# Novel Tribochemically Active Metal Chelates of Aromatic Azo Ligands

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Abstract—Novel Cu(II) and Pd(II) complexes with *o*-phenylaminoazo compounds were synthesized and studied by X-ray diffraction. Distorted tetrahedral chelate complex of Cu contains two six-membered  $CuN_3C_2$  metal cycles. The complexes under study can be used as industrial lubricant additives.

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Complex compounds of azo ligands are always in the focus of researchers' attention [1-4]. Azo ligand chelate complexes were used to establish and develop important theoretical concepts about chelate isomerization (realization of metal cycles with different members in the molecule of a complex) [3–5], about stabilization as a result of complexation of different tautomeric forms of the ligand systems [4], and isolation of *cistrans*-isomers [6, 7].

Metal complexes of azo compounds have wide practical application, including the production of dyes and pigments [1, 8, 9].

In this work, the most poorly studied atomatic azo chelates with the  $MN_4$  coordination core are synthesized and their structures are determined by X-ray diffraction. Their tribochemical activity (the possibility of using as lubricant addivites) is shown. Azo chelates are obtained by the following scheme:



# **EXPERIMENTAL**

Synthesis of ligands. The starting compounds I were prepared according to the known procedures [1, 10], i.e., by diazotization of p-toluidine or p-chloroaniline and coupling with N-phenyl-2-naphthylamine.

**Synthesis of complex compounds II.** To a solution of 4-(2'-N-phenylaminonaphthylazo)toluene (0.67 g, 2 mmol) in 50 ml methanol, a solution of Cu acetate monohydrate (0.2 g, 1 mmol) in 20 ml methanol was added (**IIa**, M = Cu) or to a solution of 4-(2'-N-pheny-laminonaphthylazo)chlorobenzene (0.72 g, 2 mmol) in 50 ml methanol, a solution of Pd acetate (0.22 g, 1 mmol) in 10 ml acetone was added (**IIb**, M = Pd). The

reaction mixture was boiled on a water bath for 1 h and cooled. The obtained precipitates of the complexes were filtered off, washed twice with 5-ml portions of methanol.

The complexes were recrystallized and their crystals for X-ray diffraction analysis were grown from methylene chloride–methanol mixture (1 : 2).

**IIa**. Dark brown crystals,  $T_{\rm m} = 232-233^{\circ}$ C.

For  $C_{46}H_{36}N_6Cu$ Anal. calcd. (%): C 75.12; H 4.95; N 11.35; Cu 8.55. Found (%): C 75.02; H 4.93; N 11.41; Cu 8.63. **IIb.** Dark brown crystals,  $T_{\rm m} = 203-204^{\circ}$ C.

**Table 1.** The main crystallographic parameters and summary of data collection for structures **IIa** and **IIb** 

Value

For C<sub>44</sub>H<sub>30</sub>N<sub>6</sub>ClPd

Anal. calcd. (%): C 64.51; H 3.70;N10.15; Cl 8.76; Pd 12.88. Found (%): C 64.44; H 3.69; N 10.25; Cl 8.65; Pd 12.98.

<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>, ppm: 4-(2'-N-phenylaminonaphthylazo)chlorobenzene (**Ib**), 12.91 (1H, s, NH), 8.88 (1H, d,  ${}^{3}J$  = 8.4 Hz, H<sub>8</sub>), 7.88–7.23 (14H, m, 4H C<sub>6</sub>H<sub>4</sub>, 5H C<sub>6</sub>H<sub>5</sub>, 5H C<sub>10</sub>H<sub>5</sub>); Pd complex **IIb**, 8.30 (2H, d,  ${}^{3}J$  = 8.6 Hz, H<sub>8</sub>) 7.79–6.83(28H, m, 8H C<sub>6</sub>H<sub>4</sub>; 10H C<sub>6</sub>H<sub>5</sub>, 10H C<sub>10</sub>H<sub>5</sub>).

**X-ray diffraction analysis.** The experimental data for single crystals **IIa** and **IIb** were collected on a Bruker AXS SMART 1000 diffractometer equipped with CCD-detector (Mo $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å, graphite monochromator,  $\omega$  scan mode). The experimental data were processed and averaged with the SAINT-*Plus* program package [11], the absorption was corrected by semiempirical method from equivalent reflections [12].

