Unusual condensation of *N*-phenylsemiquinonediimine ligands coordinated to the Ni^{II} atom with an acetone molecule to form a heterocycle

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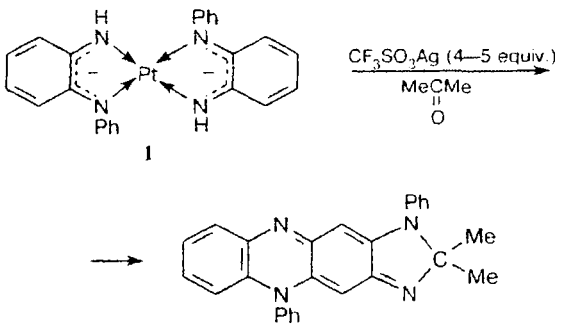
The reaction of a mononuclear Ni^{II} semiquinonediimine complex, *viz.*, $Ni[1,2\text{-}(NPh)(NH)C_6H_4]_2$, with silver triflate was investigated. The starting monomer was not oxidized in benzene or CH_2Cl_2 solutions; instead, a solvate of the complex with C_6H_6 was formed. According to the X-ray diffraction data, the solvate is characterized by an unusual molecular packing with short $C{-}H(C_6H_6)\cdots Ni$ and $C{-}H(C_6H_6)\cdots N{-}H$ contacts. An analogous effect is observed in the crystals of the solvate $Pt[1,2\text{-}(NPh)(NH)C_6H_4]_2 \cdot C_6H_6$. Grinding of the nickel complex with silver triflate (the reagent ratio was 1 : 5) in the presence of acetone led to the oxidation of the complex, yielding tetrahydroimidazophenazinium triflate, whose structure was established by X-ray diffraction analysis.

Key words: nitrogen-containing heterocyclic compounds, semiquinonediimine complexes of nickel and platinum.

Researchers engaged in directed synthesis of nitrogen-containing heterocycles face a serious problem associated with the fact that the chemical assembly of the target molecules is a complex multistage process, which often hinders control over the chemical reactions and affords many by-products.[1] However, the use of organic ligands which are coordinated to transition metal atoms and generally exhibit high reactivity can be very efficient in such a situation. For example, we have demonstrated recently that the oxidation of the platinum(II) complex, $Pt[1,2\text{-}(NPh)(NH)C_6H_4]_2$ (**1**), by silver triflate (CF_3SO_3Ag) in the presence of acetone led to the condensation of two semidiimine fragments coordinated to the platinum atom with the Me_2CO molecule to form an imidazophenazine derivative[2] (Scheme 1).

Scheme 1



In this case, the heterocycle formation involves the intermediate formation of a binuclear complex dication $\{Pt[1,2\text{-}(NPh)(NH)C_6H_4]_2\}_2^{2+}$ (**2**) containing Pt^{III} atoms. According to the NMR data, this dication can weakly coordinate acetone molecules.[2,3] This new type of conversions involving platinum atoms gave impetus to further investigations along this line. In the present work, we report data on the oxidation of a nickel analog of complex **1**.

Results and Discussion

Previously, we have demonstrated that the $Ni[1,2\text{-}(NPh)(NH)C_6H_4]_2$ complex (**3**) can be prepared in high yield by the reaction of the oligomeric nickel hydroxopivalate complex with *N*-phenyl-*o*-phenylenediamine.[4] However, the formation of the dimeric cation analogous to platinum derivative **2** was not observed in the reaction of complex **3** with 2 equiv. of CF_3SO_3Ag in benzene or CH_2Cl_2.[2,3] Recrystallization of the reaction products from benzene afforded solvate $\mathbf{3} \cdot C_6H_6$ as the major product. A solvate of analogous composition ($\mathbf{1} \cdot C_6H_6$) was obtained upon recrystallization of platinum analog **1** from benzene in the absence of silver triflate. According to the X-ray diffraction data, the principal geometric parameters of complexes **1** and **3** in both solvates are virtually identical to the corresponding characteristics determined previously for the nonsolvated molecules[2,4] (Table 1). However, a somewhat unusual molecular packing is noteworthy (Fig. 1).

