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The first polymeric pentacoordinate zinc(II) azoimidazole complex

Anatolii S. Burlov,[a] Alla S. Antsyshkina,[b] Georgii G. Sadikov,[b] Alexander A. Zubenko,[c] Sergei A. Mashchenko,[a] Igor S. Vasilchenko,*[a] Vladimir S. Sergienko,[b] Alexander D. Garnovskii[a] and Vladimir I. Minkin[a,d]

[a] *Institute of Physical and Organic Chemistry, Southern Federal University, 344090 Rostov-on-Don, Russian Federation. Fax: +7 863 243 4667; e-mail: vas@ipoc.rsu.ru*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 954 1279; e-mail: common@ionchran.msk.ru*
[c] *Southern Caucasian Regional Institute of Veterinary, 346400 Novocherkassk, Russian Federation*
[d] *Southern Scientific Center of the Russian Academy of Sciences, 344090 Rostov-on-Don, Russian Federation. E-mail: minkin@ipoc.rsu.ru*

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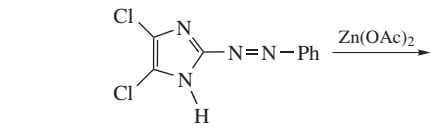
Coupling of 4,5-dichloro-2-phenyldiazenyl-1*H*-imidazole with zinc acetate gives rise to polymeric pentacoordinate Zn^{II} complex, whose structure was determined by X-ray diffraction study.

Metal complexes with aromatic and heterocyclic azo ligands are amongst the most important objects of modern coordination chemistry[1–3] since they are prospective for molecular electronics and photonics.[1–8] The previously obtained metal complexes of azo ligands, *e.g.*, Zn complexes,[9–12] are monomeric in solution while in crystal their molecules form associates stabilized by secondary bonds. The majority of described polymeric metallocomplexes are obtained based on functionalized aromatic ligands.[13]

Here we report on the first case of the formation of a polymeric pentacoordinate Zn^{II} azoimidazole complex prepared by coupling of 4,5-dichloro-2-phenyldiazenyl-1*H*-imidazole with zinc acetate (Scheme 1). Synthesis of 4,5-dichloro-2-phenyldiazenyl-1*H*-imidazole **1** has been performed by azo-coupling of 4,5-dichloroimidazole with phenyldiazonium salt.† Zinc complex **2** has been obtained by refluxing methanol solution of the reactants for 2 h.‡



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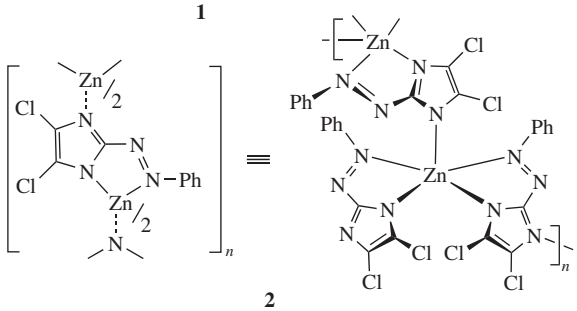

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Scheme 1

The structure of complex **2** was studied by X-ray diffraction method (Figure 1).§ An interesting feature of this complex containing two five-membered bis-chelate units is an additional short axial Zn–N bond that coordinates the ZnN_4 core to imidazole rings of the adjacent bis-chelate molecules to form slightly distorted trigonal bipyramidal ZnN_5 moieties with three shorter equatorial Zn–N bonds with N(3), N(7) and N(8A) atoms and elongated axial Zn–N(1) and Zn–N(5) bonds. The X-ray data reveal the polymeric chain directed along axis *x* of the crystal.

The chain-forming element of symmetry is the plane of sliding reflection and the repeating unit in the chain is the ZnL_2 molecular group. Atom N(8A) of the neighbouring molecule plays the bridging role and rises the coordination number of Zn to five. These chains form the layers which are parallel to crystallo-

† *Synthesis of 4,5-dichloro-2-phenyldiazenyl-1*H*-imidazole* **1**. 17.25 g (0.125 mol) of 4,5-dichloroimidazole were dissolved in 600 ml of water solution containing 30 g of Na_2CO_3 and 10 g of NaOH. The mixture was cooled to 8 °C and a solution of diazonium salt obtained by the common procedure from aniline (11.4 g, 0.125 mol), concentrated HCl (31.25 ml) and $NaNO_2$ (9 g, 0.13 mol) was added under intense stirring for 20 min with keeping the temperature in the range 6–10 °C. The mixture was then stirred for 1 h at room temperature and acidified with acetic acid to pH ~6. The precipitate was filtered off, dried and recrystallized from acetonitrile to furnish yellow-orange crystals of compound **1**. Yield 64%, mp 166–167 °C. ^{1}H NMR (DMSO-d_6) δ: 7.47–7.56 (m, 3H, H_{Ar}), 7.86–7.89 (m, 2H, H_{Ar}), 14.06 (br. s, 1H, NH). Found (%): C, 44.98; H, 2.49; N, 23.29. Calc. for $C_9H_6N_4Cl_2$ (%): C, 44.84; H, 2.51; N, 23.24.

‡ *Synthesis of bis(4,5-dichloro-2-phenyldiazenyl-1*H*-imidazoleato)zinc(II)* **2**. A solution of zinc acetate dihydrate (0.219 g, 1 mmol) in methanol (5 ml) was added to a solution of **1** (0.48 g, 2 mmol) in methanol (20 ml). The mixture was refluxed for 2 h. The precipitate formed after cooling was filtered off, washed with methanol and recrystallized from DMF to give orange crystals. Yield 30%, mp > 250 °C. ^{1}H NMR (DMSO-d_6) δ: 7.39 (br. s, 10H, H_{Ar}). Found (%): C, 39.58; H, 1.76; N, 20.49; Zn, 12.10. Calc. for $C_{18}H_{10}N_8Cl_4Zn$ (%): C, 39.63; H, 1.85; N, 20.54; Zn, 11.98.

