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Cyclometallated Ni(II) and Pd(II) Complexes of the Azomethine Compounds: Synthesis and Structures

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Abstract—New Ni(II) and Pd(II) complexes (**Ia** and **Ib**) are synthesized on the basis of the azomethine compound 2-[(*E*)-[4-methyl-2-[(*Z*)-*p*-tolylazo]phenyl]iminomethyl]phenol. The structures and properties of the complexes are characterized by IR spectroscopy, ^{1}H NMR spectroscopy, and X-ray diffraction analysis (CIF files CCDC nos. 1899223 (**Ia**) and 1899224 (**Ib**)). The complex formation affords cyclometallated chelates. According to the X-ray diffraction data, the crystals of the Ni(II) and Pd(II) complexes are isostructural with the square geometry of the coordination mode (MCN_2O, M = Ni, Pd) and formation of two five-membered and one six-membered metallocycles.

Keywords: azo-azomethines, metal complexes, cyclometallation, X-ray diffraction analysis
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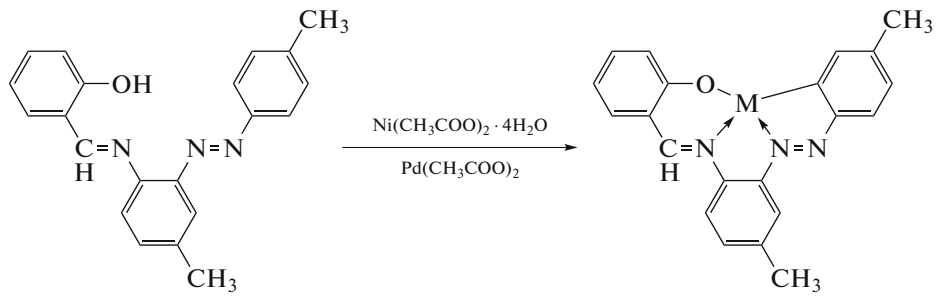
INTRODUCTION

Azomethine ligands are important objects of the modern chemistry of coordination compounds. A number of monographs and reviews are devoted to compounds of this class [1–5]. Metal complexes of the azomethine ligands have a series of useful properties, which allow one to prepare multifunctional materials from them. These are the magnetically active [6–8] and luminescent [9] complexes and chemisensors [10–12]. The complexes of the azomethine ligands are widely presented among biocoordination systems [13, 14]. The complexes of the azomethine ligands are highly catalytically active in various reactions at high (>100°C) temperatures and in the presence of moisture [15, 16].

The study of the coordination compounds of azomethines containing the azobenzene moiety that is not involved in coordination plays an important role in investigations of the molecular magnetic materials and systems [17, 18] exhibiting the thermo- and photoinduced crossover effect [19, 20]. The ability of the azobenzene moiety to undergo photoinduced *E/Z* isomerization is very significant for the preparation of coordination compounds with the properties of molecular switches [21].

New coordination Ni(II) (**Ia**) and Pd(II) (**Ib**) complexes with the azomethine compound 2-[(*E*)-[4-methyl-2-[(*Z*)-*p*-tolylazo]phenyl]iminomethyl]phenol (HL) were synthesized in this work.



HL (**I**) M = Ni (a), Pd (b)

EXPERIMENTAL

Commercially available (Alfa Aesar) salicylaldehyde and 6-amino-4,4'-dimethylazobenzene, palladium acetate, and nickel acetate tetrahydrate (analytical grade) were used.

Synthesis of HL. 6-Amino-4,4'-dimethylazobenzene (5.63 g, 2.5 mmol) in isopropyl alcohol (40 mL) was added to a solution of salicylaldehyde (3.05 g, 2.5 mmol) in isopropyl alcohol (10 mL), and the mixture was refluxed using a reflux condenser for 2 h. The precipitate formed on cooling was filtered off, recrystallized from a chloroform–methanol (1 : 2) mixture, and dried in a vacuum drying box. The yield of the red crystals of HL was 7.68 g (96%), mp = 88–89°C.