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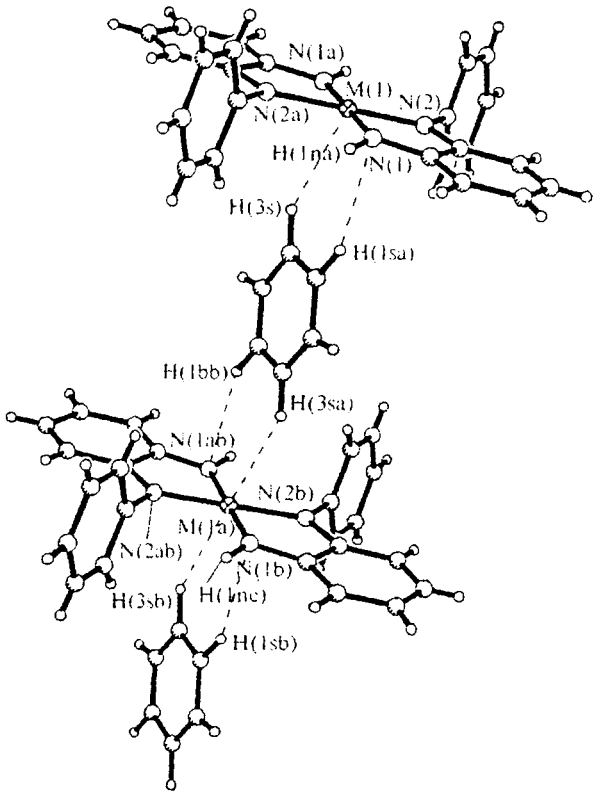


Fig. 1. Fragments of the molecular packings of the solvates $1 \cdot C_6H_6$ (M = Pt) and $3 \cdot C_6H_6$ (M = Ni).

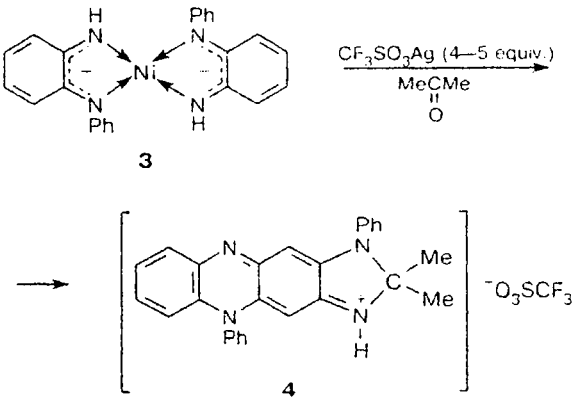
In the crystals of both solvates, the benzene molecules are located between molecules of the complexes in such a manner that the hydrogen atoms of the C_6H_6 molecules of solvation form weak nonbonded interactions with the metal centers ($M \cdots H(C_6H_6)$ are 3.071(7) and 3.004(4) Å for M = Pt and Ni, respectively) and the nitrogen atoms of the NH groups (H...NH are 2.983(14) and 2.843(4) Å for M = Pt and Ni, respectively). It should be noted that these interactions were not detected by NMR spectroscopy in solutions in C_6D_6 in a wide temperature range (from −55 to 80 °C). Probably,

Table 1. Principal bond lengths (d) and bond angles (ω) in the complexes [M(1,2-(NH)(NPh)C_6H_4)$_2$] (M = Pt (**1**) or Ni (**3**)) and their solvates with benzene

