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NICKEL(II) AND COPPER(II) COMPLEXES WITH AMIDRAZONE-BASED LIGANDS: STRUCTURE AND CATALYTIC ACTIVITY

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Abstract—Nickel(II) and copper(II) complexes MeL, where H_2L = [9-(2′-hydroxyphenyl)-6-methyl-3-acetyl-5,7,8-triazanona-3,6,8-trien-2-one], have been synthesized by template reaction of salicylaldehyde acetamidrazone with corresponding $Me(acac)_2$ and Hacac in the presence of the orthoformic ester at 110°C. The crystal structure of CuL has been determined by X-ray diffraction. The square-planar mode of coordination is realized in CuL. Comparison of geometrical parameters of CuL with those of the corresponding derivative based on *S*-allylisothiosemicarbazide showed that substitution of the —SR group by methyl in the quadridentate ligand does not affect the mode of binding nor the main interatomic distances and angles in the ligand. The data from magnetic measurements, ^1H NMR and EI mass spectra indicate that NiL has a similarly structured coordination polyhedron. Epoxidation of norbornene can be performed efficiently with molecular oxygen (1 atm) in THF (or THF–EtOAc) in the presence of CuL at 70°C. The corresponding copper(II) derivatives based on *S*-substituted isothiosemicarbazides are much less active as catalysts.

The ligands based on the *S*-alkylated isothiosemicarbazides $H_2NNC(SR)NH_2$ form various coordination compounds with transition metals.[1,2] Recently, it was shown that these ligands are also capable of stabilizing unusual oxidation states of 3*d* metals. For example, salicylaldehyde *S*-propylisothiosemicarbazide in its doubly deprotonated form gives a complex $[Mn^{IV}L_2]$.[3] Also, *S*-methyl-1,4 - bis(salicylidene)isothiosemicarbazidate(2−) gives a μ-oxo-tetranuclear mixed-valence complex $[(Fe_2L_2O)_2][I_3]\cdot I_2$[4] and pentan-2,4-dione bis(*S*-alkylisothiosemicarbazones), in their trianionic form, stabilize iron(IV) and copper(III) in the corresponding complexes.[5–7]

In order to get an insight into the influence of a sulphur atom on the electron-donor properties of the atoms and groups in the corresponding ligands

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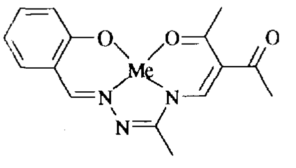
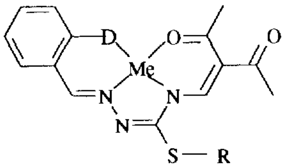
and their capability to stabilize unusual oxidation states of the 3*d* metal ions, we began to study the closely related systems based on amidrazones. In this paper we report data on the synthesis, structure and catalytic properties of the coordination compounds of nickel(II) and copper(II) of the general formula MeL:



MeL

Me = Ni **(1)**
Me = Cu **(2)**

We compare these results with those reported earlier[8,9] for closely related systems based on *S*-alkylisothiosemicarbazides (MeQ):



MeQ

D = O, R = CH_3, Me = Ni **(3)**
D = O, R = C_2H_5, Me = Ni **(4)**
D = O, R = n-C_3H_7, Me = Cu **(5)**
D = O, R = C_3H_5, Me = Cu **(6)**
D = NH, R = CH_3, Me = Cu **(7)**
D = NTs, R = CH_3, Me = Cu **(8)**

EXPERIMENTAL

All chemicals used were analytical reagent grade. Acetamidrazone hydrochloride was prepared according to a known procedure described in ref. 10.

Synthesis of salicylaldehyde acetamidrazone

To a warm solution of salicylaldehyde (2.1 cm^3, 20 mmol) in ethanol (15 cm^3), acetamidrazone hydrochloride (2.19 g, 20 mmol) in water (8 cm^3) and then Na_2CO_3 (1.06 g, 10 mmol) in water (7 cm^3) were added. After cooling the precipitate was separated by filtration washed with mixture of ethanol–water (1 : 1), ethanol and ether. Yield 1.9 g, 53.6%. *M* (mass spectrum) 177.