Structures **IIa** and **IIb** were solved by the direct method and refined on  $F_{hkl}^2$  by least-squared method in anisotropic approximation for non-hydrogen atoms. The H atoms were located geometrically and refined in the rider model. The main crystallographic parameters and summary of data collection are presented in Table 1. All calculations were performed with the SHELXTL-*Plus* program package [13].

The <sup>1</sup>H NMR spectra were measured on a Varian Unity-300 instrument in CDCl<sub>3</sub> solution (300 MHz). Tribochemical study was performed on a friction-testing machine of AE-5 type.

## **RESULTS AND DISCUSSION**

Metal chelates **II** were synthesized by the direct reaction of components, i.e., azo compound **I** and metal acetates [5].

The <sup>1</sup>H NMR spectrum of **Ib** exhibits a pronounced singlet from a proton of the NH group at 12.91 ppm, which is absent in the case of the Pd complex **IIb**. This fact indicates the formation of chelate structures of type **II**.

Taking into account the literature data, the complexes under consideration were expected to contain five- and(or) six-membered metal cycles [3–7, 14]. In the previous publication [15], Price proposed the formation of five-membered chelate rings in the Co complexes similar to **II** ( $\mathbf{R} = \mathbf{H}$ ,  $\mathbf{M} = \mathbf{Co}^{2+}$ ), which were described in manual [1]. At the same time, X-ray diffraction data confirmed the formation of six-membered

Parameter IIa IIb М 736.35 820.04 Crystal system Monoclinic Monoclinic Space group C2/c $P2_{1}/c$ *T*, K 120 120 Ζ 8 2 a, Å 25.919(2) 8.4146(3) b, Å 12.3992(8) 17.4835(6) *c*, Å 23.476(2) 12.2616(5)  $\beta$ , deg 105.113(2)97.987(1) V, Å<sup>3</sup> 7283.8(8) 1786.4(1) $\rho$  (calcd), g cm<sup>-3</sup> 1.343 1.525  $\mu$ , cm<sup>-1</sup> 6.42 7.12  $2\theta_{\text{max}}$ , deg 58 58 Number of measured 22550 (0.0358) 13638 (0.0253) reflections  $(R_{int})$ Number of independent 9614 4715 reflections Number of reflections 3906 6073 with  $I > 2\sigma(I)$ Number of refined pa-480 245 rameters GOOF 0.982 1.070 0.0513 0.0597  $R_1$  $wR_2$ 0.1251 0.0851  $\Delta \rho_{\rm max} / \Delta \rho_{\rm min}, e {\rm \AA}^{-3}$ 0.77/-0.281.246/-0.891

coordination cores in analogous Ni complexes with 4-aryl-5-aminopyrazoles (III) [16].



The question of stereochemistry of chelates **II** also remained open [4, 6, 7]. These questions were solved in the course of X-ray diffraction analysis of complexes **IIa**  $(M = Cu^{2+}, R = CH_3)$  and **IIb**  $(M = Pd^{2+}, R = Cl)$ . The data obtained showed that in the structures of chelates **IIa** (Fig. 1) and **IIb** (Fig. 2), as in the case with complexes of type **III** and analogous complexes of azomethin series [4, 17, 18], two six-membered metal rings are closed. The analysis of bond lengths and bond angles in structures **IIa** and **IIb** showed that aryl substituents contained in the ligands at atoms N(1) and

Vol. 32 No. 9 2006



Fig. 1. General view of complex IIa (the H atoms are omitted).



Fig. 2. General view of complex IIb (the H atoms are omitted).

N(2) make these complexes sterically overloaded, as a result of which their geometry is distorted.

Indeed, in both complexes, the aromatic substituents at the N atoms have "face-to-face" arrangement, such that a number of shortened contacts are realized between the aryl substituents of the neighboring chelates:  $C(11)\cdots C(17')$  ( $C(11')\cdots C(17)$ ) 3.217(3) Å in **IIa**,  $C(11)\cdots C(17A)$  3.074(3) Å in **IIb**. Note that the letter contact is shorter than the contact between the planes of aromatic rings in [2.2]-paracyclophane (3.099(1) Å) [19].