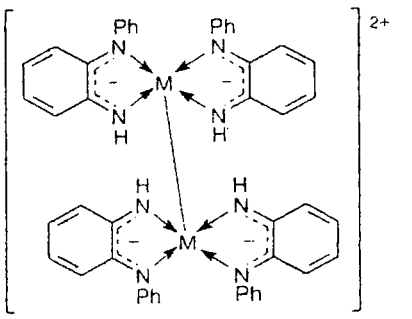
Parameter	**1**[2]	**3**[4]	$1 \cdot C_6H_6$	$3 \cdot C_6H_6$
Bond		d/Å		
M—N(H)	1.954(4)	1.826(3)	1.976(9)	1.832(3)
M—N(Ph)	1.989(6)	1.863(4)	1.959(8)	1.855(4)
C—N(H)	1.368(7)	1.345(6)	1.326(14)	1.341(7)
C—C	1.443(8)	1.423(6)	1.415(14)	1.427(5)
C—N(Ph)	1.331(9)	1.364(5)	1.336(14)	1.351(6)
N···H(C_6H_6)			2.983	2.843
M···H(C_6H_6)			3.071	3.004
Angle		ω/deg		
N(H)—M—N(Ph)	79.7(2)	84.2	78.4(4)	83.6(2)

it is for this reason that complex **3** was most efficiently oxidized upon grinding of the solid crystalline nonsolvated complex with a large excess of CF_3SO_3Ag (4—5 equiv.) in the presence of several drops of acetone. In the absence of benzene of solvation, mechanochemical treatment can result in reorientation of molecules **3** in such a way that the C—H groups of the phenylene rings of the coordinated ligands fulfill the function of the analogous groups of the benzene fragments. As a result, the formation of new M...H—C (the phenylene fragment of the ligand of the adjacent molecule) and N...H—C contacts is quite possible. These contacts stimulate activation of C—H bonds for subsequent condensation of the ligands of the adjacent molecules. In this case, H atoms can be accepted by either atmospheric oxygen or O atoms of acetone molecules, which (as has been mentioned previously[3]) can be weakly coordinated to the metal atoms. This reaction of nickel complex **3**, like that of platinum derivative **1**, afforded heterocycle **4**. The latter appeared to be protonated due apparently to a too large excess of silver triflate, which can readily be hydrolyzed by water eliminated in the course of the reaction (Scheme 2).

Scheme 2



It should be noted that this scheme formally does not exclude the formation of a short-lived dimer containing Ni^{III} atoms (**5**), which should be substantially less stable than the platinum analog **2** prepared previously, due to



M = Pt (**2**), Ni (**5**)

steric hindrances between the planar mononuclear fragments, resulting in substantial weakening of the M—M bond. For example, the Pt—Pt bond lengths in complex **2** are 3.260 Å.[2]

The structure of heterocyclic compound **4** was established by X-ray diffraction analysis (Fig. 2, Table 2).

In conclusion, it should be noted that the involvement of an acetone molecule in the transformations which include complexes **1**[2] or **3** is a very unusual phenomenon. There are only two examples of condensation of *o*-phenylenediamine ligands coordinated to the copper(II) or nickel(II) atoms in the complexes $[M(1,2\text{-}(NH_2)_2C_6H_4)_2](ClO_4)_2$,[5,6] whose oxidation with atmospheric oxygen in acetonitrile gave rise to 2,3-diaminophenazine[5] or its protonated form.[6] Apparently, the latter reaction also proceeded through the formation of metal complexes with coordinated semidiimine fragments, but the involvement of solvent molecules has not been observed.

Experimental

The complexes were synthesized both in air and under an inert atmosphere with the use of anhydrous solvents. The starting complexes **1** and **3** were prepared according to known procedures.[2,4] The IR spectra were recorded on a Specord M80 instrument in KBr pellets. The ^1H and ^{13}C NMR spectra were measured on a Varian VXR-400 spectrometer operating at 400 MHz (^1H). The solvents, *viz.*, C_6D_6, CD_2Cl_2, and $CDCl_3$, were purchased from Fluka; Me_4Si was used as the standard.

