Seven-membered metallocycle in the Cu^{II} complex with deprotonated 2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide

P. A. Petrov,[a] E. V. Tret´yakov,[a] G. V. Romanenko,[b] V. I. Ovcharenko,[a]★ and R. Z. Sagdeev[a]

[a]*International Tomography Center, Siberian Branch of the Russian Academy of Sciences,*
3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 33 1399. E-mail: ovchar@tomo.nsc.ru
[b]*Novosibirsk State University,*
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation

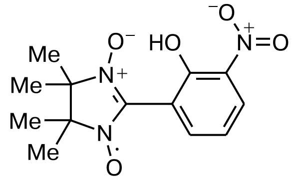
The reaction of $CuCl_2$ with deprotonated 2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide afforded a bis-chelate complex containing seven-membered metallocycles.

Key words: nitroxides, copper complexes, X-ray diffraction analysis.

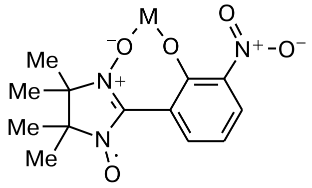
The development of procedures for the synthesis of molecular magnets and the corresponding magnetically active materials is a topical problem in modern coordination chemistry. As part of this line of investigation, we studied the reactions of copper(II) salts with the paramagnetic ligand, *viz.*, 2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (HL).

Results and Discussion

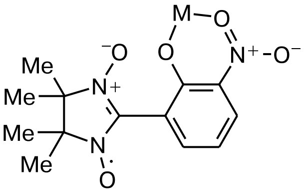
X-ray diffraction study demonstrated that the reactions afforded a bis-chelate complex with seven-membered metallocycles. This result was unexpected because the structure of the L^- ligand allows the formation of six-membered metallocycles as a result of bidentate coordination of L^- through the O atom of the deprotonated phenol group and one of the O atoms of the nitro group.



The bidentate coordination of the L^- ligand giving rise to six-membered metallocycles seemed to be more favorable not only from general considerations of higher stability of six-membered metallocycles compared to seven-membered metallocycles but also reasoning from the data on the structures of complexes with organic ligands containing functional groups analogous to those present in the L^- ligand. The Cambridge Structural Database (CSD)[1] includes 53 entries related to transition metal complexes (among them 21 Cu^{II} complexes) with various bidentate organic ligands, which bear six-membered $\overline{\text{M–O–C–C–N–O}}$ metallocycles (M is metal) involving the deprotonated oxynitro fragment (structure **B**). However, data on the structures containing the seven-membered $\overline{\text{M–O–C–C–C–N–O}}$ metallocycle are unavailable in the CSD, *i.e.*, no transition metal complexes containing an **A**-type fragment were structurally characterized.



A



B

M is metal

We isolated the Cu^{II} bis-chelate as mixed-ligand complexes with a coordinated solvent molecule, *viz.*, $CuL_2(AcOEt)$ and $CuL_2(MeCN)$. As can be seen from Fig. 1, the O atoms of the nitro groups are uncoordinated. The environment about the Cu atom in the $CuL_2(AcOEt)$ molecule is formed by the O atoms of two N—O groups, two deprotonated oxy groups, and AcOEt. The coordination polyhedron is a square pyramid with a distorted base, which can be considered as a strongly flattened tetrahedron.

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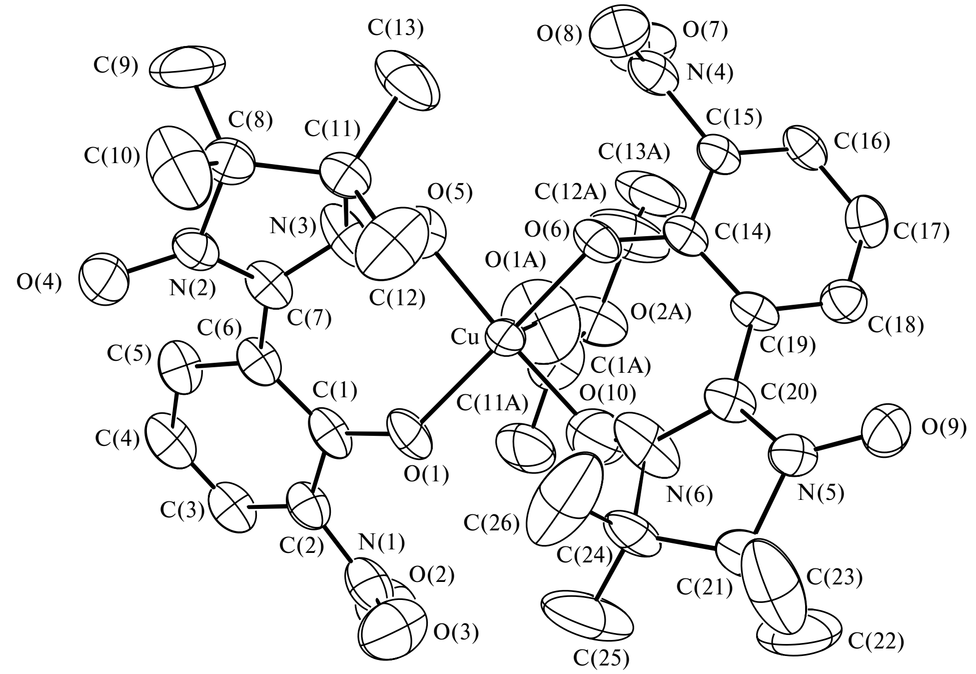