Synthesis of complexes

NiL (**1**). A mixture of salicylaldehyde acetamidrazone (1.77 g, 10 mmol), $Ni(acac)_2$ (2.56 g, 10 mmol), orthoformic ester (4 cm^3) and pentan-2,4-dione (16 cm^3) was heated in a sealed ampoule at 110°C for 8 h. After cooling the deposited precipitate was removed by filtration and washed with ethanol and ether. The red–orange product was purified by dissolving the precipitate in a minimum quantity of chloroform, filtration of the solution, evaporation of the filtrate until ~ 1/4 of the initial volume and adding an equal volume of methanol. Yield 0.65 g, 18.9%. Found: Ni, 17.2; C, 52.1; H, 4.30; N, 11.7. Calc. for $C_{15}H_{15}NiN_3O_3$ (fw 344.00): Ni, 17.1; C, 52.4; H, 4.4; N, 12.2. *M* (mass spectrum) 343.

CuL (**2**). The corresponding copper(II) complex was prepared in an analogous way to that described for NiL with a yield of 0.41 g, 11.8%. Found: C, 51.2; H, 4.2; N, 12.0. Calc. for $C_{15}H_{15}CuN_3O_3$ (fw 348.85): C, 51.6; H, 4.3; N, 12.0. *M* (mass spectrum) 348.

Complexes **3–8** were synthesized according to the literature procedures.[11–13] Single crystals of CuL of sufficient quality for X-ray analysis were grown from a saturated chloroform–hexane (1 : 1) solution at room temperature.

The carbon, hydrogen and nitrogen contents were determined by standard micro-methods. The nickel content was determined by the gravimetric method as $Ni(DMG)_2$.

Electron impact mass spectra were measured on an MX-1320 double-focusing mass spectrometer (PO 'Nauchpribor', Orel, Russia) using a direct inlet system at 110–140°C, a temperature of the ionization chamber 60–70°C higher than the evaporation temperature, an emission current of 10 mA, and an ionization energy of 70 eV.

Magnetic susceptibilities were measured on a Gouy balance. Effective magnetic moments were calculated from the relation $\mu_{eff} = 2.828\,(X_M \cdot T)^{1/2}$, taking into account the diamagnetic corrections.[14]

X-ray crystallographic studies

A suitable brown–red plate like single crystal of CuL, dimensions 0.40 × 0.30 × 0.15 mm, was placed in an RED-4 diffractometer (Mo-K_α radiation, ω-scanning method, constant speed 8 grad min^{-1}) to collect reflection data. In order to determine and refine the crystal structure, 2069 unique reflections satisfying $I \geqslant 3\sigma(I)$ were used; the dependent reflections were averaged. The structure was solved by the heavy-atom technique in combination with direct methods and refined by least-squares using the SHELXTL program[15] on an SM-4 computer. The non-hydrogen atoms found from Fourier synthesis were refined anisotropically and the hydrogen atoms, which were located objectively, were refined isotropically. The refinement was carried out using the weighting scheme $w = [\sigma^2|F_o| + 0.0050|F_o|^2]^{-1}$. The final R factor is 0.049. The crystallographic data and interatomic distances and bond angles are presented in Tables 1 and 2, respectively.

RESULTS AND DISCUSSION

The heating of salicylaldehyde acetamidrazone with pentan-2,4-dione and corresponding Me $(acac)_2$ in the presence of orthoformic ester gives rise to the complex MeL, where Me = Ni, Cu. Both the red–orange nickel(II) chelate and the brown copper(II) product are crystalline, soluble in chloroform, less soluble in methanol and ethanol, and insoluble in hexane, ether and water.

The nickel compound is diamagnetic. The copper complex has effective magnetic moment 1.67 B.M. at 293 K, which is close to the pure spin value for a system with $S = 1/2$.

