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CRYSTAL STRUCTURE OF A TRINUCLEAR COMPLEX OF ZINC(II) WITH 2,6-DI-*TERT*-BUTYL-*p*-QUINONE 1′-PHTHALAZINYLHYDRAZONE

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2,6-Di-*tert*-butyl-*p*-quinone 1′-phthalazynylhydrazone (HL) is synthesized; the total energies and geometry of the possible hydrazone tautomeric forms are calculated by quantum chemical methods. The hydrazone phthalazone tautomer is shown to be the most stable, which is well consistent with the ^{1}H NMR spectroscopic data for hydrazone. An X-ray crystallographic analysis is performed of the hydrazone-based Zn(II) trinuclear complex, in which zinc atoms are linked by the diazine bridge of the phthalazine cycle and two pivalate bridges. The geometric properties of the monodeprotonated hydrazone residue in the complex are similar to the calculated data for the phthalazone hydrazone tautomeric form.

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1-Hydrazinephthalazine and its derivatives, as well as 1,4-dihydrazinephthalazines, are known to act as N-donor chelating–bridging ligands in the complexation with transition metal ions [1]. The possibility of their transition to the ion form allows one to obtain molecular binuclear complexes with inorganic metal salts (cobalt(II), nickel(II), and copper(II)), where metal centers are linked by chelating–bridging molecules of hydrazine phthalazine derivatives and contribute to the coordination of monodentate ligands, solvent molecules, and/or inorganic anions [2-10]. The metal skeleton of these systems can be enhanced by adding other bridging ligands (e.g., carboxylate anions, which are known to facilitate the formation of polynuclear systems of a molecular and polymeric structure) into the reaction systems [11-13].

This article presents the results of synthesizing a new trinuclear complex $Zn_3(Piv)_4L_2$ on the basis of zinc(II) pivalate ($[Zn(Piv)_2]_n$) and 2,6-di-*tert*-butyl-4-(phthalazine-1(2*H*)-ylidenehydrazono)cyclohexa-2,5-dienone (HL).

EXPERIMENTAL

The HL hydrazone compound was synthesized using commercially available 2,6-di-*tert*-butyl-*para*-quinone (Aldrich) and 1-hydrazinephthalazine hydrochloride (Alfa Aesar). Polymeric zinc(II) pivalate was synthesized by a well-known technique described in [14].

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TABLE 1. Main Bond Lengths (*d*, Å) and Angles (ω, deg) according to the Calculated Results for the HL Molecule (tautomeric forms a–c) and L^- Monoanion in Complex **1** (atomic notation corresponds to that of complex **1** in Fig. 2)

Bond	HLa	HLb	HLc	L^-	Angle	HLa	HLb	HLc	L^-
N(1)–N(2)	1.350	1.346	1.357	1.366(2)	C(20)–C(19)–C(32)	119.05	118.59	119.95	119.78(19)
N(1)–C(11)	1.295	1.310	1.311	1.296(3)	C(19)–C(20)–C(21)	122.00	122.24	121.99	121.6(2)
N(2)–C(18)	1.370	1.323	1.316	1.339(3)	C(20)–C(21)–C(26)	118.82	118.82	116.55	118.6(2)
N(3)–C(18)	1.320	1.392	1.415	1.355(3)	C(21)–C(26)–C(27)	119.07	118.88	123.11	119.21(19)
N(3)–N(4)	1.354	1.323	1.254	1.351(3)	C(26)–C(27)–C(32)	118.17	118.27	117.12	117.8(2)
N(4)–C(19)	1.316	1.317	1.409	1.333(3)	C(19)–C(32)–C(27)	122.89	123.19	121.28	122.6(2)
C(19)–C(20)	1.446	1.445	1.398	1.429(3)					
C(20)–C(21)	1.353	1.355	1.389	1.353(3)					
C(21)–C(26)	1.502	1.504	1.424	1.490(3)					
O(5)–C(26)	1.230	1.230	1.367	1.235(3)					
C(26)–C(27)	1.495	1.491	1.416	1.484(3)					
C(27)–C(32)	1.353	1.353	1.391	1.349(3)					
C(19)–C(32)	1.444	1.444	1.396	1.426(3)					

