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Oxidative dehydrogenation of *N*-methyl-*o*-phenylenediamine coordinated to the Pd^{II} and Pt^{II} atoms

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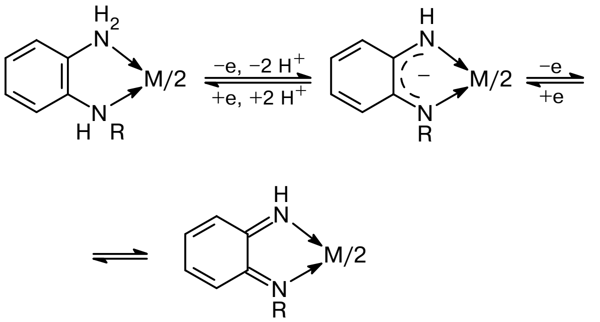
The reactions of *N*-methyl-*ortho*-phenylenediamine (**1**) with K_2MCl_4 (M = Pd or Pt) were investigated. At the first stage, the tetraamine dicationic complexes $[(C_6H_4(NH_2)(NMeH))_2M]Cl_2$ were formed. Oxidation of these compounds with atmospheric oxygen in an alkaline medium afforded the neutral semiquinonediimine complexes $[C_6H_4(NH)(NMe)]_2M$. The structures of the $\{[(C_6H_4)(NH_2)(NHMe)]_2Pd\}Cl_2$ and $[C_6H_4(NH)(NPh)]_2Pt$ complexes were established by X-ray diffraction analysis.

Key words: 1,2-diamines, platinum and palladium complexes, semiquinonediimines, oxidative dehydration, X-ray diffraction analysis.

One of the most important properties of aromatic *ortho*-diamines coordinated to transition metal atoms is their ability to undergo in-sphere oxidative dehydrogenation.[1] This property is associated with a decrease in the basicity and, correspondingly, with an increase in the acidity of the amino groups due to the electron density redistribution upon the formation of metal—nitrogen bonds. It is assumed that this process involves a sequence of one-electron stages accompanied by a loss of protons.[2] For the elements of the nickel triad, the first stage of these conversions gives rise to stable planar-square ML_2 complexes, where L is the *o*-semiquinonediimine ligand (Scheme 1).[1—4]

Scheme 1



Previously,[3] when studying oxidation of *ortho*-phenylenediamine and its *N*-phenyl-substituted analog (**1**) in the presence of K_2MCl_4 (M = Pt or Pd), we have found that this reactions afforded semiquinonediimine complexes whose metal centers are coordinated by the deprotonated ligands with the *trans* arrangement of the phenyl substituents at the nitrogen atoms.

To gain a detailed knowledge of the oxidation process of aromatic diamines coordinated to the platinum or palladium metals, we studied the reactions involving *N*-methyl-substituted *ortho*-phenylenediamine. The results of the present investigation provide an idea of intermediates formed at the first stage of the reactions of diamines with the tetrachlorometallate dianion.

Results and Discussion

As mentioned above, oxidation of compound **1** in the presence of K_2PtCl_4 in aqueous alkali in air afforded the semiquinonediimine platinum(II) complex $[C_6H_4(NH)(NPh)]_2Pt$ (**2**) with the *trans* arrangement of the phenyl substituents.[3]

In the reactions of *N*-methyl-substituted phenylenediamine with K_2MCl_4 (M = Pd or Pt), we detected the bis-chelate dicationic complex $\{[(C_6H_4)(NH_2)(NHMe)]_2Pd\}Cl_2$ (**3**), which was formed as an intermediate at the initial stage, and isolated this complex as a solvate with a water molecule (Scheme 2).

The IR spectrum of complex **3** · H_2O has symmetric and asymmetric stretching bands ν(N—H) at 3278, 3141, and 3037 cm^{-1} and a medium intensity band δ(H—O—H) at 1602 cm^{-1}. According to the data from X-ray diffraction analysis of dark-red crystals of solvate **3** · H_2O (Figs. 1 and 2, Table 1), the metal atom in the