Fig. 1. Molecular structure of the $CuL_2(AcOEt)$ complex.

The angle between the O(1)—Cu—O(5) and O(6)—Cu—O(10) planes is 25.2°. The Cu—O_L distances are in the range of 1.912(2)—1.932(2) Å (Table 1).

The Cu atom has a coordination number of five due to additional coordination by the carbonyl oxygen atom of ethyl acetate; the length of this coordination bond is 2.359(3) Å. The atoms of the nitronyl nitroxide fragment O—N—C—N—O are in a single plane. The bond lengths in the coordinated N—O groups are noticeably larger (~1.30 Å) than the corresponding bond lengths in the uncoordinated N—O groups (~1.27 Å). These values are equal to the average bond lengths determined from the CSD data on 104 transition metal complexes containing the O—N—C—N—O—M fragment. The angle between the planes of the NCN fragment of the imidazoline ring and the Ph ring of the L^- ligand (~49°; in Table 1, this angle is denoted as NCN—Ph) characterizes a nonplanar structure of the seven-membered chelate rings. In two crystallographically independent ligands, the planes of the NO_2 groups form angles of 55.5 and 49.0° with the planes of the Ph rings.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the molecules under study

Parameter	HL	$CuL_2(AcOEt)$	$CuL_2(MeCN)$	$CuL'_2\cdot$ $\cdot MeCN$
Bond		*d*/Å		
Cu—O	—	1.912(2), 1.918(2)	1.906(2), 1.924(2)	1.889(3), 1.896(3)
$M—O_{NO}$	—	1.932(2), 1.919(2)	1.917(2), 1.944(2)	—
M—N	—	—	2.343(5)	1.944(3), 1.967(3)
N—O [a]	1.296(2)	1.299(3), 1.299(3)	1.300(4), 1.292(4)	—
N—O [b]	1.271(2)	1.267(3), 1.271(3)	1.268(4), 1.274(4)	1.265(5), 1.269(5)
Angle		ω/deg		
NCN—Ph	45.4(1)	49.8(2), 49.2(2)	46.8(3), 41.0(2)	23.2(4), 25.8(3)
$Ph—NO_2$	32.1(2)	55.5(3), 49.0(4)	54.7(5), 61.5(6)	22.7(6), 48.0(8)

[a] For the coordinated N—O group or the N—O group involved in hydrogen bonding.

[b] For the uncoordinated N—O group, which is not involved in hydrogen bonding.

The structure of the $CuL_2(MeCN)$ molecule differs only slightly from that of $CuL_2(AcOEt)$. The angle between the O(1)—Cu—O(5) and O(6)—Cu—O(10) planes is 27.8°; the Cu—O_L distances are in the range of 1.906(2)—1.944(2) Å; the Cu—N(1A) distance is 2.343(5) Å. The angles between the planes of the NCN group and the Ph rings of two L^- ligands are 41.0 and 46.8°. The angles between the Ph rings and the nitro groups are 54.7 and 61.5°, respectively. Selected bond lengths and bond angles in the $CuL_2(MeCN)$ complex are given in Table 1.