2,6-Di-*tert*-butyl-4-(phthalazine-1(2*H*)-ylidenehydrazono)cyclohexa-2,5-dienone (HL). 0.164 g (2 mmol) sodium acetate was added to a hot suspension of 0.391 g (2 mmol) 1-hydrazinephthalazine hydrochloride in 20 ml EtOH. The mixture was boiled for 10 min, and 0.44 g (2 mmol) 2,6-di-*tert*-butyl-*para*-quinone was added. The reaction mixture was boiled under reflux for 4 h. Then 50 ml water was added, and the mixture was left overnight. The orange precipitate was filtered and washed with water and ethanol. Recrystallized from DMFA.

Yield 0.396 g (55%); m.p. 207°C. Elemental analysis: gross formula $C_{22}H_{26}N_4O$; calculated, %: C 72.90, H 7.23, N 15.46; found, %: C 72.65, H 7.39, N 15.62. IR spectrum (Varian Scimitar 1000 FT-IR, nujol mull, ν, cm^{-1}): 3371 ν(NH), 1684 ν(C=O), 1636, 1597 ν(C=N). PMR spectrum (Varian Unity 300, $CDCl_3$, δ, ppm, *J*, Hz): 10.928 s (1H, NH); 8.50-8.60 m (1H, CH_{arom}); 8.044 s (1H, CH_{arom}); 7.70-7.80 m (2H, CH_{arom}); 7.56-7.67 m (1H, CH_{arom}); 8.094 d (1H, CH_{arom}, $J = 2.5$ Hz); 7.101 d (1H, CH_{arom}, $J = 2.5$ Hz); 1.328 s (9H, *t*-Bu); 1.356 s (9H, *t*-Bu). EAS (Varian Cary 5000, toluene, nm): 471 ($\varepsilon = 34500$ l·cm^{-1}·mol^{-1}).

$Zn_3(Piv)_4L_2$ (1). A suspension of 0.035 g (0.1 mmol) HL and 0.030 g (0.11 mmol) $[Zn(Piv)_2]_n$ in 30 ml MeCN was stirred while heating (80°C) for 2 h. The resulting red fine-crystalline precipitate was washed with MeCN and DMFA.

Yield: 0.040 g (80%); m.p. > 250°C. Elemental analysis: gross formula $C_{64}H_{86}N_8O_{12}Zn_3$; calculated, %: C 58.08, H 7.02, N 8.47; found, %: C 57.4, H 7.3, N 8.6. IR spectrum (KBr, ν, cm^{-1}): 3600-3300 w, 2959 m, 2868 w, 1605 m, 1591 s, 1581 s, 1566 vs, 1546 s, 1506 m, 1485 s, 1461 m, 1453 m, 1423 s, 1402 s, 1377 vs, 1357 vs, 1331 s, 1307 vs, 1257 s, 1231 m, 1192 s, 1171 w, 1164 w, 1136 s, 1085 w, 1064 m, 1021 s, 960 vs, 938 m, 912 w, 899 w, 884 w, 799 w, 788 w, 760 m, 678 w, 616 w, 606 w, 544 vs, 436 w.

Quantum chemical calculations of the electronic and spatial structure of the HL hydrazone were conducted in Gaussian'03 [15] within the density functional theory (DFT). The calculations used the B3LYP hybrid exchange–correlation functional [16] with the Becke exchange part [17] and Lee–Yang–Parr correlation part [18]. The 6-311+G(*d*,*p*) split-valence basis was used. The geometric structure of the molecules was optimized with respect to all natural variables with no symmetry restrictions. Potential energy surface minima were identified for each structure by calculating the matrix of force constants and normal vibration frequencies. The ChemCraft program [19] was used to prepare the data and presentation images and visualize the calculated results. The total energies of the tautomeric forms and selected bond lengths and valence angles are presented in Table 1.

