.2 kcal/mol.

It is of interest that all the three compounds crystallize in the same space group $R\bar{3}c$ with close parameters if the complexes were synthesized in the liquid phase. An analysis of the molecular and crystal structures of ligand L and complexes **I** and **II** shows that the ligand structure remains almost unchanged upon the formation of the complexes. Since a sufficient space remains unoccupied in the crystal structure of the ligand for the arrangement of metal ions, the crystal structures of the complexes are determined by the ligand packing.

The calculations performed using the VASP 5.3.3 software (Vienna ab-initio simulation program) by the

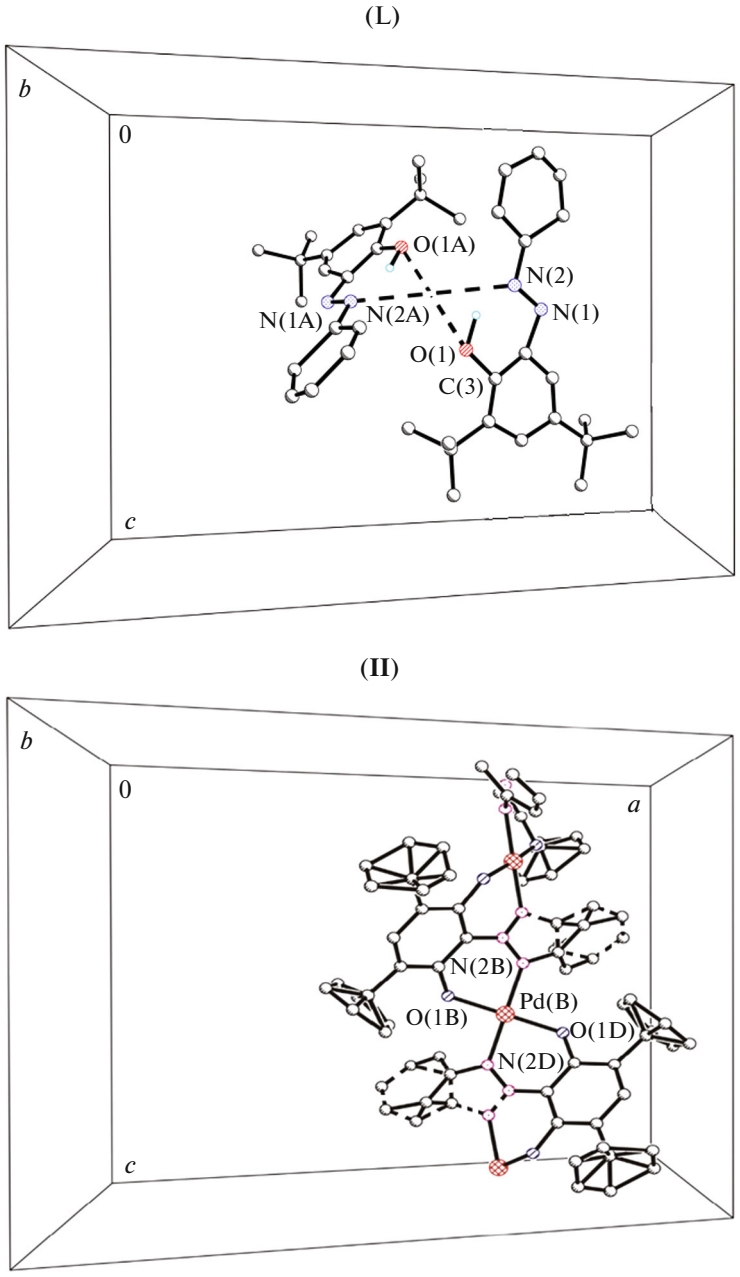


Fig. 4. Character of packing of ligand L and complex **II** lying on the 3-fold axis in the projection along parameter *b* on the *a*0*c* plane.

Table 3. Selected bond lengths in ligand L calculated for its isolated state and experimentally determined by XRD

Bond length, Å	Calculation	Experiment
O(1)–C(2)	1.346	1.438(9)
N(1)–N(2)	1.273	1.261(4)
N(1)–C(1)	1.414	1.468(12)
N(2)–C(15)	1.394	1.399(6)

in box method, i.e., taking into account the crystalline environment, confirm the above conclusions.

Thus, the calculations performed completely confirm our conclusion about the determining role of the crystal structure of ligand L in the formation of the unusual crystal structures of its complexes.

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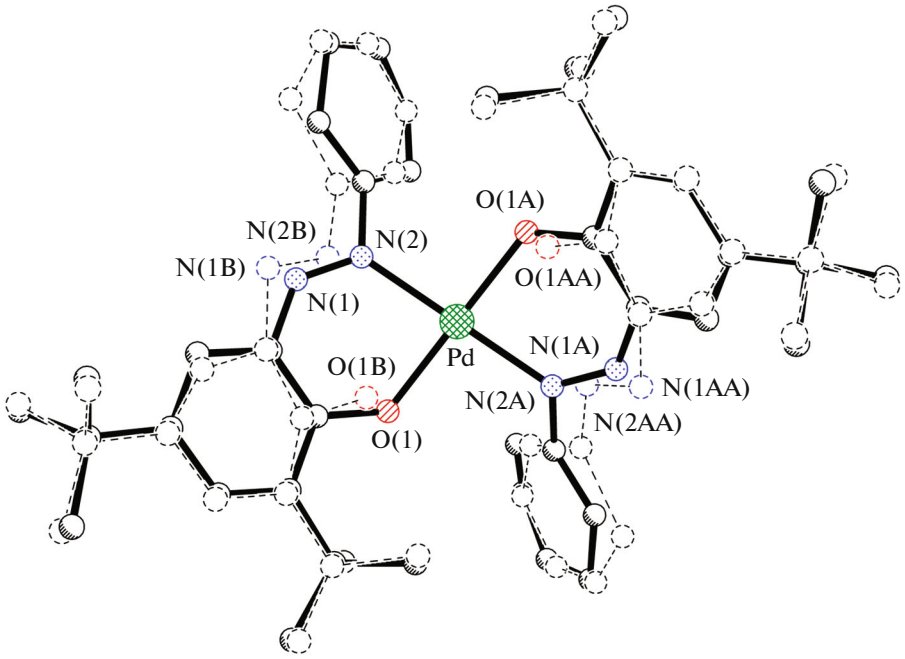

Fig. 5. Superposition of complex **II** (solid line) with two L molecules (dashed lines) over atoms O(1)(O(1B)), N(2)(N(2B)), O(1A)(O1AA)), and N(2A)(N(2AA)).

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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