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Crystal Structures of Copper(II) and Nickel(II) Complexes with 1,3-Bis(3,5-Di-*tert*-Butylsalicylideneamino)propan-2-ol

L. D. Popov[a], S. I. Levchenkov[b, *], I. N. Shcherbakov[a], K. Yu. Suponitskii[c], Yu. P. Tupolova[a], V. V. Lukov[a], and V. A. Kogan[a]

[a] *Southern Federal University, Rostov-on-Don, Russia*
[b] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*
[c] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*
**e-mail: s.levchenkov@gmail.com*

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Abstract—Mononuclear copper(II) and nickel(II) complexes with 1,3-bis(3,5-di-*tert*-butylsalicylideneamino)propan-2-ol (H_3L) of the general formula [M(HL)] were obtained and structurally characterized. It was demonstrated that the presence of the *tert*-butyl groups precludes intermolecular hydrogen bonding in the crystals of the complexes and that their molecules are only linked by hydrophobic interactions.

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INTRODUCTION

Bisazomethines synthesized by condensation of salicylaldehyde derivatives with 1,3-diaminopropan-2-ol are very popular ligand systems in modern coordination chemistry, primarily because of their tendency to form binuclear complexes with the alkoxide O atom and an exogenic group as two bridges [1–4]. At the same time, compounds of this class often behave like so-called "salen-type" ligands in reactions with metal ions [5, 6]: coordination involves their dideprotonated form, while the alcohol OH group remains free. So these ligand systems can produce both mono- and polynuclear complexes. It should be noted that transition metal complexes with salen ligands are under extensive study because of their inherent good catalytic properties [6–8].

We synthesized new mononuclear copper(II) and nickel(II) complexes with 1,3-bis(3,5-di-*tert*-butylsalicylideneamino)propan-2-ol (H_3L) of the general formula [M(HL)] (M = Cu (**I**) and Ni (**II**)) and examined their structures by IR spectroscopy, magnetochemistry, and X-ray diffraction.

EXPERIMENTAL

The ligand H_3L was prepared as described in [9].

Synthesis of complexes I and II. A solution of copper(II) perchlorate or nickel(II) perchlorate (1 mmol) in methanol (10 mL) was added to a hot solution of H_3L (1 mmol) in methanol (20 mL). The reaction mixture was refluxed for 1 h. On cooling, the precipitate that formed was filtered off and recrystallized from ethanol.

The yield of complex **I** was 0.38 g (65%), $\underline{T}_m$ > 250°C.

For $C_{33}H_{48}N_2O_3Cu$ (**I**)

anal. calcd., %:	C, 67.8;	H, 8.28;	N, 4.79;	Cu, 10.9.
Found, %:	C, 67.4;	H, 8.22;	N, 4.92;	Cu, 11.3.

IR (ν, cm^{-1}): 3302 ν(OH), 1625, ν(C=N). μ_{eff} 1.85 (300 K) and 1.80 μ_B (77.4 K).

The yield of complex **II** was 0.29 g (50%), $\underline{T}_m$ > 250°C.

For $C_{33}H_{48}N_2O_3Ni$ (**II**)

anal. calcd., %:	C, 68.4;	H, 8.35;	N, 4.83;	Ni, 10.1.
Found, %:	C, 68.9;	H, 8.20;	N, 4.77;	Ni, 10.7.

IR (ν, cm^{-1}): 3261 ν(OH), 1621 ν(C=N).

IR spectra (Nujol) were recorded on a Varian Scimitar 1000 FTIR instrument in the 400–4000 cm^{-1} range. Specific magnetic susceptibility was measured using the relative Faraday method in a temperature range from 77.4 to 300 K.