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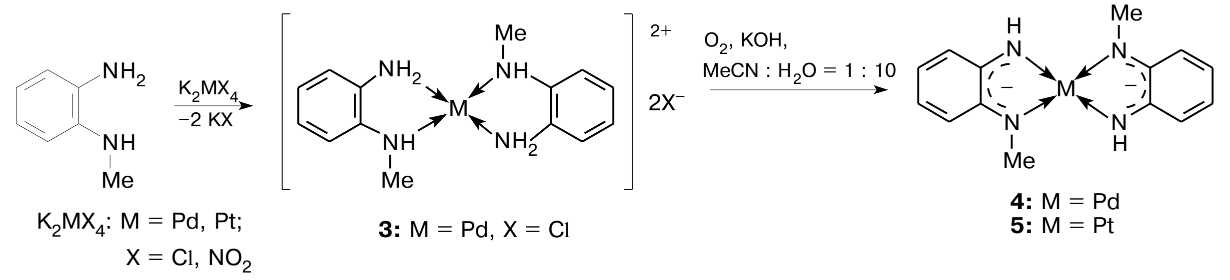
Scheme 2



dication has a square-planar environment formed by four nitrogen atoms of two ligands with the nonequivalent Pd—N distances (1.996(7) and 2.08(1) Å).

Apparently, the observed distortions are caused by a complex system of hydrogen bonds with the participation of the water molecules, the dications, and the chloride ions responsible for the molecular packing in the crystal. The adjacent $\{[(C_6H_4)(NH_2)(NHMe)]_2Pd\}^{2+}$ dications are linked in infinite layers through intermolecular interactions between the oxygen atoms of the water molecules and the hydrogen atoms of the N(Me)H groups (O...H are 2.17(3) and 2.38(3) Å) (Fig. 1). In the layer, short contacts between the chloride anions and the amino groups (Cl...H are 2.13(3) and 2.17(3) Å) are observed. In addition, the chloride anions form symmetrical contacts with the hydrogen atoms of the water molecules of solvation (Cl...HOH...Cl is 2.24(3) Å). The layers are linked *via* hydrogen bonds between the hydro-

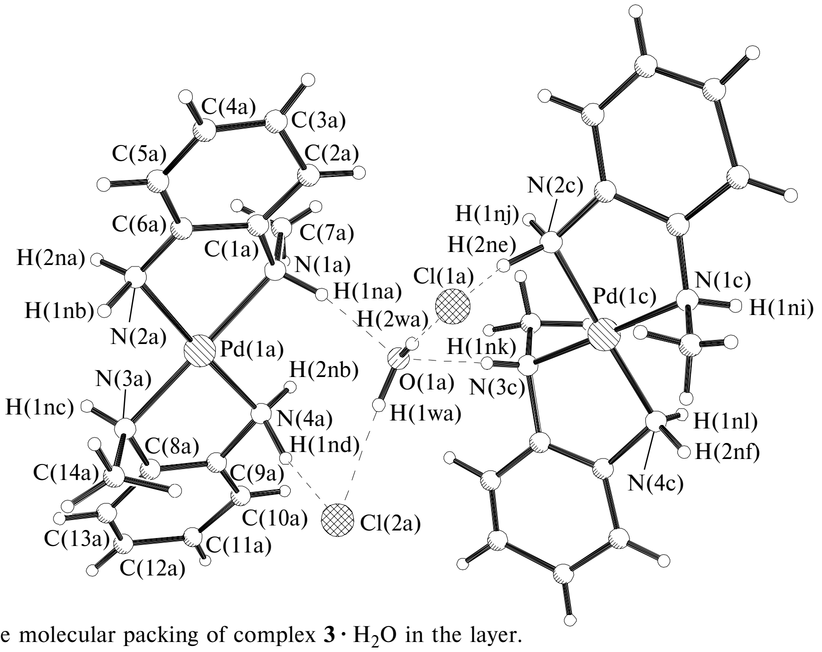


Fig. 1. Fragment of the molecular packing of complex **3** · H_2O in the layer.