The highly conjugated systems MeL are stable to electron impact. The most intense peaks in their mass spectra are at m/z 343 (NiL) and 348 (CuL) corresponding to the molecular ions $[M]^+$. The most characteristic ions formed on fragmentation are the following: $[M]^{2+}$, $[M-CH_3]^{2+}$, $[M-COCH_3]^+$.

Table 1. Crystallographic data for CuL

Chemical formula	$C_{15}H_{15}CuN_3O_3$
Formula weight	348.84
System	Triclinic
Space group	$P\bar{1}$
a (Å)	12.796 (3)
b (Å)	8.461 (4)
c (Å)	7.325 (3)
α (°)	73.04 (3)
β (°)	75.71 (3)
γ (°)	76.77 (2)
V (Å^3)	724 (1)
Z	2
T (°C)	20
λ (Å)	0.71069
$F(000)$	358
μ (cm^{-1})	15.84
$2\theta_{max}$ (°)	75.1
D_o (g cm^{-3})	1.599 (3)
No. of reflections measured	2079
No. of unique reflections	2069
R	0.049
R_w	0.055

Figure 1 shows the molecular structure of the compound CuL. The general mode of coordination of the quadridentate ligand is the same as in the related nickel(II) and copper(II) complexes based on S-alkylisothiosemicarbazides.[8,9] The square-planar coordination of the copper atom is realized via the two end nitrogen atoms of the acetamidrazone fragment [N(1) and N(3)], the phenolic oxygen atom O(1) and the oxygen atom of the 3-formylacetylacetonate residue O(2). The interatomic distances Cu—O(1) and Cu—O(2) are different (due to the different nature of binding groups—deprotonated hydroxyl and carbonyl) and equal to 1.876 and 1.926 Å, respectively. The same difference was revealed for the copper(II) chelate **(6)** based on S-allylisothiosemicarbazide (1.879 and 1.934 Å, respectively). The bond lengths Cu—N(1) and Cu—N(3) are identical in the limits of 3σ (Table 2). In spite of this, the comparison of these distances with the corresponding bond lengths for copper(II) chelate **6** described in ref. 9 shows that there is a tendency towards shortening of the Cu—N(1) distance compared with the Cu—N(3) bond length.

It should be noted that the ligand under discussion acts as a doubly charged anion, deprotonated at O(1) and N(3). Upon coordination with copper(II), three metallo-rings are formed: two six-membered $CuNC_3O$ and one five-membered CuN_3C. The five-membered metallocycle is practically planar. However, the electron density is lower because the electron donating —SR group is lacking. The six-membered salicylidene ring exhibits a tendency to adopt the conformation of a half-boat. The fragment O(1), C(11), C(10), C(9), N(1) is almost planar and the displacement of the copper atom from the mean plane of that cycle is 0.14 Å. Another $CuNC_3O$ ring adopts the conformation of an almost flattened boat; the atoms O(2), C(7), C(3) and N(3) are practically coplanar. The Cu and C(4) atoms deviate from the mean plane by 0.021 and 0.024 Å, respectively. The distortion of the coordinating donor atoms relatively to the mean plane is ±0.007 Å. The copper atom is displaced from this plane by 0.06 Å toward N(3) of the molecule connected with basical by symmetry transformation. This fact could be due to the specific intermolecular interactions between neighbouring square-planar copper(II) complexes in the crystal. The apical positions are occupied by the donor atoms of adjacent molecules. Thus, the distances Cu—N(3) $(-x, -y, -z)$ and Cu—O(1) $(-x, -y, 1-z)$ are 3.323 and 3.232 Å, respectively. The same

Table 2. Bond lengths (Å) and bond angles (°) for CuL and MeQ (Me = Ni, Cu)[8,9]

Coordination polyhedron of Cu^{II}

	CuL	CuQ **(6)**		CuL	CuQ **(6)**
Cu—O(1)	1.876(3)	1.879	Cu—O(2)	1.926(3)	1.934
Cu—N(1)	1.908(3)	1.914	Cu—N(3)	1.900(3)	1.921
Cu—N(3a)	3.323(3)		Cu—O(1b)	3.232(3)	