Preparation of the solvates $M[1,2\text{-}(NPh)(NH)C_6H_4]_2 \cdot C_6H_6$, *trans*-bis(*N*-phenyl-*o*-benzosemiquinonediimino)nickel(II) [and platinum(II)] benzene monosolvates. A solution of CF_3SO_3Ag (0.610 g, 2.374 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $Ni[1,2\text{-}(NPh)(NH)C_6H_4]_2$ (1 g, 2.374 mmol) in benzene (50 mL). The reaction mixture was refluxed for 3 h, the color of the solution remaining unchanged. The solvent was

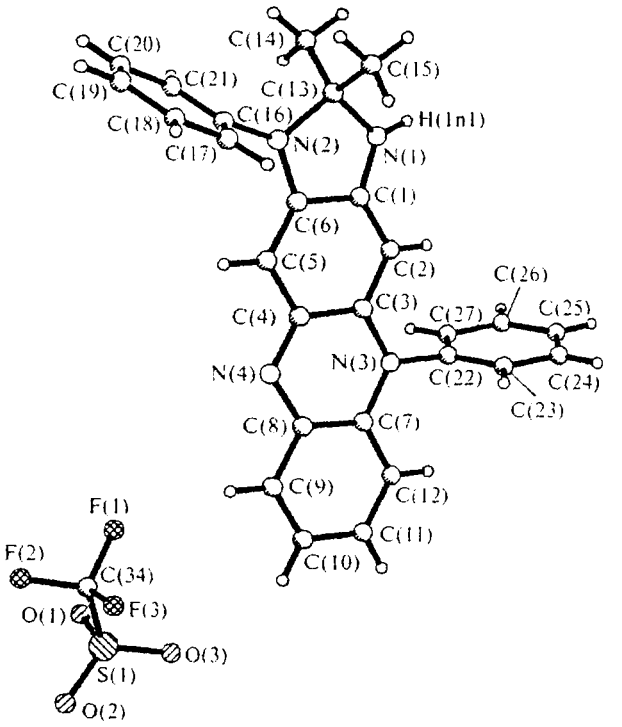


Fig. 2. Structure of compound **4**.

Table 2. Selected geometric characteristics of heterocycle **4**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
N(1)—C(1)	1.327(2)	N(2)—C(16)	1.439(2)	C(5)—C(6)	1.357(2)
N(1)—C(13)	1.472(2)	N(3)—C(22)	1.452(2)	C(7)—C(8)	1.406(2)
N(2)—C(6)	1.363(2)	C(13)—C(14)	1.525(2)	C(8)—C(9)	1.407(2)
N(2)—C(13)	1.488(2)	C(13)—C(15)	1.527(2)	C(9)—C(10)	1.376(2)
N(3)—C(3)	1.370(2)	C(1)—C(6)	1.450(2)	C(10)—C(11)	1.404(2)
N(3)—C(7)	1.391(2)	C(1)—C(2)	1.386(2)	C(11)—C(12)	1.380(2)
N(4)—C(4)	1.323(2)	C(2)—C(3)	1.390(2)	C(7)—C(12)	1.407(2)
N(4)—C(8)	1.371(2)	C(4)—C(5)	1.429(2)	C(3)—C(4)	1.467(2)
Angle	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**
N(1)—C(13)—N(2)	100.17(2)	C(2)—C(3)—C(4)	121.4(2)	C(7)—C(8)—C(9)	118.9(2)
N(1)—C(13)—C(14)	111.01(14)	C(3)—N(3)—C(7)	121.75(14)	C(4)—N(4)—C(8)	118.8(2)
N(1)—C(13)—C(15)	109.88(14)	C(3)—N(3)—C(22)	117.50(14)	N(4)—C(4)—C(3)	122.2(2)
N(2)—C(13)—C(14)	112.04(14)	C(7)—N(3)—C(22)	120.70(13)	N(4)—C(4)—C(5)	118.6(2)
N(2)—C(13)—C(15)	110.65(14)	N(3)—C(7)—C(8)	117.7(2)	C(3)—C(4)—C(5)	119.1(2)
C(14)—C(13)—C(15)	112.44(14)	N(3)—C(7)—C(12)	121.9(2)	C(4)—C(5)—C(6)	118.9(2)
C(13)—N(1)—C(1)	112.19(14)	C(8)—C(7)—C(12)	120.5(2)	N(2)—C(6)—C(1)	106.79(14)
N(1)—C(1)—C(2)	129.0(2)	C(7)—C(12)—C(11)	119.1(2)	N(2)—C(6)—C(5)	132.2(2)
N(1)—C(1)—C(6)	108.72(14)	C(12)—C(11)—C(10)	121.0(2)	C(1)—C(6)—C(5)	120.9(2)
C(2)—C(1)—C(6)	122.2(2)	C(10)—C(9)—C(8)	120.6(2)	C(6)—N(2)—C(13)	111.10(13)
C(1)—C(2)—C(3)	117.4(2)	N(4)—C(8)—C(7)	122.7(2)	C(6)—N(2)—C(16)	124.70(14)
N(3)—C(3)—C(2)	121.8(2)	N(4)—C(8)—C(9)	118.4(2)	C(13)—N(2)—C(16)	121.33(13)
N(3)—C(3)—C(4)	116.9(2)				