Table 1. Principal geometric characteristics of compound **3**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Pd(1)—N(1)	2.08(1)	N(1)—Pd(1)—N(2)	81.2(4)	N(1)—Pd(1)—N(3)	179.3(3)
Pd(1)—N(3)	2.04(1)	N(2)—Pd(1)—N(3)	98.0(3)	N(1)—Pd(1)—N(4)	96.2(4)
N(1)—C(1)	1.36(1)	N(2)—Pd(1)—N(4)	177.1(4)	N(3)—Pd(1)—N(4)	84.6(4)
N(2)—C(6)	1.41(2)	Pd(1)—N(1)—C(1)	109.3(6)	Pd(1)—N(1)—C(7)	113.3(7)
N(3)—C(14)	1.492(6)	C(1)—N(1)—C(7)	109.3(6)	Pd(1)—N(2)—C(6)	108.7(5)
Pd(1)—N(2)	2.075(7)	Pd(1)—N(3)—C(8)	106.6(5)	Pd(1)—N(3)—C(14)	112.0(7)
Pd(1)—N(4)	1.996(7)	C(8)—N(3)—C(14)	112.4(5)	Pd(1)—N(4)—C(9)	109.1(6)
N(1)—C(7)	1.517(7)	N(1)—C(1)—C(2)	122.6(7)	N(1)—C(1)—C(6)	118.4(10)
N(3)—C(8)	1.53(1)	N(2)—C(6)—C(1)	115.0(7)	N(2)—C(6)—C(5)	124.3(7)
N(4)—C(9)	1.51(2)	N(3)—C(8)—C(9)	116.9(10)	N(3)—C(8)—C(13)	121.2(7)
		N(4)—C(9)—C(8)	117.2(7)	N(4)—C(9)—C(10)	121.8(9)

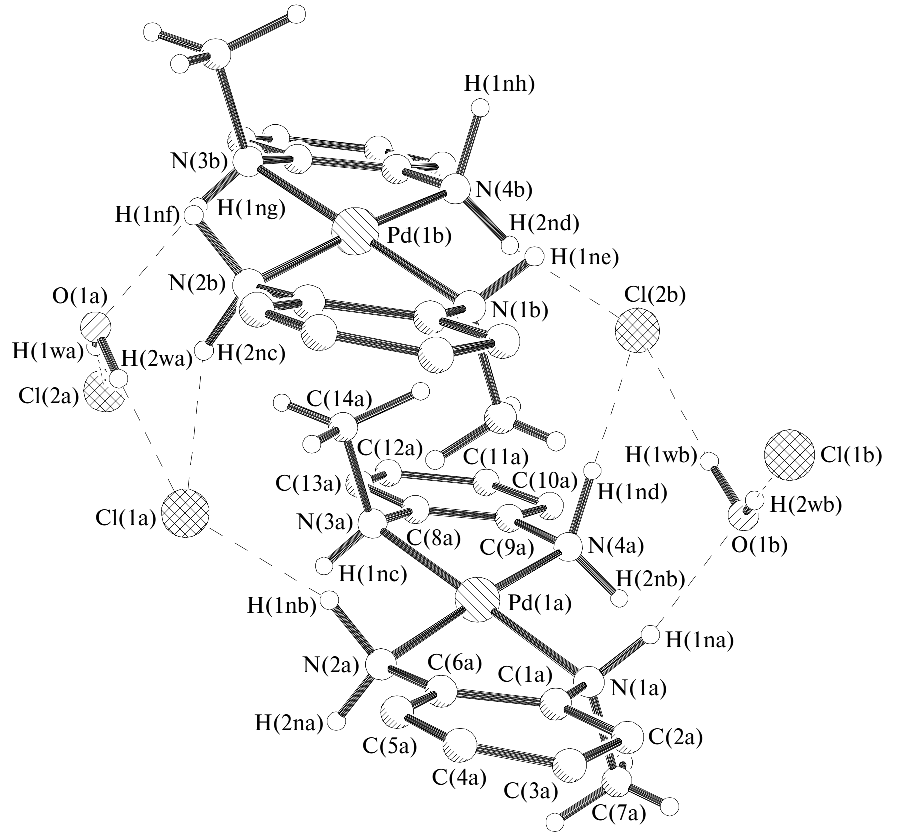


Fig. 2. Fragment of the molecular packing of complex $3 \cdot H_2O$ between the layers.

gen atoms of the amino groups and the chloride anions (Cl...H—N are in the range of 2.22(3)—2.23(3) Å) (Fig. 2). The methyl substituents at the nitrogen atoms (N—C are 1.517(7) and 1.492(6) Å) are in *trans* positions with respect to each other.

In an alkaline solution of MeCN, complex **3** is oxidized with atmospheric oxygen to form blue crystals of the only compound $[C_6H_4(NH)(NMe)]_2Pd$ (**4**), which was characterized by the data of elemental analysis, IR spectroscopy, and mass spectrometry.

We failed to isolate the pure dicationic platinum-containing intermediate (an analog of **3**) because it was almost immediately oxidized to form the semiquinonediimine complex $[C_6H_4(NH)(NMe)]_2Pt$ (**5**). The overall geometry of molecule **5** is analogous to that observed for *N*-phenyl-substituted complex **2** [3] (Fig. 3).