§ *Crystal data for* **2**: $C_{18}H_{10}N_8Cl_4Zn$, orange, prismatic, M = 545.5, orthorhombic, space group $Pna2_1$, at 293 K: a = 11.118(3), b = 21.900(5) and c = 9.512(4) Å, V = 2251(5) Å^3, Z = 4, d_{calc} = 1.609, $F(000)$ = 1088, μ = = 6.09 mm^{-1}, R_1 = 0.0550 for 1718 independent reflections with $F > 4\sigma(F_0)$, wR_2 = 0.1682 for all data, GOF = 1.014. 2438 reflections (unique, R_{int} = = 0.083) were measured on an Enraf-Nonius Cad-4 diffractometer (CuKα-radiation, graphite monochromator, $\theta/2\theta$ scan mode, $2\theta_{max}$ = 60°).

The structure was determined by direct method and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. One of Cl atoms was disordered by two positions. The hydrogen atoms were placed in calculated positions and refined in the riding model with fixed isotropic displacement parameters. The structure was solved by direct method SHELXS-86[14] and refined by the SHELXL-97 program.[15]

CCDC 772819 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

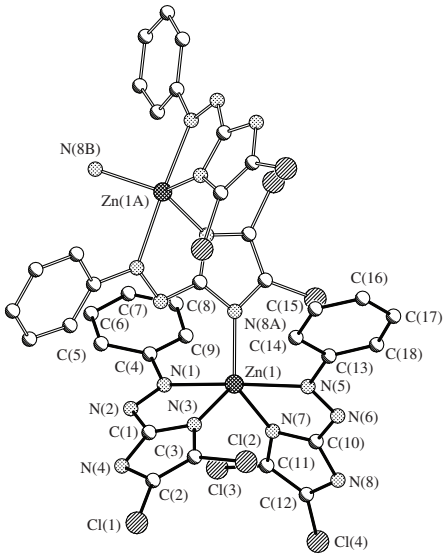

Figure 1 Fragment of the polymer **2**. Selected bond lengths (Å) and angles (°): Zn–N(3) 1.96, Zn–N(7) 2.04, Zn–N(1) 2.18, Zn–N(5) 2.25, Zn–N(8A) 2.01; N(8A)–Zn–N(7) 129.3, N(3)–Zn–N(7) 105.4, N(3)–Zn–N(8A) 125.3, N(1)–Zn–N(5) 176.7.

graphic plane *ac*. Chlorine atoms of neighbouring chains involve the shortened contact Cl–Cl 3.51 Å (Figure 2). The ligating atoms in the metal chelate five-membered rings form a plane with deviations no more than ±0.07 Å. Two identical 2-phenyldiazenyl-1*H*-imidazole ligands play different roles in the crystal: one of them serves as a bidentate chelate whereas the second one participates in the tridentate chelate bridging.

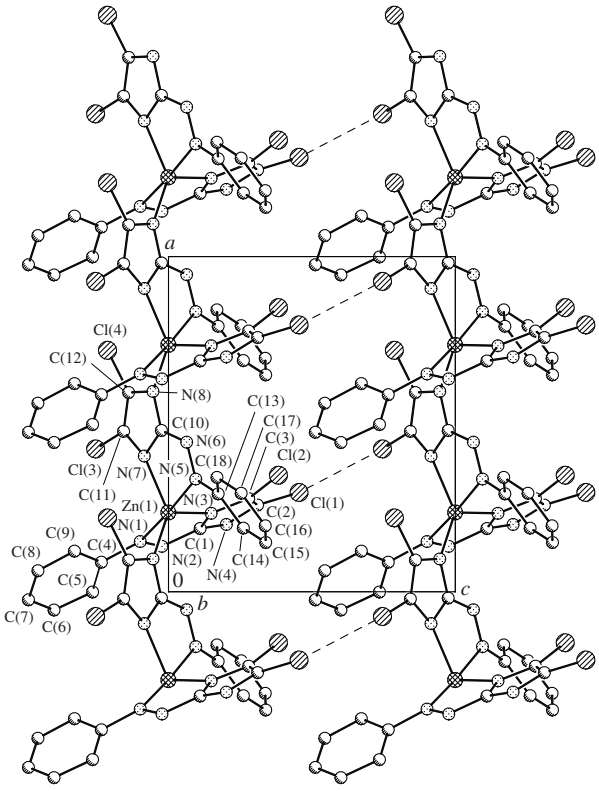

Figure 2 Crystal packing of polymeric complex **2**.

The polymeric structure of **2** results from the intermolecular interaction of the central zinc atoms with donor nitrogen centres of the imidazole moiety of the adjacent molecule. Such mode of binding is met in crystal structures of some other metal complexes of nitrogen-containing heterocycles.[16–18] An example[15] is tetranuclear copper complexes with 1-alkyl-2-aryldiazenylimidazole ligands, but the intermolecular coordination is furnished by nitrogen centres in the azo group. Bis(4,5-dichloro-2-phenyldiazenyl-1*H*-imidazoleato)zinc is the first example of complexes in which the polymeric structure is achieved *via* intermolecular Zn–N coordination provided by heterocyclic nitrogen centres.

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