IIa				IIb	
bond	d, Å	bond	<i>d</i> , Å	bond	d, Å
Cu(1)–N(1)	1.934(2)	Cu(1)–N(1')	1.947(2)	Pd(1)–N(1)	2.017(2)
Cu(1)–N(3)	1.940(2)	Cu(1)–N(3')	1.946(2)	Pd(1)–N(3)	2.029(2)
N(1)–N(2)	1.289(2)	N(1')–N(2')	1.297(2)	N(1)–N(2)	1.299(3)
N(2)–C(1)	1.353(3)	N(2')-C(1')	1.350(3)	N(2)–C(1)	1.339(3)
N(3)–C(2)	1.341(3)	N(3')–C(2')	1.330(3)	N(3)–C(2)	1.331(3)
C(1)–C(2)	1.433(3)	C(1')–C(2')	1.440(3)	C(1)–C(2)	1.446(3)
C(1)–C(6)	1.467(3)	C(1')–C(6')	1.470(3)	C(1)-C(6)	1.462(3)
C(2)–C(3)	1.446(3)	C(2)–C(3)	1.446(3)	C(2)–C(3)	1.461(3)
C(3)–C(4)	1.353(3)	C(3')–C(4')	1.349(3)	C(3)–C(4)	1.355(3)
C(4)–C(5)	1.425(3)	C(4')–C(5')	1.421(3)	C(4)–C(5)	1.423(4)
C(5)–C(6)	1.402(3)	C(5')–C(6')	1.402(3)	C(5)–C(6)	1.413(3)
C(5)–C(7)	1.423(3)	C(5')–C(7')	1.419(3)	C(5)–C(7)	1.407(3)
C(6)–C(10)	1.407(3)	C(6')–C(10')	1.403(3)	C(6)–C(10)	1.409(3)
C(7)–C(8)	1.375(3)	C(7')–C(8')	1.356(4)	C(7)–C(8)	1.382(4)
C(8)–C(9)	1.402(3)	C(8')–C(9')	1.395(4)	C(8)–C(9)	1.404(4)

Table 2. Selected bond lengths in structures IIa and IIb

Minimization of steric repulsion of substituents in the complexes under study is realized due to distortion of the Cu coordination polyhedron in complex **IIa** and distortion of chelate in complex **IIb**.

Thus, in complex **IIa**, the coordination polyhedron of the Cu(1) atom is significantly distorted: the dihedral angle between the planes Cu(1)N(1)N(2) and Cu(1)N(1')N(2') is equal to 88.8°, the bond angles at the Cu(1) atom vary within a range of 92.04(7)°–138.94(8)°. In this case, six-membered metal rings Cu(1)N(1)N(2)N(3)C(1)C(2) and Cu(1)N(1')N(2)N(3')C(1')C(2') in **IIa** are sufficiently flattened to give chair conformation with 0.36 and 0.27 Å deviation of the Cu(1) atom from the N<sub>3</sub>C<sub>2</sub> plane, respectively. The angles of bending along the N(1)···N(3) and N(1')···N(3') lines are 9.6° and 11.3°, respectively.

On the contrary, the Pd atom in complex **IIb** lies in the symmetry center and has ordinary square coordination, whereas metal rings and naphthalene fragment are significantly distorted (Fig. 2). Unlike complex IIa, the metal ring Pd(1)N(1)N(2)C(1)C(2)N(3) in complex IIb has the conformation of a slightly twisted boat with the Pd(1) and C(1) atoms deviating by 0.87 and 0.23 Å from the plane N(1)N(2)C(2)N(3), respectively. The angle of bending along the N(1)...N(3) line is equal to 35.7°. As a result of the metal ring distortion, the naphthalene ring C(1)–C(6) in **IIb** is also distorted and acquires the boat conformation with the C(2) and C(6)atoms deviating from the plane C(1)C(3)C(4)C(5) by 0.22 and 0.10 Å, respectively. The analysis of molecules containing analogous disubstituted naphthalene fragment (as follows from the Cambridge Structural Database [20]) indicated that the violation of planarity of a ring observed in **IIb** (the torsional angles C(6)C(1)C(2)C(3) and C(1)C(2)C(3)C(4) are equal to 21.1° and 18.3°) is maximum. In particular, analogous torsional angles in **IIa** are 0.9° and 1.6°.

In addition to the above mentioned distortions of naphthalene ring, complex **IIb** also exhibits significant twisting about the double bond N(1)=N(2) (the torsional angles Pd(1)N(1)N(2)C(1) and C(1)N(1)N(2)C(11) are equal to 28.3° and 167°, respectively). For comparison, the corresponding torsional angles in **IIa** are equal to 8.6°–9.9° and 178°, respectively.