Table 3. Crystallographic parameters and details of X-ray diffraction study of complexes $1 \cdot C_6H_6$, $3 \cdot C_6H_6$, and **4**

Parameter	$1 \cdot C_6H_6$	$3 \cdot C_6H_6$	**4**
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	8.812(2)	8.883(2)	13.7557(8)
b/Å	8.889(2)	8.932(2)	14.2955(8)
c/Å	9.190(2)	9.042(2)	15.2898(9)
α/deg	83.06(3)	67.83(3)	90
β/deg	66.61(3)	84.66(3)	99.1420(10)
γ/deg	68.91(3)	67.14(3)	90
V/Å^3	616.2(2)	611.0(3)	2968.5(3)
Z	1	1	4
ρ_{calc}/g cm^{-3}	1.718	1.362	1.411
μ/cm^{-1}	5.719	0.820	0.171
θ-2θ scanning range/deg	2.42—56.0	3.0—55.0	1.85—60.06
Number of measured reflections	3154	3120	23903
Number of reflections with $I > 4\sigma$	2964	2934	8608
$F(000)$	312	262	1312
GOOF	1.917	0.471	0.865
R_1	0.079	0.094	0.089
wR_2	0.196	0.127	0.127

removed at 60 °C (0.1 Torr). The solid residue was extracted with benzene (70 mL). The extract was filtered, concentrated to 15 mL at 20 °C (0.1 Torr), and kept at 10 °C for 24 h. The blue-green prismatic crystals that formed were separated by decantation and dried in air. The solvate $3 \cdot C_6H_6$ was obtained in a yield of 85% (0.93 g). Found (%): C, 72.19; H, 4.51; N, 10.98. $C_{30}H_{24}N_4Ni$. Calculated (%): C, 72.14; H, 4.81; N, 11.22. ^{1}H NMR ($CDCl_3$), δ: 7.63 (dd, 4 H, H(8)); 7.52 (dd, 4 H, H(9)); 7.46 (tt, 2 H, H(10)); 6.68 (ddd, 2 H, H(4)); 6.62 (dd, 2 H, H(6)); 6.57 (dd, 2 H, H(3)); 6.51 (ddd, 2 H, H(5)); 6.06 (br.s, 2 H, NH). ^{13}C NMR ($CDCl_3$), δ: 154.3 (C(2)); 153.9 (C(7)); 148.8 (C(1)); 128.2 (C(9)); 128.0 (C(8)); 126.0 (C(10)); 123.5 (C(4)); 123.0 (C(5)); 118.6 (C(6)); 116.2 (C(3)). IR (KBr), ν/cm^{-1}: 3232 w, 3086 w, 1616 s, 1512 m, 1464 w, 1384 w, 1336 w, 1248 m, 1168 w, 1096 m, 1032 s, 1008 m, 960 w, 744 s, 969 m, 640 s, 472 m, 408 m.