	CuL	CuQ **(6)**
O(1)—Cu—O(2)	92.7(1)	93.4
O(1)—Cu—N(1)	94.2(1)	94.3
O(2)—Cu—N(3)	91.8(1)	90.7
N(1)—Cu—N(3)	81.1(1)	81.7
O(1)—Cu—N(3)	175.4(1)	175.4
O(2)—Cu—N(1)	173.0(1)	172.2

Ligand

	CuL	NiQ **(3)**	CuQ **(6)**		CuL	NiQ **(3)**	CuQ **(6)**
N(1)—N(2)	1.393(5)	1.422	1.411	N(2)—C(1)	1.307(6)	1.278	1.266
C(1)—N(3)	1.390(5)	1.393	1.409	C(1)—C(2)	1.493(6)	—	—
N(3)—C(3)	1.343(5)	1.310	1.304	C(3)—C(4)	1.389(6)	1.409	1.395
C(4)—C(5)	1.484(6)	1.461	1.466	C(5)—C(6)	1.514(8)	1.524	1.509
C(5)—O(3)	1.202(6)	1.210	1.219	C(4)—C(7)	1.424(6)	1.458	1.446
C(7)—C(8)	1.494(7)	1.498	1.497	C(7)—O(2)	1.270(5)	1.254	1.252
N(1)—C(9)	1.303(5)	1.289	1.273	C(9)—C(10)	1.432(6)	1.439	1.434
C(10)—C(11)	1.418(6)	1.437	1.431	C(11)—C(12)	1.401(7)	1.419	1.428
C(12)—C(13)	1.393(6)	1.355	1.351	C(13)—C(14)	1.384(7)	1.393	1.398
C(14)—C(15)	1.361(7)	1.388	1.370	C(15)—C(10)	1.425(6)	1.387	1.392
C(11)—O(1)	1.317(5)	1.307	1.290				

	CuL	NiQ **(3)**	CuQ **(6)**
N(2)—N(1)—C(9)	116.5(3)	116.5	116.1
N(1)—N(2)—C(1)	110.9(4)	110.4	110.4
C(1)—N(3)—C(3)	120.9(3)	122.8	122.8
N(2)—C(1)—N(3)	118.8(4)	121.6	119.7
N(2)—C(1)—C(2)	118.8(4)		
N(3)—C(1)—C(2)	122.6(4)		
N(3)—C(3)—C(4)	125.8(4)	128.0	126.4
C(3)—C(4)—C(5)	116.5(4)	118.0	117.8
C(3)—C(4)—C(7)	122.5(4)	119.6	119.6
C(5)—C(4)—C(7)	120.8(4)	122.2	122.5
O(3)—C(5)—C(4)	122.7(5)	123.5	123.1
O(3)—C(5)—C(6)	117.8(5)	116.9	116.6
C(4)—C(5)—C(6)	119.3(4)	119.6	120.4
O(2)—C(7)—C(4)	123.7(4)	124.0	122.9
O(2)—C(7)—C(8)	112.9(4)	115.2	115.8
C(4)—C(7)—C(8)	123.2(4)	120.7	121.3
N(1)—C(9)—C(10)	123.4(4)	123.6	124.6
C(9)—C(10)—C(11)	123.5(4)	122.1	120.1
C(9)—C(10)—C(15)	117.2(4)	117.0	118.2
C(11)—C(10)—C(15)	119.1(4)	120.8	121.0
O(1)—C(11)—C(10)	124.3(4)	125.9	125.3
O(1)—C(11)—C(12)	117.6(4)	118.9	119.1
C(10)—C(11)—C(12)	117.9(4)	115.2	115.5
C(11)—C(12)—C(13)	121.0(4)	122.4	121.8
C(12)—C(13)—C(14)	120.9(4)	122.3	121.8
C(13)—C(14)—C(15)	119.3(4)	117.3	118.4
C(10)—C(15)—C(14)	121.5(4)	122.1	121.3