In molecule **5** (Fig. 3, Table 2), the platinum atom has a square-planar environment formed by the nitrogen atoms of two chelate ligands existing in the semiquinonediimine form (Pt—N, 1.954(9)—1.978(12) Å). The N—C and C—C distances (1.341(16)—1.406(16) Å and 1.415(17) Å, respectively) in both C_2N_2Pt metallocycles are shortened. Both phenylene fragments are in a single plane. The methyl substituents are in the *trans* arrangement (N—C is 1.505(16) Å).

In molecule **5**, the positions of the hydrogen atoms of both the rings and the NH groups (N—H is 0.84(5) Å) were revealed. The ^1H NMR spectrum of complex **5** in

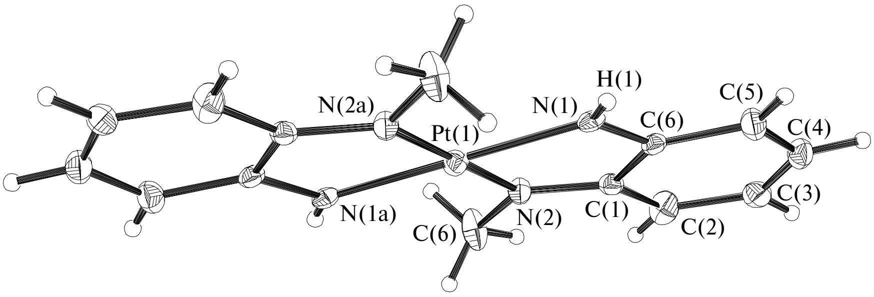


Fig. 3. Structure of the semiquinonediimine complex $Pt[C_6H_4(NH)(NMe)]_2$ (**5**).

Table 2. Principal geometric characteristics of monomer **5**

Bond	*d*/Å	Angle	ω/deg
Pt(1)—N(1)	1.978(12)	N(1)—Pt(1)—N(2)	80.0(4)
Pt(1)—N(1A)	1.978(12)	N(2)—Pt(1)—N(1A)	100.0(4)
N(1)—C(6)	1.403(16)	N(2)—Pt(1)—N(2A)	180.0(1)
N(2)—C(7)	1.505(16)	Pt(1)—N(1)—C(6)	113.3(8)
C(1)—C(6)	1.415(17)	Pt(1)—N(2)—C(7)	125.1(9)
C(3)—C(4)	1.357(20)	N(2)—C(1)—C(2)	127.9(12)
C(5)—C(6)	1.422(22)	N(1)—C(6)—C(1)	115.6(12)
Pt(1)—N(2)	1.954(9)	N(1)—Pt(1)—N(1A)	180.0(1)
Pt(1)—N(2A)	1.954(9)	N(1)—Pt(1)—N(2A)	100.0(4)
N(2)—C(1)	1.341(16)	N(1A)—Pt(1)—N(2A)	80.0(4)
C(1)—C(2)	1.409(18)	Pt(1)—N(2)—C(1)	118.5(8)
C(2)—C(3)	1.405(22)	C(1)—N(2)—C(7)	116.1(10)
C(4)—C(5)	1.366(21)	N(2)—C(1)—C(6)	112.1(11)
		N(1)—C(6)—C(5)	124.5(12)

$CDCl_3$ has a broad singlet ($\Delta\nu_{1/2}$ = 34.5 Hz) at δ 8.02 (2 H), which is in agreement with the presence of the proton of the NH group.

The reactions with the use of the corresponding nitrites, *viz.*, $K_2[M(NO_2)_4]$, instead of potassium tetrachloropalladate(II) or potassium tetrachloroplatinate(II) as the staring compounds afforded the final mononuclear semiquinonediimine complexes **4** and **5** in substantially higher yields. However, attempts to detect intermediate "tetraamine" dications in these reactions failed.

Experimental

The complexes were synthesized under an inert atmosphere in anhydrous solvents. The initial K_2MCl_4 complexes were prepared according to known procedures.[5] New compounds were synthesized with the use of *N*-methyl-*o*-phenylenediamine (Fluka). The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets. The ^1H NMR spectra were measured on a Varian VXR-400 spectrometer operating at 400 MHz in $CDCl_3$ (Fluka) with Me_4Si as the internal standard. The mass spectra (electrospray ionization, ESI) of complex **4** were obtained on a Finnigan LCQ instrument.