X-ray diffraction study of complexes **I** and **II** was performed on a Bruker Smart 1000 CCD diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The collected set of reflection intensities was processed with the SAINT [10] and SADABS programs [11]. The structures were solved by the direct methods and refined anisotropically on F^2_{hkl} by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms were located geometrically and refined using a riding model (U_{iso}(H) = nU_{iso}(C), where n = 1.5 for the methyl C atoms and

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
M	584.27	579.44
Crystal dimensions, mm	0.18 × 0.12 × 0.09	0.22 × 0.14 × 0.08
Temperature, K	120(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	P_{bcn}	P_{bcn}
a, Å	26.986(3)	26.5633(12)
b, Å	11.0080(13)	11.2405(5)
c, Å	10.2986(12)	10.4600(5)
V, Å^3	3059.3(6)	3123.2(2)
Z	4	4
ρ_{calcd}, g/cm^3	1.269	1.232
μ, mm^{-1}	0.749	0.655
F(000)	1252	1248
$2\theta_{max}$, deg	52.0	60.0
Ranges of h, k, and l indices	$-33 \le h \le 33$, $-13 \le k \le 13$, $-12 \le l \le 12$	$-37 \le h \le 37$, $-15 \le k \le 15$, $-14 \le l \le 14$
Number of measured reflections	25078	37387
Number of unique reflections	3009	4538
Number of reflections with $I \ge 2\sigma(I)$	2343	3659
Number of parameters refined	192	192
GOOF (for all reflections)	1.016	1.068
R_1 ($I > 2\sigma(I)$)	0.0463	0.0338
wR_2 (for all reflections)	0.1244	0.0821
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.982/–0.435	0.360/–0.307

$n = 1.2$ for the other C atoms). All calculations were performed with the SHELX program package [12]. The molecular and crystal structures of the complexes were analyzed with the PLATON program [13].

Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II** are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2. The atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (nos. 927601 (**I**) and 927602 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complexes **I** and **II** were obtained by reactions of 1,3-bis(3,5-di-*tert*-butylsalicylideneamino)propan-2-ol with copper(II) perchlorate and nickel(II) perchlorate, respectively, in methanol. Single crystals suitable for X-ray diffraction were prepared by recrystallization from ethanol.

The azomethine ligands in the isostructural crystals of both complexes are dideprotonated and make up a tetrahedral environment around the metal center. The alcohol OH group is not involved in the coordination. The O(2) atom and the methine C atom are disordered over two crystallographic positions with equal occupancies.

The coordination polyhedron of the copper atom in complex **I** is a planar square with a tetrahedral distortion (Fig. 1); the dihedral angle between the planes O(1)Cu(1)N(1) and O(2)Cu(1)N(2) is 30.6°.

It is worth noting that the distortion of the chelate ring is not unique to copper complexes with the *tert*-butyl groups in the *ortho*-position. In other structurally characterized mononuclear copper complexes with ligands obtained by condensation of salicylaldehyde [14], 3-*tert*-butyl-5-methylsalicylaldehyde [15], 5-nitrosalicylaldehyde [16], and 4-diethylaminosalicylaldehyde [17] with 1,3-diaminopropan-2-ol, the coordination polyhedron of the Cu atom also shows substantial tetrahedral distortions; the dihedral angles between the planes OCuN in those complexes are 35.7°, 15.7°, 15.4°, and 28.4°, respectively. At the same time, in a vanadyl(IV) complex with 1,3-bis(3-methoxysalicylideneamino)propan-2-ol [18], the electron-donating O and N atoms are virtually coplanar.

The effective magnetic moment of complex **I** at room temperature is 1.85 μ_B and remains nearly the same on cooling to 77.4 K. This suggests the absence of intermolecular magnetic exchange between the copper(II) ions.

As in complex **I**, the coordination polyhedron of the Ni atom in complex **II** is a planar square with a tetrahedral distortion; the dihedral angle between the planes O(1)Ni(1)N(1) and O(2)Ni(1)N(2) is 21.7°. Despite a considerable tetrahedral distortion of the coordination polyhedron, the nickel ion in complex **II** is in a low-spin state ($S = 0$), which is evident from the diamagnetism of this complex.

Note that no data on mononuclear nickel(II) complexes with bisazomethines derived from salicylaldehyde derivatives and 1,3-diaminopropan-2-ol have been available hitherto from the Cambridge Structural Database. In a number of structurally characterized trinuclear complexes, the phenoxide O atoms perform a bridging function [19–22]. In all those complexes, the coordination polyhedron of the nickel ions is an octahedron. In complex **II**, the phenoxide O atom cannot form an additional coordination bond because the *tert*-butyl groups are in the *ortho*-position of the benzene ring.