TABLE 2. Selected Interatomic Distances (*d*, Å) and Valence Angles (ω, deg) in Zn Atoms Coordination Polyhedra in the Structure of **1**

Bond	*d*	Angle	ω	Bond	ω
Zn(1)–N(2)	2.007(2)	N(2)–Zn(1)–N(4)	77.66(7)	O(3)–Zn(1)–O(4)	55.60(7)
Zn(1)–N(4)	2.060(2)	N(2)–Zn(1)–O(1)	120.61(8)	N(1)–Zn(2)–O(2)	92.04(7)
Zn(1)–O(1)	1.926(2)	N(2)–Zn(1)–O(3)	115.08(7)	N(1)–Zn(2)–O(4)	92.26(7)
Zn(1)–O(3)	1.970(2)	N(2)–Zn(1)–O(4)	82.38(7)	N(1)–Zn(2)–N(1A)	180.00(7)
Zn(1)–O(4)	2.572(2)	N(4)–Zn(1)–O(1)	115.02(7)	N(1)–Zn(2)–O(2A)	87.96(7)
Zn(1)···Zn(2)	3.4000(3)	N(4)–Zn(1)–O(3)	106.80(7)	N(1)–Zn(2)–O(4A)	87.74(7)
Zn(2)–N(1)	2.092(2)	N(4)–Zn(1)–O(4)	143.43(7)	O(2)–Zn(2)–O(4)	89.82(7)
Zn(2)–O(2)	2.111(2)	O(1)–Zn(1)–O(3)	115.05(8)	O(2)–Zn(2)–O(2A)	180.00(7)
Zn(2)–O(4)	2.104(2)	O(1)–Zn(1)–O(4)	101.49(7)	O(2)–Zn(2)–O(4A)	90.18(7)
Zn(2)–N(1A)	2.092(2)				
Zn(2)–O(2A)	2.111(2)				
Zn(2)–O(4A)	2.104(2)				

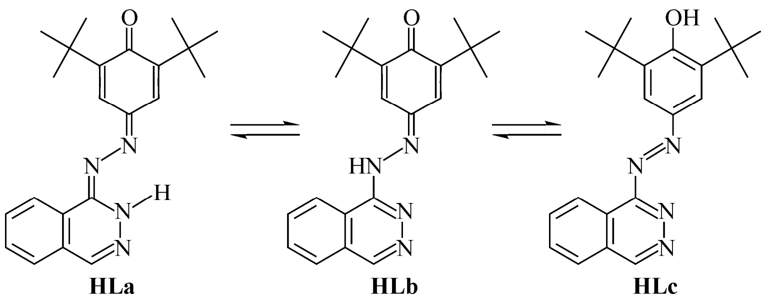
X-Ray crystallographic study. The crystal of complex **1** has a red-brown color and prismatic habit; dimensions: 0.16×0.14×0.02 mm ($C_{64}H_{86}N_8O_{10}Zn_3$, $M = 1323.52$); monoclinic; space group $P2_1/n$ at $T = 183(2)$ K: $a = 10.5014(9)$ Å, $b = 9.7816(8)$ Å, $c = 32.018(3)$ Å, $\beta = 91.9220(10)°$, $V = 3287.1(5)$ Å^3, $Z = 2$, $d_x = 1.337$ g/cm^3, $F(000) = 1392$, $\mu = 1.147$ mm^{-1}.

The unit cell parameters and the intensities of 27,442 reflections ($R_{int} = 0.0507$) were measured with a Bruker Apex II diffractometer with a CCD detector ($T = 183(2)$ K, MoK_α radiation, graphite monochromator, ω-scanning, $\theta_{max} = 28.39°$) [20]. A semiempirical correction for X-ray absorption ($T_{min}/T_{max} = 0.8378/0.9556$) was made with SADABS [21]. The structure was solved by the direct method and refined by full-matrix least squares in an anisotropic approximation for nonhydrogen atoms against F^2_{hkl}. Hydrogen atoms were put into geometrically calculated positions and refined in the rider model ($U_{iso}(H) = 1.5U_{eq}(C)$ for *tert*-butyl groups; $U_{iso}(H) = 1.2U_{eq}(C)$ for all the other fragments). The final divergence factors $R_1 = 0.0388$ and $wR_2 = 0.0938$ for 6018 independent reflections with $I > 2\sigma(I)$ and $R_1 = 0.0652$ and $wR_2 = 0.1092$ for all the 8212 independent reflections; 385 refinement parameters; *GOOF* = 1.039. All the calculations were made in the SHELX-97 programs [22]. The main bond lengths and valence angles are given in Table 2. The atomic coordinates and temperature factors have been deposited with the Cambridge Crystallographic Data Centre (No. 950157; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The HL hydrazone was obtained by condensation of 1-hydrazine phthalazine and 2,6-di-*tert*-butyl-*para*-quinone and identified by elemental analysis and IR and ^{1}H NMR spectroscopy.