The solvate Pt[1,2-(NPh)(NH)C_6H_4]$_2 \cdot C_6H_6$ ($1 \cdot C_6H_6$) was prepared by recrystallization of complex **1** from benzene. ^{1}H NMR ($CDCl_3$), δ: 7.62 (dd, 4 H, (H(8)); 7.57 (dd, 4 H, H(9)); 7.43 (tt, 2 H, H(10)); 7.20 (br.s, 2 H, NH); 6.89 (dd, 2 H, H(6)); 6.82 (dd, 2 H, H(3)); 6.70 (ddd, 2 H, H(4)); 6.60 (ddd, 2 H, H(5)). ^{13}C NMR ($CDCl_3$), δ: 155.7 (C(7)); 148.7 (C(2)); 147.9 (C(1)); 128.6 (C(9)); 127.5 (C(8)); 126.5 (C(10)); 123.6 (C(4)); 123.1 (C(5)); 119.2 (C(6)); 115.8 (C(3)).

Oxidation of Ni[1,2-(NPh)(NH)C_6H_4]$_2$ with an excess of CF_3SO_3Ag in acetone. A mixture of Ni[1,2-(NPh)(NH)C_6H_4]$_2$ (1 g, 2.37 mmol), CF_3SO_3Ag (3.04 g, 11.85 mmol), and acetone (3—5 drops) was ground in an agate mortar for 3 h, acetone being added as it was evaporated. Hexane (10 mL) was added to the resulting greenish-black powder and the suspension was applied onto a column with zeolite (5×10 cm). The red product was eluted with benzene (50 mL). The eluent was concentrated to 20 mL at 50 °C (0.1 Torr) and kept at 20 °C for 24 h. The dark-red needle-like crystals of 2,2-dimethyl-3,10-diphenyl-2,3,4,10-tetrahydroimidazo[4,5-*b*]phenazin-1-ium triflate (**4**) that formed were separated by decantation and dried in air. Compound **4** was obtained in a yield of 0.425 g (65%). Found (%): C, 61.55; H, 4.19; N, 9.89. $[C_{22}H_{23}N_4] \cdot O_3SCF_3$. Calculated (%): C, 60.87; H, 4.17; N, 10.14. ^{1}H NMR ($CDCl_3$), δ: 8.98 (br.s, 1 H, NH^+); 7.75 (dd, 2 H, H(3)); 7.70 (ddd, 1 H, H(8)); 7.64 (dd, 1 H, H(9)); 7.60 (dd, 2 H, H(4)); 7.55 (tt, 1 H, H(12)); 7.49 (dd, 2 H, H(10)); 7.44 (tt, 1 H, H(5)); 7.38 (dd, 2 H, H(11)); 7.31 (ddd, 1 H, H(7)); 6.91 (dd, 1 H, H(6)); 6.37 (s, 1 H, H(2)); 6.02 (s, 1 H, H(1)); 1.81 (s, 6 H, $-CH_3$). IR (KBr), ν/cm^{-1}: 3430 w, 2920 m, 2856 m, 1688 w, 1608 s, 1520 s, 1488 s, 1443 w, 1384 m, 1352 w, 1288 s, 1240 s, 1160 m, 1071 w, 1024 m, 952 w, 912 m, 816 m, 760 m, 720 w, 680 m, 632 s, 608 w, 552 m, 512 m, 472 w, 424 w.

X-ray diffraction study. The X-ray diffraction data sets for the solvates $1 \cdot C_6H_6$ and $3 \cdot C_6H_6$ and compound **4** were collected on a four-circle automated Siemens R3/PC diffractometer (Mo-K_α radiation, λ = 0.71074 Å, T = 22 °C). The unit cell parameters were determined and refined based on 24 equivalent reflections with 2θ < 24—28°. Three strong reflections with $0 < \chi < 65°$ were used as the standards and were measured after each 100 reflections. The standard reflections revealed no significant intensity variation in the course of data collection, and therefore, no corrections were applied.

All structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The H atoms were located from difference Fourier syntheses and refined isotropically. All calculations were carried out with the use of the SHELXTL PLUS program package (PC version).[7] The principal geometric parameters of the complexes are given in Tables 1 and 2. The crystallographic parameters and details of the structure refinements are listed in Table 3.

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