In the structure of the free HL molecule, the phenol group is linked by an intramolecular hydrogen bond to the NO group of the nitronyl nitroxide fragment (O...O,

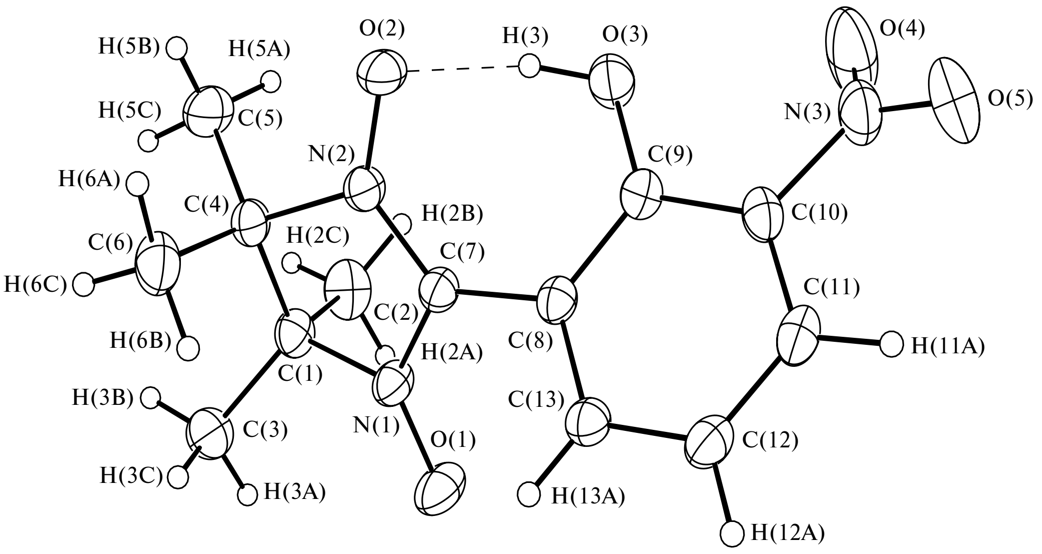
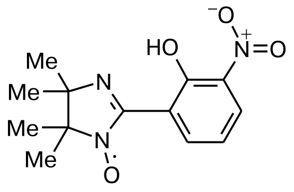


Fig. 2. Structure of the HL molecule.

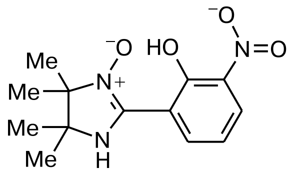
2.589(2) Å; H...O, 1.66(3) Å; O—H—O, 167(3)°) giving rise to a seven-membered ring (Fig. 2).

As a consequence, the N—O bond lengths in the nitronyl nitroxide fragment, like those in the N—O groups coordinated to the metal ion, are substantially different (see Table 1). However, the formation of the seven-membered ring involving a hydrogen bond in the structure of the free HL molecule is not surprising, because the nitrone group is, generally, a stronger proton acceptor compared to the nitro group. It should be noted that the angle between the NCN fragment of the imidazoline ring and the Ph ring is 45.4° in both complexes occurring in the solid state. The closure of the seven-membered ring both upon the formation of the metallocycle and through an intramolecular hydrogen bond results in virtually the same geometry of the L^- ligand without regard for the orientation of the nitro group. In the structures of the compounds under study, the angle between the planes of the nitro group and the Ph ring varies over a very wide range (see Table 1), which indicates that there are no additional interactions and the nitro group can undergo free rotation.

When kept in a solution in MeCN over a long period of time, the CuL_2 complex gradually loses the O atoms, which are eliminated from the nitrone groups of the L^- ligands, and the $CuL'_2 \cdot MeCN$ complex with the anion of the corresponding imino nitroxide L'^- (Fig. 3) crystallizes from the concentrated solution. This result is of interest on its own, because imino nitroxide HL′ is unstable and an attempt to isolate this compound led to its transformation into the corresponding nitrone HL″.[2] Hence, spontaneous deoxygenation of the CuL_2 complexes can be used as a method for the synthesis of complexes with imino nitroxides, when attempts to prepare these compounds by the direct reactions of metal ions with imino nitroxide failed.



HL′



HL″

The $CuL'_2 \cdot MeCN$ complex has a molecular structure. The coordination polyhedron of the Cu atom is a distorted tetrahedron formed by the imine N atoms and the O atoms of the deprotonated oxy groups of two L'^- ligands (see Fig. 3). The angle between the N(1)—Cu—O(4) and N(4)—Cu—O(8) planes is 58.0°. The MeCN molecules are not involved in coordination. The angle between the planes of the NCN fragment of the imidazoline ring and the Ph ring in the ligand (~24°) is substantially smaller than those in the complexes with seven-membered metallocycles. In one of the ligands, the O atoms of the nitro group are statistically disordered. Selected bond lengths and bond angles for $CuL'_2 \cdot MeCN$ are given in Table 1.