Due to NH-proton mobility, the HL hydrazone can exist in three main tautomeric forms: phthalazonic (HLa), hydrazonic (HLb), and azophenolic (HLc).



HLa **HLb** **HLc**

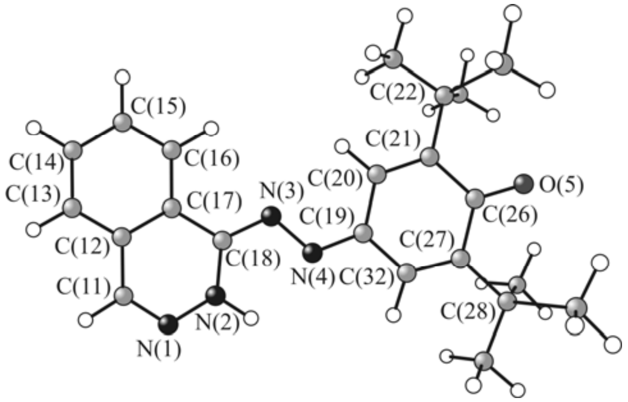


Fig. 1. Structure of the most stable HL hydrazone form in vacuum (atomic numbering corresponds to that of complex **1** in Fig. 2).

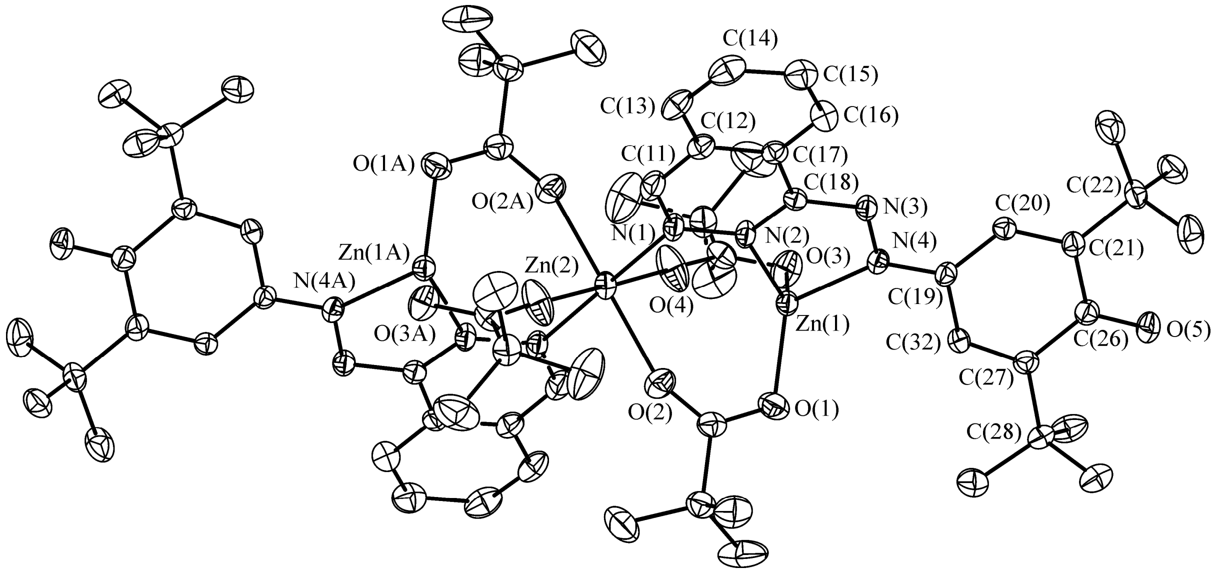


Fig. 2. Structure of complex **1** (hydrogen atoms are not shown; thermal ellipsoids are drawn at 50% probability).