Synthesis of bis[η²-*N*,*N*′-(*N*-methyl-*o*-phenylenediamine)]palladium(II) dichloride monohydrate, $[\{C_6H_4(NH_2)(NMeH)\}_2Pd]^+Cl_2^- \cdot H_2O$ (3). *N*-Methyl-*o*-phenylenediamine (0.56 g, 4.6 mmol) was added to a solution of $K_2[PdCl_4]$ (0.5 g, 2.27 mmol) in a 1 : 1 MeCN—water mixture (100 mL) in air. The reaction mixture was stirred until the pink residue that intially formed was dissolved. The resulting red solution was kept at ~20 °C for 18 h. The dark-red crystals that formed were separated from the solution by decantation, washed successively with water and hexane, and dried under a stream of argon at ~20 °C. Compound **3** was obtained in a yield of 0.22 g (92%). Found (%): C, 38.3; H, 5.1; N, 12.6. $C_{14}H_{22}N_4PdCl_2O$. Calculated (%): C, 38.23; H, 5.0; N, 12.75.

IR, ν/cm^{-1}: 3278 s, 3141 s, 3037 v.s, 2976 s, 2805 s, 1611 w, 1607 m, 1602 w, 1324 v.s, 1321 m, 1316 m, 1028 m, 1023 w, 1012 s, 1007 w, 1002 m, 724 m, 717 m, 711 s, 709 s, 707 v.s, 702 m, 424 w, 417 w, 414 w, 405 s.

Synthesis of bis[η²-*N*,*N*′-(*N*-methyl-*o*-benzosemiquinonediimine)]palladium(II), $[C_6H_4(NH)(NMe)]_2Pd$ (4). ***A.*** *N*-Methyl-*o*-phenylenediamine (0.36 g, 3 mmol) and solid KOH (1 g) were added to a solution of K_2PdCl_4 (0.5 g, 1.5 mmol) in water (25 mL). The resulting solution was kept at 90 °C for 1 h. The black precipitate that formed was filtered off from the mother liquor, washed with water, dried on a filter, and dissolved in CH_2Cl_2 (50 mL). The dark-violet solution was concentrated to 10 mL and transferred to a chromatography column (Al_2O_3, 3×5 cm). The blue band (R_f 0.10) was eluted with CH_2Cl_2 (30 mL). An equal volume of hexane was added to the resulting solution and the mixture was concentrated to 5 mL *in vacuo* (0.1 Torr). The black-violet needle-like crystals that formed upon storage at ~20 °C for two days were separated from the solution by decantation, washed with hexane, and dried in air. Compound **4** was obtained in a yield of 11 mg (2%).

B. A mixture of $K_2[Pd(NO_2)_4]$ (0.5 g, 1.4 mmol) and *N*-methyl-*o*-phenylenediamine (0.33 g, 2.7 mmol) was dissolved in a 10 : 1 MeCN—water mixture (40 mL) and the solution was heated at 90 °C. Then solid KOH (10 g) was added and the reaction mixture was heated for 3 h. Then the solution was cooled to ~20 °C and kept for 24 h. The black precipitate that formed was filtered off, washed with hexane, and dissolved in CH_2Cl_2 (30 mL). The dark-violet solution was transferred on a chromatography column (Al_2O_3, 3×5 cm) and the blue band (R_f 0.10) was eluted with CH_2Cl_2 (30 mL). An equal volume of hexane was added to the resulting solution. The mixture was concentrated to 30 mL *in vacuo* (0.1 Torr) and kept at ~20 °C for two days. The black-violet needle-like crystals that formed were separated from the solution by decantation, washed with hexane, and dried under a stream of argon at ~20 °C. Compound **4** was obtained in a yield of 0.28 g (60%). Found (%): C, 48.6; H, 4.6; N, 16.2. $C_{14}H_{16}N_4Pd$. Calculated (%): C, 48.50; H, 4.62; N, 16.17.

MS (*m/z*): 344 [M]$^+$. IR, ν/cm^{-1}: 3019 w, 2970 w, 2928 m, 2852 w, 1645 m, 1535 m, 1468 m, 1450 m, 1363 s, 1332 s, 1283 s, 1141 s, 1116 m, 1061 m, 927 w, 831 m, 740 v.s, 622 s, 610 s, 561 m, 512 m, 480 m.