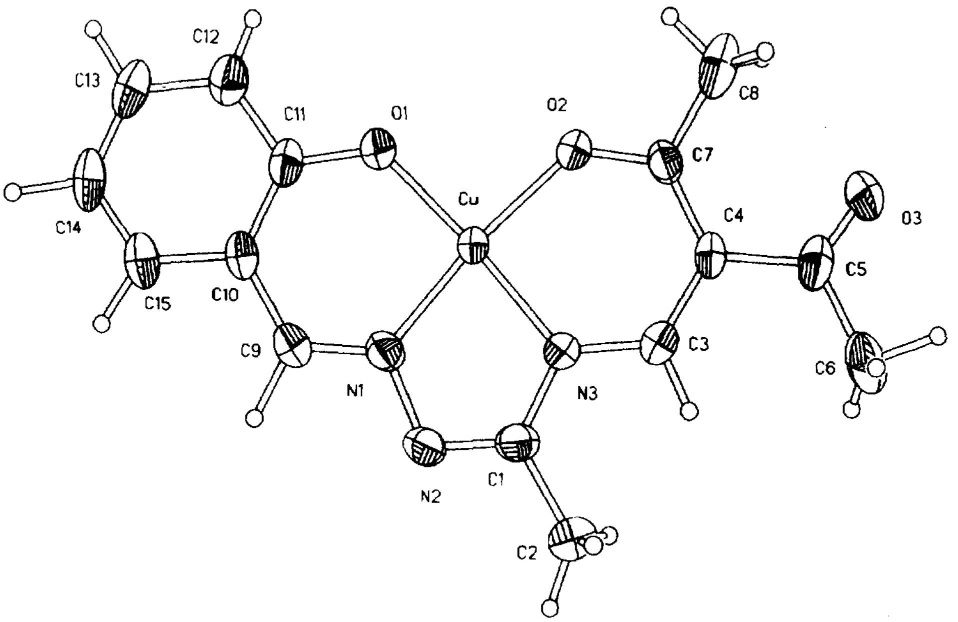
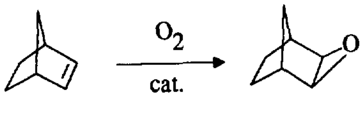


Fig. 1. Molecular structure of complex CuL, showing the thermal vibration ellipsoids and the atom numbering scheme.

intermolecular interaction was shown for a number of other square-planar copper(II) complexes.[16]

Therefore, on passing from *S*-alkylisothiosemicarbazide metal-derivatives CuQ to CuL, the mode of coordination and bond distances methyl–ligand are not altered significantly. At the same time the displacement of the —SR group by a methyl affects the packing of the square-planar molecules. In the first case the molecular structure can be explained by van der Waals interactions between molecules, and in the second case—the stacked structure (Fig. 2)—by van der Waals interactions between covalently bound stacks.

Recently, it was shown that 3*d*-metal salts or Schiff base complexes exhibit catalytic activity in aerobic epoxidation of olefins in the presence of aldehydes or ketones.[17–23] In order to compare the properties of MeL and MeQ compounds, the catalytic activity of nickel(II) and copper(II) complexes was examined in the oxidation of norbornene with molecular oxygen:



In a typical experiment, norbornene (2 mmol) and catalyst (0.04 mmol) in THF (2 cm^3) in oxygen (1 atm) were stirred for 24 h at 70°C. Aliquots of the THF layer were analysed by GLC and compared to