For $C_{21}H_{19}N_3O$

Anal. calcd., %	C, 76.57	H, 5.81	N, 12.76
Found, %	C, 76.49	H, 5.75	N, 12.68

IR (ν, cm^{-1}): 1616 (CH=N), 1284 (Ph–O).

^{1}H NMR (DMSO-d^6; δ, ppm): 2.40 (s, 6H, CH_3), 6.98–7.83 (m, 11H, C_{Ar}–H), 9.05 (s, 1H, CH=N), 13.92 (s, 1H, OH).

Synthesis of metal complexes Ia and Ib. Sodium methoxide (0.054 g, 1 mmol) in methanol (5 mL) was poured to a suspension of HL (0.33 g, 1 mmol) in methanol (30 mL). The mixture was boiled to the complete dissolution of azomethine. Nickel acetate tetrahydrate (0.25 g, 1 mmol) in methanol (10 mL) or palladium acetate (0.23 g, 1 mmol) in acetone (10 mL) was added to the obtained solution. The mixture was refluxed for 2 h. The formed precipitates of the complexes were filtered off, washed with boiling methanol (two times by 5 mL), recrystallized from a dichloromethane–methanol (2 : 1) mixture, and dried in a vacuum drying box.

The yield of the green crystals of (2-[(*E*)-[4-methyl-2-[(*Z*)-*p*-tolylazo]phenyl]iminomethyl]phenolato)nickel(II) (**Ia**) was 0.38 g (99%), mp > 250°C.

For $C_{21}H_{17}N_3ONi$

Anal. calcd., %	C, 65.34	H, 4.44	N, 10.88	Ni, 15.20
Found, %	C, 65.28	H, 4.39	N, 10.91	Ni, 15.87

IR (ν, cm^{-1}): 1611 (CH=N), 1322 (Ph–O).

Since the complex is diamagnetic and almost insoluble in organic solvents, we failed to detect the ^{1}H NMR spectrum.

The yield of the brown crystals of (2-[(*E*)-[4-methyl-2-[(*Z*)-*p*-tolylazo]phenyl]iminomethyl]phenolato)palladium(II) (**Ib**) was 0.38 g (87%), mp > 250°C.

For $C_{21}H_{17}N_3PdO$

Anal. calcd., %	C, 58.14	H, 3.95	N, 9.69	Pd, 24.53
Found, %	C, 58.21	H, 4.02	N, 9.72	Pd, 24.53

IR (ν, cm^{-1}): 1609 (CH=N), 1319 (Ph–O).

^{1}H NMR (DMSO-d^6; δ, ppm): 2.36 (s, 6H, CH_3), 6.55–7.93 (m, 10H, C_{Ar}–H), 9.01 (s, 1H, CH=N).

Elemental analyses to C, H, and N were carried out on a Carlo Erba Instruments TCM 480 instrument. Analyses to metals were conducted by the gravimetric method.

IR spectra were recorded on a Varian Excalibur-3100 FT–IR instrument in powders using the attenuated total internal reflection technique (ATR). ^{1}H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in the internal stabilization mode of the ^{2}H resonance line in $CDCl_3$.

X-ray diffraction analyses of single crystals of the NiL and PdL complexes were conducted on a Bruker Apex II diffractometer (CCD detector, MoK_α, λ = 0.71073 Å, graphite monochromator) [22]. A semiempirical absorption correction was applied [23]. The structures were solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were geometrically generated and refined in the riding model. The calculations were performed using the SHELX-2014/7 program package [24]. The crystallographic parameters of NiL and PdL are presented in Table 1.