Table 2. Selected bond lengths and bond angles in structures **I** and **II**

Bond	d, Å	Bond	d, Å
		I	
Cu(1)–O(1)	1.8920(17)	Cu(1)–N(1)	1.938(2)
		II	
Ni(1)–O(1)	1.8520(9)	Ni(1)–N(1)	1.8668(11)
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(1)Cu(1)O(1*A*)	88.25(10)	O(1)Cu(1)N(1)	93.67(8)
O(1)Cu(1)N(1*A*)	157.70(9)	N(1*A*)Cu(1)N(1)	92.90(13)
		II	
O(1)Ni(1)O(1*A*)	84.84(6)	O(1)Ni(1)N(1)	93.91(4)
O(1)Ni(1)N(1*A*)	163.83(5)	N(1*A*)Ni(1)N(1)	91.68(7)

The crystal structures of complexes **I** and **II** differ noticeably from those described earlier for mononuclear complexes with bisazomethines synthesized by condensation of salicylaldehyde and its derivatives with 1,3-diaminopropan-2-ol. The main difference is that the uncoordinated alcohol OH group is not involved in intermolecular hydrogen bonding, which, in copper complexes, serves to combine complex molecules into infinite chains in the crystal [14, 16, 17] or to form hydrogen-bonded dimers [15].

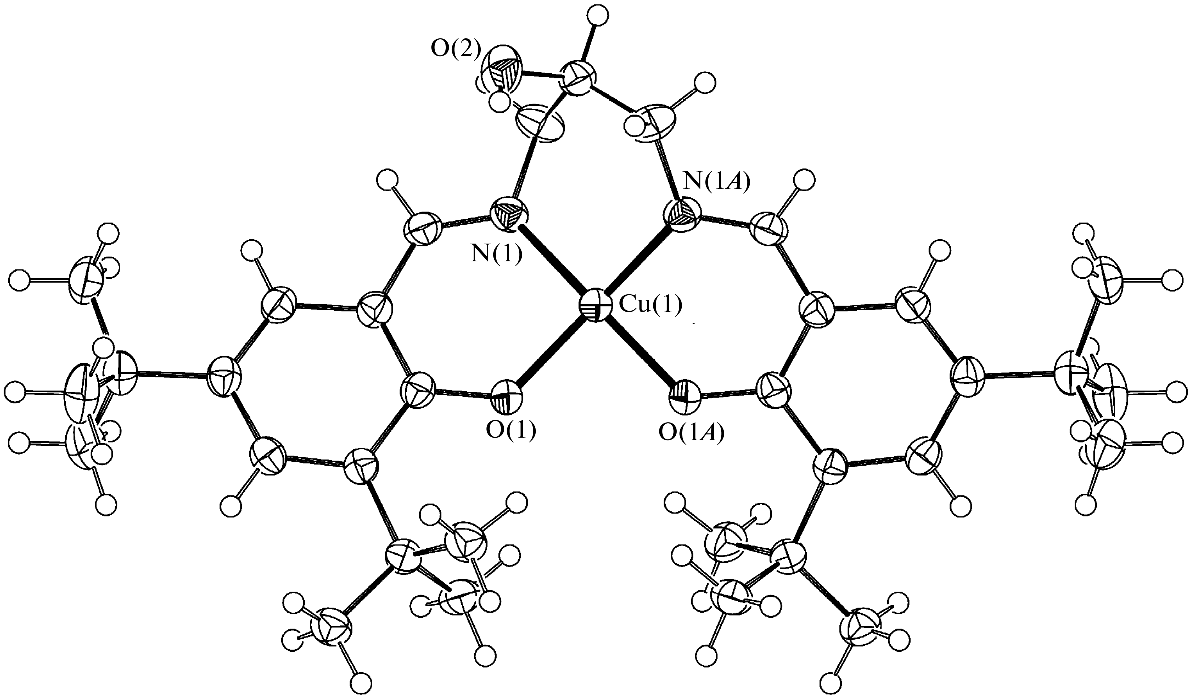

Fig. 1. Structure **I** with atomic thermal displacement ellipsoids (50% probability).