Synthesis of bis[η²-*N*,*N*′-(*N*-methyl-*o*-benzosemiquinonediimine)]platinum(II), $[C_6H_4(NH)(NMe)]_2Pt$ (5). ***A.*** *N*-Methyl-*o*-phenylenediamine (0.29 g, 2.4 mmol) was added to a solution of K_2PtCl_4 (0.5 g, 1.1 mmol) in water (25 mL). The resulting solution was treated with solid KOH (1 g) and stirred at 90 °C for 1 h. The black precipitate that formed was filtered off, washed with water, dried on a filter, and dissolved in CH_2Cl_2 (50 mL). The dark-violet solution was transferred to a chromatography column (Al_2O_3, 3×5 cm) and the blue band was eluted with CH_2Cl_2 (30 mL) (R_f 0.90). An equal volume of hexane was added to the resulting solution. The mixture was concentrated to 30 mL *in vacuo* (0.1 Torr) and kept at ~20 °C for two days. The copper-colored needle-like crystals that formed were separated from the solution by decantation, washed with hexane, and dried under a stream of argon at ~20 °C. Compound **5** was obtained in a yield of 24 mg (5 %).

B. A mixture of $K_2[Pt(NO_2)_4]$ (0.5 g, 1.1 mmol) and *N*-methyl-*o*-phenylenediamine (0.27 g, 2.19 mmol) was dissolved in a 10 : 1 MeCN—water mixture (40 mL) and kept at 80 °C for 2 h. The resulting violet solution was slowly cooled to ~20 °C and kept for 18 h. The copper-colored finely crystalline product that formed was separated from the violet mother liquor by decantation, washed with hexane, and dried *in vacuo* (0.1 Torr). Compound **5** was obtained in a yield of 0.40 g (85%). Found (%): C, 38.6; H, 3.6; N, 12.9. $C_{14}H_{16}N_4Pt$. Calculated (%): C, 38.62; H, 3.68; N, 12.87.

IR, ν/cm^{-1}: 3018 w, 2969 w, 2926 m, 2851 w, 1647 m, 1536 m, 1468 m, 1450 m, 1363 s, 1332 s, 1283 s, 1141 s,

Table 3. Crystallographic parameters of complexes **3** and **5**

Parameter	**3** · H$_2$O	**5**
Molecular formula	$C_{14}H_{20}N_4PdCl_2 \cdot H_2O$	$C_{14}H_{16}N_4Pt$
Space group	*Cc*	$P2_1/c$
a/Å	25.498(8)	5.224(2)
b/Å	5.438(2)	10.608(3)
c/Å	15.136(4)	12.047(4)
α/deg	90	91.594(3)
β/deg	121.18(2)	90.18(2)
γ/deg	90	107.632(3)
V/Å^3	1796(2)	667.7(4)
Z	4	2*
ρ_{calc}/g cm^{-3}	1.676	2.154
μ/cm^{-1}	13.33	10.50
Radiation	MoKα (λ = 0.71073 Å)	
θ—2θ scan range/deg	3—52	2—60
Number of independent reflections	2001	1206
Number of reflections with $I > 4\sigma$	1731	789
Weighting scheme,	$w^{-1} = \sigma^2(F) + kF^2$	
k	0.00417	0.00001
R_1	0.041	0.040
wR_2	0.047	0.051

* The molecule occupies the crystallographic inversion center.

1116 m, 1061 m, 925 w, 832 m, 740 v.s, 622 s, 610 s, 561 m, 511 m, 480 m.

X-ray diffraction study. Single crystals of **5** suitable for X-ray diffraction study were prepared by slow evaporation of a solution of complex **5** in CH$_2$Cl$_2$ at ~20 °C. The X-ray diffraction data sets for complexes **3** and **5** were collected on an automated four-circle Siemens R3/PC diffractometer (22 °C). The unit cell parameters were determined and refined based on 24 equivalent reflections with $2\theta < 24—28°$. In both cases, three strong standard reflections with $0 < \chi < 65°$ were monitored after each 100 reflections. The intensities of the standard reflections showed no decrease in the course of data collection, and therefore, the corresponding corrections were ignored. The crystallographic parameters and details of the refinement of both structures are given in Table 3.

The structures of both complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms in both structures were located from difference Fourier syntheses and refined isotropically. Absorption corrections were applied for both structures.[6] All calculations were carried out using the SHELXTL PLUS program package (PC version).[7] The principal geometric parameters of complexes **3** and **5** are given in Tables 1 and 2, respectively. The complete tables of the atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database.

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X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences).

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