The full set of X-ray structural data was deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1899223 (**Ia**) and 1899224 (**Ib**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The structure of azo-azomethine HL was determined by elemental analysis, IR spectroscopy, and ^{1}H NMR spectroscopy. The IR spectrum of HL exhibits absorption bands at 1616 cm^{-1} (ν(CH=N)) and 1284 cm^{-1} (ν(Ph–O)). The signals of all protons according to the empirical formula were found in the ^{1}H NMR spectrum. The signals of the CH=N protons are detected at 9.05 ppm, and the signals of the protons of the OH groups are observed at 13.92 ppm.

We previously synthesized the metal complexes of azomethine compounds ML_2, the derivatives of 2-hydroxy- and 2-tosylaminobenzaldehydes and 1-phenyl-3-methyl-4-formyl-5-pyrazolone (thione). They have the azo group in the *ortho* position of the amine fragment in which the azo group of the amine fragment participates or does not participate in coordination to the metal ion depending on the nature of the ligand and metal [25–32].

According to the elemental analysis data, metal complexes **Ia** and **Ib** obtained from HL have the composition ML, unlike those described previously. In the IR spectra of complexes **Ia** and **Ib**, the absorption

Table 1. Crystallographic parameters and structure refinement details for complexes **Ia** and **Ib**

Parameter	Value	
	Ia	**Ib**
FW	386.09	433.78
T, K	173(2)	120(2)
Crystal system	Monoclinic	
Space group	$P2_1/n$	
a, Å	11.9303(14)	11.6714(11)
b, Å	7.3913(9)	7.5075(7)
c, Å	18.661(2)	19.288(2)
β, deg	90.388(2)	90.347(1)
V, Å^3	1645.5(3)	1690.1(3)
Z	4	
ρ_{calc}, g/cm^3	1.558	1.705
μ, mm^{-1}	1.19	1.11
θ_{max}, deg	26.96	29.18
T_{min}/T_{max}	0.465/0.746	0.632/0.746
Number of measured reflections	7736	11122
Number of independent reflections	3484	4510
Number of reflections with $I > 2\sigma(I)$	2491	3614
R_{int}	0.055	0.036
Number of refined parameters	235	235
GOOF	0.96	0.98
R_1 ($I > 2\sigma(I)$)	0.050	0.033
wR_2 ($I > 2\sigma(I)$)	0.116	0.081

bands of stretching vibrations at 1619 cm^{-1} ν(CH=N) of the ligand are shifted to the long-wavelength range by 8–10 cm^{-1} upon complex formation, and the ν(Ph–O) stretching vibration bands of the ligands at 1284 cm^{-1} are shifted to the shortwave-length range by 35–38 cm^{-1}. These IR spectral changes are characteristic of the complex formation of the chelate structures [33]. Complexes **Ia** and **Ib** are diamagnetic.

The metal complexes of the azomethine ligands with the cyclometallated structures ML are described [34–40]. The X-ray diffraction analyses of complexes **Ia** and **Ib** also indicate the formation of the cyclometallated nickel and palladium complexes.

The crystals of complexes **Ia** and **Ib** are isostructural. In both compounds, the L^{2-} dianion is coordinated to the metal atoms and their environment (MCN_2O, M = Ni, Pd) corresponds to the distorted square geometry (Fig. 1). The molecules of complexes **Ia** and **Ib** are planar, and the deviation of the atoms from the root-mean-square plane is 0.067 and 0.085 Å, respectively.

Selected bond lengths and angles in the molecules of complexes **Ia** and **Ib** are given in Table 2 (numerations of the N, C, and O atoms coincide in both structures).

In complex **Ia**, the Ni–N(azo) (1.806 Å) and Ni–N(imine) (1.899 Å) bond lengths differ due to the *trans* effect of the aryl carbon atom, which is stronger than the *trans* effect of the phenol oxygen atom [34]. The Ni–C bond length (1.877 Å) is comparable with the similar length for the Ni(II) *ortho*-metallated complexes with azobenzene [35]. The Ni–O bond length (1.820 Å) is close to the Ni–O bond lengths in the square nickel(II) complexes with *N*,*N*′-bis(salicylidene)ethylenediamine [36, 37].