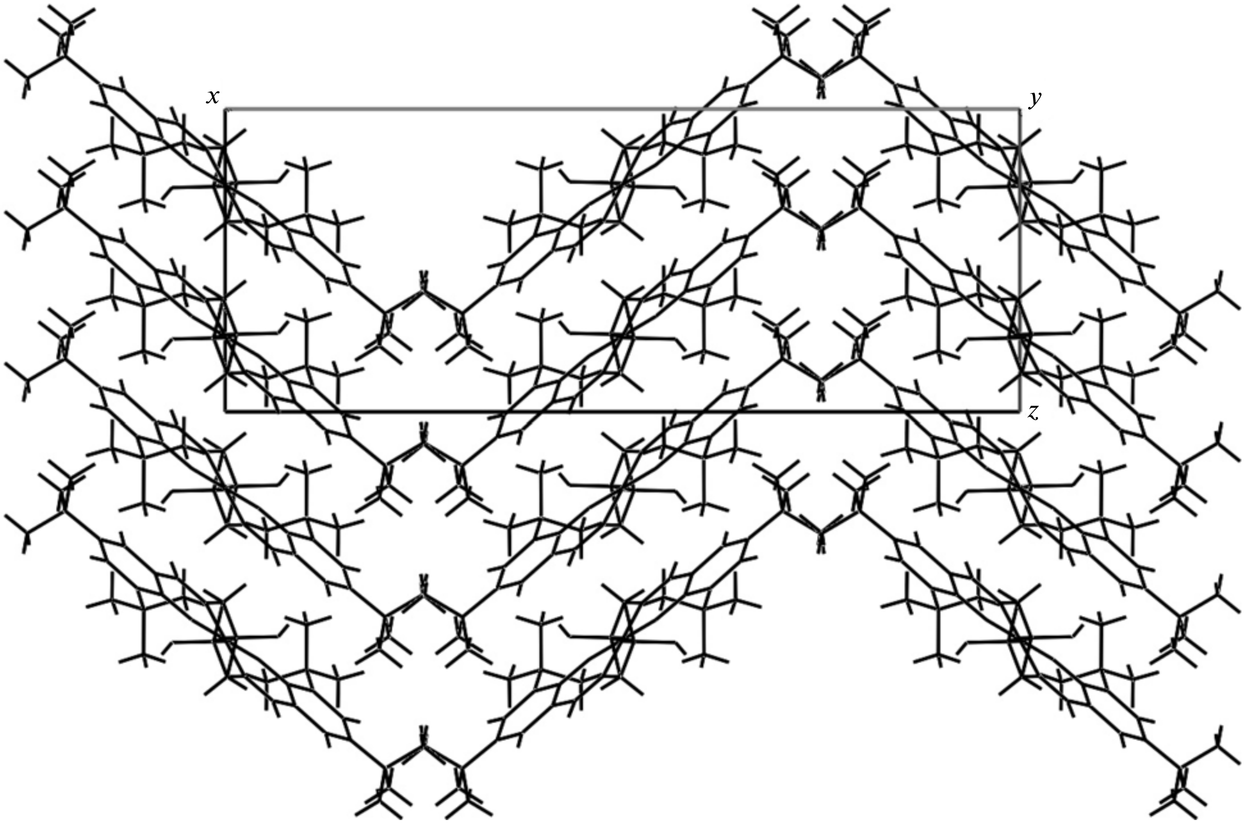

Fig. 2. Molecular packing of complex **I** in the crystal (viewed along the crystallographic axis *y*).

Since the crystallographic parameters of complexes **I** and **II** are close (Table 1), here we describe only the crystal packing of complex **I** (Fig. 2). The molecules of both complexes in the crystals make up layers running parallel to the crystallographic plane *y*0*z*, the *tert*-butyl groups being on the surface of each layer. Hydrophobic interactions occur between the layers; within each layer, the molecules are also linked by hydrophobic interactions alone. A similar crystal packing has been reported for nickel(II), palladium(II), and platinum(II) complexes with bisazomethines derived from 3,5-di-*tert*-butylsalicylaldehyde and 1,2-ethylenediamine and 1,3-diaminopropane [23, 24].

To sum up, we obtained and structurally characterized mononuclear copper(II) and nickel(II) complexes with 1,3-bis(3,5-di-*tert*-butylsalicylideneamino)propan-2-ol. We demonstrated that the presence of the *tert*-butyl groups precludes intermolecular hydrogen bonding in the crystals of the complexes, so their molecules are only linked by hydrophobic interactions.

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