Despite the observed ligand distortions, the bond lengths in **Ha** and **Hb** are close: the differences for the C(1)-C(6) ring do not exceed 0.015 Å (Table 2). Hence, violation in the naphthalene ring planarity and twisting about the double bonds N=N do not result in weakening of the  $\pi$ -system coupling of a ligand.

In order to study in detail the nature of intramolecular interactions in complexes **II**, we performed the quantum-chemical calculations of chelate **IIa** in terms of DFT (UPBEPBE/DGDZVP/DGA1). The full optimization of the molecular geometry and further calculation of the electron density distribution function ( $\rho(r)$ ) were performed with the G03W program package [21]. The topological analysis of  $\rho(r)$  in terms of the Bader "atoms in molecules" (**AM**) theory [22] was carried out with the MORPHY-98 program [23]. The geometry of **IIa** obtained in the quantum-chemical calculation agrees well with the experimental data. Thus, the Cu–N and N(1)–N(2) bond lengths in an isolated complex are equal to 1.984–1.992 and 1.301 Å, respectively. A significant tetragonal distortion of the Cu

polyhedron is also retained: the dihedral angle Cu(1)N(1)N(2)/Cu(1)N(1')N(2') is equal to 72.4°, while the bond angles NCuN vary within 92.9°–132.3°. Note that the metal ring in an isolated molecule is flattened and the angle of bending along the N(1)…N(3) line does not exceed 3°. The metal ring flattening substantially strengthens the intramolecular contact between the aryl substituents (C(11)...C(17') 3.457 Å). Therefore, one can assume that flattening of a six-membered metal cycle confirmed by X-ray diffraction data for complex **IIa** arises, first of all, due to steric repulsion of the aryl substituents.

The search for the critical points  $\rho(r)$  (3, -1), which are the criteria of the chemical bond in the terms of the AM theory [22], revealed that they are localized in interatomic space of all expected interaction (Cu-N, N-C, C-C, N-N, C-H), but are absent for the abovedescribed shortened intramolecular contacts C---C between the aryl rings. The analysis of topological characteristics in the critical points (3, -1) of a metal ring showed that, despite its flattening, the Cu atom is not practically involved in the coupling with the  $\pi$ -system of a ligand. Indeed, the ellipticity values ( $\epsilon$ ), which determine the deviation in  $\rho(r)$  from cylindrical symmetry in a cross-section perpendicular to the bond line [22], remain almost unchanged for the bonds C-C, N–N, and N–C in a six-membered metal ring and vary within 0.12–0.19, while in the critical points (3, -1) of the Cu–N bonds, the values of  $\varepsilon$  do not exceed 0.05.

Thus, X-ray diffraction and quantum-chemical studies of complexes **IIa** and **IIb** indicate that the shortened intramolecular contacts C···C in both isolated molecule and in crystal are likely to be induced and do not correspond to the charge transfer. In this case, depending on "rigidity" of the metal polyhedron, the steric contacts realized in the complexes under consideration between substituents at the N atoms can be minimized due to distortion of both the metal center and the ligands.

With the aim to study tribochemical properties of metal complexes and developing new lubricant compositions on their base [24–32] with the wearless friction effect [25, 33], tribochemical parameters of ligand I ( $R = CH_3$ ) and its complexes II were investigated.

The obtained data revealed that the addition to the industrial lubricant I-20 of the indicated azo ligands and coordination compounds on their base improves the lubricating characteristics, including the load characteristic (1.5-2 times) and antiwear and antifriction characteristics (2–3 times).