An analysis of the molecular packing of the complex in crystal revealed the formation of dimers $\{Ni_2\}$ of the adjacent molecules in which the Ni···Ni distance is 3.182 Å. The $\{Ni_2\}$ dimers also interact with the adjacent dimers due to π–π-stacking interactions between the phenyl fragments C(1)–C(6) and C(8)–C(13), and the distance between the centroids of the aromatic rings is 3.632 Å (Fig. 2). These intermolecular interactions result in the formation of the supramolecular chain (Fig. 2) in which the Ni···Ni interatomic distance between two $\{Ni_2\}$ dimers is 4.876 Å.

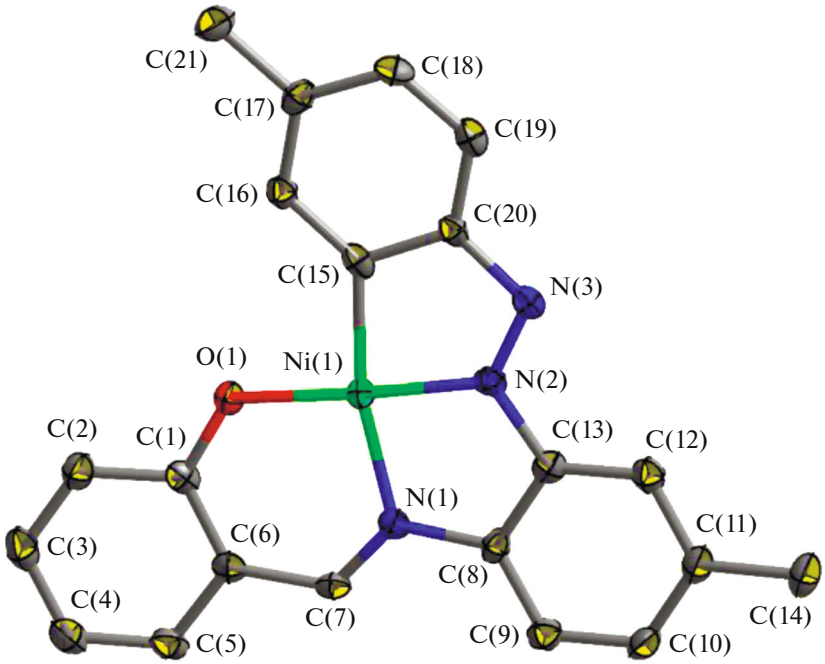


Fig. 1. Structure of complex **Ia** (hydrogen atoms are omitted, ellipsoids of 50% probability).

In complex **Ib**, the Pd–N(azo) (2.030 Å) and Pd–N(imine) (1.920 Å) bond lengths, as in complex **Ia**, differ due to the *trans* effect of aryl carbon stronger than that of phenol oxygen [38]. The Pd–C (1.983 Å) and Pd–O (1.993 Å) bond lengths are comparable with similar bond lengths for the known Pd(II) complexes [38–40]. An analysis of the molecular packing of the complex in crystal revealed the formation of $\{Pd_2\}$ dimers of the adjacent molecules in which the Pd···Pd distance is 3.274 Å. The $\{Pd_2\}$ dimers interact with the adjacent dimers due to π–π-stacking interactions between the phenyl C(1)–C(6) and C(8)–C(13) fragments, and the distance between the centroids of the aromatic rings is 3.646 Å. The Pd···Pd interatomic distance between two $\{Pd_2\}$ dimers in the formed supramolecular chain is 5.057 Å.