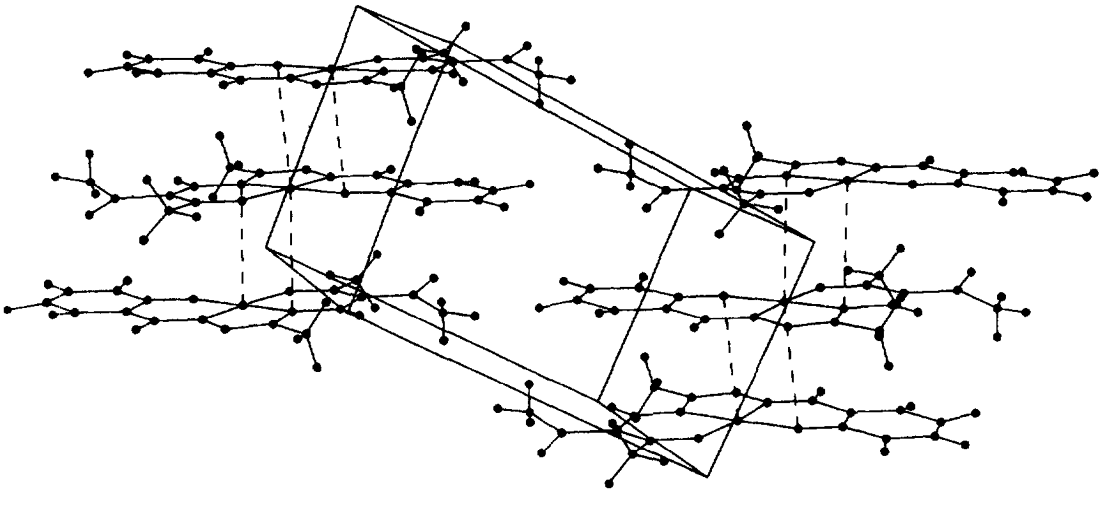


Fig. 2. A view of the unit cell packing diagram for CuL.

Table 3. Nickel(II) and copper(II)-catalysed epoxidation of norbornene with molecular oxygen (1 atm) at 70°C

Catalyst	Solvent	Conversion (%)[a]	Yield (%) of *exo*-epoxide[b]
1	THF	46	100
2	THF	83	100
4	THF	13	100
5	THF	13	100
6	THF	16	100
7	THF	22	100
	THF–CH_3CN	1	
8	THF–EtOAc	38	100
	Toluene	0	

[a] Determined by GLC analysis based on the starting norbornene.

[b] Determined by GLC analysis based on the converted substrate; the identity of the *exo*-epoxide was verified by co-injection with authentic sample and GC–MS analysis.

an internal standard. The representative results of the catalytic aerobic oxidation of norbornene are summarized in Table 3.

Copper(II) complexes proved to be more effective catalysts than the nickel(II) analogues. The presence of —SR group in the quadridentate ligand diminishes the catalytic activity of the corresponding complexes. Nickel and copper complexes of amidrazone-based ligands (**1** and **2**) are much more effective in this process (see Table 3). This fact can be explained taking into account that the —SR group, as shown by a series of X-ray diffractions,[16] may occupy the axial coordination site of the copper atom of the neighbouring molecule and influence in such a way the reactivity of the metal centre. It is necessary to note that a mixture of CuCl and the ligand H_2Q (D = NTs, R = CH_3) does not promote the epoxidation reaction. The results presented in Table 3 show that the nature of the donor group D influences the catalytic activity of the copper complex as well. Complex **8** proved to be the most effective catalyst among nickel(II) and copper(II) complexes based on isothiosemicarbazides. One can suppose that the corresponding amidrazone derivatives of **7** and **8** will prove to be more effective catalysts for the process of alkene epoxidation. Systems with NTs groups as in **8** but lacking —SR moieties should be the most effective of all catalysts. Such experiments are underway in our laboratories.

CONCLUSIONS

X-ray diffraction shows that substitution of the —SR group by a methyl in the quadridentate ligand does not affect the mode of binding nor the main geometrical parameters of the ligand. At the same time the displacement changes the packing of planar molecules. In the epoxidation of norbornene by molecular oxygen, copper(II) complexes are much more efficient catalysts than the nickel(II) analogues. In the copper(II) series, complex **2** is currently the most active catalyst.

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