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## REFERENCES

- 1. *The Chemistry of Synthetic Dyes*, Venkataraman, K.L., Ed., New York: Academic, 1971, vol. 3.
- 2. Emeleus, L.C., Cupertino, D.C., Harris, S.G., et al., *J. Chem. Soc., Dalton Trans.*, 2001, no. 8, p. 1239.
- 3. Kogan, V.A. and Shcherbakov, I.N., *Ross. Khim. Zh.*, 2004, vol. 48, no. 1, p. 69.
- 4. Garnovskii, A.D. and Vasil'chenko, I.S., Usp. Khim., 2005, vol. 74, no. 3, p. 211.
- 5. Synthetic Coordination and Organometallic Chemistry, Garnovskii, A.D. and Kharisov, B.I., Eds., New York: Marchel Dekker, 2003.
- Kogan, V.A., Kochin, S.G., Antsyskina, A.S., et al., *Mendeleev Commun.*, 1999, no. 1, p. 82.
- Kogan, V.A., Antsyshkina, A.S., Sadikov, G.G., et al., *Zh. Neorg. Khim.*, 2004, vol. 49, no. 12, p. 1988.
- 8. Gordon, P.F. and Gregori, P., Organic Chemistry in Color, Berlin: Springer, 1983.
- 9. Zollinger, H., Color Chemistry. Syntesis, Properties, and Application of Organic Dyes and Pigments, Weinheim: Wiley, 2003, p. 637.
- Zollinger, H., Diazochemistry of Aromatic and Heteroaromatic Compounds, Weinheim: VCH, 1994, vol. 1, p. 324.
- 11. SMART. Bruker Molecular Analysis Research Tool. Version 5.059, Bruker AXS, Madison (WI, USA), 1998.
- Sheldrick, G.M., SADABS. Version 2.01. Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS. Madison (WI, USA), 1998.
- 13. Sheldrick, G.M., SHELXTL. Version 5.10. Structure Determination Softwate Suite, Bruker AXS. Madison (WI, USA), 1998.
- D'yachenko, O.A., Avtomyan, L.O., Aldoshin, S.M., and Tkachev, V.V., *Zh. Strukt. Khim.*, 1978, vol. 19, no. 5, p. 829.
- 15. Price, R., J. Chem. Soc., Sect. A, 1967, no. 12, p. 2048.
- Nivorozhkin, A.L., Toflund, H., Nivorozhkin, L.E., et al., *Transition Met. Chem.* (London), 1994, vol. 19, no. 4, p. 319.
- 17. Larin, G.M., Koord. Khim., 1993, vol. 19, no. 5, p. 335.
- Hernandes-Molina, R. and Mederos, A., *Comprehensive Coordination Chemistry*, McCleverty, J.A. and Meyer, T.J., Eds., Amsterdam: Elsevier-Pergamon, 2003, vol. 1, p. 411.
- Lyssenko, K.A., Antipin, M.Yu., and Antonov, D.Yu., J. Chem. Phys., 2003, no. 4, p. 817.
- 20. Cambridge Crystallographic Database. Release 2004, Cambridge, UK.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., *Gaussian 03. Revision B.01*, Pittsburgh (PA, USA): Gaussian Inc., 2003.
- 22. Bader, R., Atoms in Molecules. A Quantum Theory, Oxford: Oxford Univ., 1990.
- 23. Popelier, P.L.A., *MORPHY-98. A Topological Analysis Program*, UMIST, Engl., EU, 1998.

- 24. Chigarenko, G.G., Ponomarenko, A.G., Bolotnikov, V.S., et al., *Trenie i Iznos*, 1989, vol. 10, no. 6, p. 1041.
- 25. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., and Garnovskii, A.D., *Effekt Bezyznosnosti i Tribotekh*nologiya, 1994, nos. 3–4, p. 64.
- 26. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., et al., *Izv. Vyssh. Uchebn. Zaved., Severo-Kavkaz. Region*, 2004, no. 9(21), p. 50.
- 27. Kuzharov, A.S., Burlakova, V.E., Zadoshchenko, E.G., et al., *Trenie i Iznos*, 2005, vol. 26, no. 6, p. 628.
- Barchan, G.P., Chigarenko, G.G., Kogan, V.A., et al., USSR Inventor's Certificate no. 810778, *Byull. Izobret.*, 1981, no. 9.

- 29. Barchan, G.P., Chigarenko, G.G., Bolotnikov, V.S., et al., USSR Inventor's Certificate no. 910741, *Byull. Izobret.*, 1982, no. 9.
- Barchan, G.P., Chigarenko, G.G., Bolotnikov, V.S., et al., USSR Inventor's Certificate no. 941 409, *Byull. Izobret.*, 1982, no. 25.
- Chigarenko, G.G., Kogan, V.A., Bolotnikov, V.S., et al., USSR Inventor's Certificate no. 1027187, *Byull. Izobret.*, 1983, no. 25.
- 32. RF Patent 2 238 302, Byull. Izobret., 2004, no. 29.
- 33. Garkunov, D.N., *Tribotekhnika (iznos i bezyznosnost')* (Tribotechnics (Wear and Non-Wear)), Moscow: MSKhA, 2001.