Table 2. Selected bond lengths and bond angles in complexes **Ia** and **Ib**

Bond length, Å	**Ia**	**Ib**	Angle, deg	**Ia**	**Ib**
M–N(1)	1.899(3)	2.030(2)	O(1)M(1)N(1)	97.59(11)	95.59(9)
M–N(2)	1.806(3)	1.920(2)	O(1)M(1)N(2)	176.65(12)	179.28(9)
M–O(1)	1.820(2)	1.993(2)	O(1)M(1)C(15)	94.75(12)	100.72(10)
M–C(15)	1.877(3)	1.983(3)	N(1)M(1)N(2)	85.76(12)	83.93(10)
O(1)–C(1)	1.314(4)	1.308(3)	C(15)M(1)N(1)	167.39(12)	163.65(10)
N(2)–N(3)	1.278(4)	1.273(3)	C(15)M(1)N(2)	81.90(13)	79.76(10)
N(1)–C(7)	1.294(4)	1.295(4)	M(1)(C15)C(16)	132.4(2)	133.2(2)
N(1)–C(8)	1.422(4)	1.425(3)	M(1)(C15)C(20)	110.4(3)	109.4(2)
N(2)–C(13)	1.413(4)	1.418(4)	M(1)O(1)C(1)	124.6(2)	122.0(2)
N(3)–C(20)	1.399(4)	1.407(3)	M(1)N(1)C(7)	125.0(2)	123.9(2)
C(1)–C(6)	1.422(5)	1.440(4)	M(1)N(1)C(8)	111.6(2)	110.3(2)
C(8)–C(13)	1.397(5)	1.417(4)	M(1)N(2)C(13)	115.9(2)	114.7(2)
C(15)–C(20)	1.415(4)	1.425(4)	M(1)N(2)N(3)	123.7(2)	123.2(2)
			N(3)N(2)C(13)	120.5(3)	122.1(2)
			N(2)N(3)C(20)	108.0(3)	109.2(2)

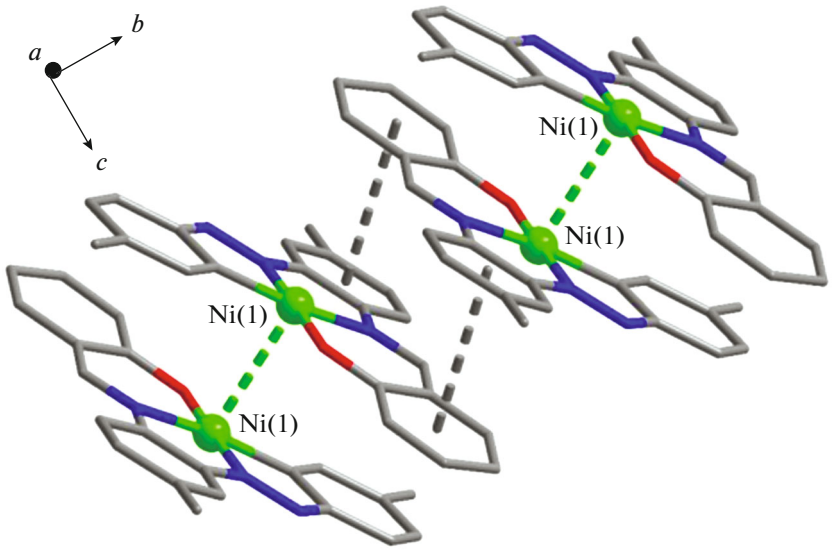


Fig. 2. Packing fragment of the molecules of complex **Ia** in crystal along the *b* axis. Hydrogen atoms are omitted, and contacts between the Ni atoms and between the centroids of the C_6 aromatic fragments of the adjacent molecules are shown by dashed lines.

Thus, new Ni(II) and Pd(II) complexes were synthesized on the basis of the azomethine compound 2-[(*E*)-[4-methyl-2-[(*Z*)-*p*-tolylazo]phenyl]iminomethyl]phenol. It is shown that the complex formation affords the isostructural cyclometallated chelates with the square geometry of the coordination mode and the nitrogen atoms of the azomethine and azo groups involved in the coordination to the metal atoms to form two five-membered and one six-membered metallocycles.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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