Since there are two signals from *tert*-butyl group protons in the PMR spectrum of HL (see Experimental), priority can be given to one of the quinoid forms, i.e., HLa or HLb. As to the azophenolic form HLc, here one can expect a fast (in the NMR time scale) rotation of the phenol moiety around the single bond N–C, whereupon the signals from the two *t*-Bu groups in the PMR spectra must be detected as an 18-proton singlet. The available literature data lead us to assume that, as in the case of other hydrazinephthalazine hyrdrazones [1, 23-27], the HL compound exists primarily as a phthalazone hydrazone tautomer HLa.

To find evidence supporting this assumption, we calculated the electronic and spatial structure of the HLa–c tautomers by quantum chemical methods within the density functional theory (DFT). The structure of the most stable HL form is shown in Fig. 1; selected bond lengths and bond angles are given in Table 1. It follows from the calculated results that the most stable HL form is the phthalazone hydrazone tautomer HLa, which is stabilized by a strong intramolecular hydrogen bond N(2)–H…N(4). The hydrazonic HLb and azophenolic HLc tautomers are destabilized relative to HLa by 9.34 kcal/mol and 15.13 kcal/mol, respectively.

The $Zn_3(Piv)_4L_2$ (**1**) trinuclear complex was obtained in the reaction between HL and zinc(II) pivalate $[Zn(Piv)_2]_n$. Previously, this reaction was carried out in MeCN, EtOH, and CH_2Cl_2 to produce, in all the cases, a fine-crystalline precipitate that was low soluble in polar and nonpolar solvents. Single crystals of the resulting compound were obtained by solvothermal recrystallization of the precipitate (DMFA, 140°C, 48 h).

The molecule of **1** is centrosymmetric; the Zn(2) atom is located at the center of inversion (Fig. 2). The zinc atoms Zn(1) and Zn(2) (Zn···Zn distance is 3.4000(3) Å) are linked by two carboxylate groups and the phthalazine moiety of the L ligand. The central Zn(2) atom has a distorted octahedral ZnN_2O_4 environment consisting of the N atoms of two L molecules and the O atoms of four carboxylate groups (*d*(Zn–O) distances are 2.1038(18) Å and 2.1105(18) Å; *d*(Zn–N) is 2.0920(19) Å; Table 2). The peripheral Zn(1) atoms have a distorted tetrahedral ZnN_2O_2 environment due to the coordination of the O atoms of two carboxylate groups (*d*(Zn–O) are 1.9261(18) Å and 1.9697(17) Å) and the azomethine and heterocyclic N atoms of the hydrazinephthalazine moiety (*d*(Zn–N) are 2.0069(18) Å and 2.0605(18) Å).

The *para*-quinone moiety of the monodeprotonated L ligand in the $Zn_3(Piv)_4L_2$ molecule has a quinoid form, which is confirmed by the short (C(20)–C(21) 1.353(3) Å and C(27)–C(32) 1.349(3) Å) and long (C(19)–C(20) 1.429(3) Å, C(19)–C(32) 1.426(3) Å, C(21)–C(26) 1.490(3) Å, and C(26)–C(27) 1.484(3) Å) carbon–carbon distances in the cycle. The short lengths of C(26)–O(5) (1.235(3) Å) and C(19)–N(4) (1.333(3) Å) correspond to the double bonds C=O and C=N, respectively [28]. The geometric properties of the L^- anion in **1** are very close to the calculated data for the phthalazone hydrazone tautomeric form HLa (Table 1).

Thus, it is shown by PMR and quantum chemical methods that the product of the interaction of 1-hydrazinephthalazine and 2,6-di-*tert*-butyl-*para*-quinone HL has a phthalazone hydrazone tautomeric form, which is stabilized in the $Zn_3(Piv)_4L_2$ molecular complex. The compound $Zn_3(Piv)_4L_2$ is the first example of a trinuclear complex on the basis of 1-hydrazine phthalazine and its derivatives, in which the metal skeleton is enhanced by strengthening the metal centers with the bridging anions of pivalic acid.

The X-ray crystallographic analysis was conducted at the resource sharing center of the Institute of General and Inorganic Chemistry (Moscow).

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