To summarize, the investigation of the structure of the Cu^{II} complex with the phenol-substituted nitronyl nitroxide ligand demonstrated that the paramagnetic ligand tends to be coordinated through the O atoms of the deprotonated phenol group and the nitronyl nitroxide fragment to form rather unusual seven-membered chelate rings, in spite of the alternative possibility of formation of six-membered metallocycles. For this reason, when developing a strategy for the synthesis of molecular magnets

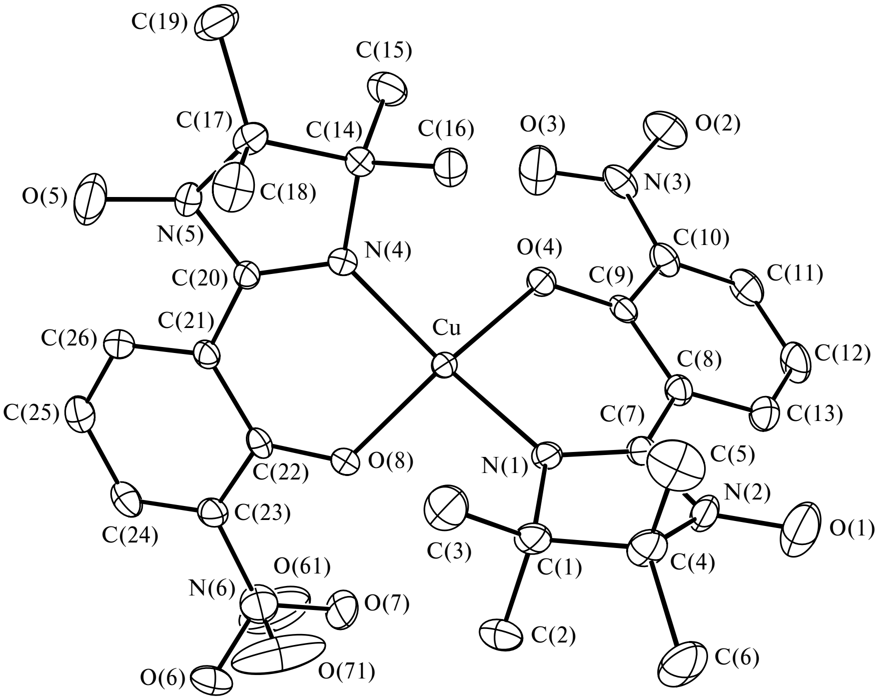


Fig. 3. Molecular structure of the CuL´$_2$·MeCN complex.

Table 2. Crystallographic characteristics and details of X-ray diffraction study

Parameter	HL	CuL$_2$(AcOEt)	CuL$_2$(MeCN)	CuL´$_2$·MeCN
Molecular weight	294.29	738.20	691.15	659.15
T/K	295	295	295	295
Molecular formula	$C_{13}H_{16}N_3O_5$	$C_{30}H_{38}CuN_6O_{12}$	$C_{28}H_{33}CuN_7O_{10}$	$C_{28}H_{33}CuN_7O_8$
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.312(1)	11.9147(9)	11.610(2)	9.720(1)
b/Å	10.678(1)	12.5499(9)	12.510(2)	10.817(1)
c/Å	12.458(1)	14.0921(10)	12.888(2)	15.354(2)
α/deg	90	107.488(1)	108.192(3)	103.811(2)
β/deg	113.355(2)	98.527(1)	91.618(2)	96.254(2)
γ/deg	90	117.578(1)	115.854(2)	102.923(2)
V/Å^3	1381.5(3)	1675.3(2)	1570.4(4)	1505.3(3)
Z	4	2	2	2
d_{calc}/g cm^{-3}	1.415	1.461	1.462	1.454
μ/mm^{-1}	0.110	0.723	0.732	0.787
θ-Scan range/deg	1.96—23.24	1.96—23.28	1.94—23.33	2.38—23.36
I_{hkl}*	5812/1978	7246/4774	6850/4490	6554/4310
R_{int}	0.0495	0.0134	0.0151	0.1156
$I_{hkl} > 2\sigma(I)/N$**	1785/255	4392/571	3990/503	3367/539
GOOF	0.806	1.012	0.982	0.855
R_1 ($I > 2\sigma(I)$)	0.0385	0.0403	0.0490	0.0580
wR_2	0.1060	0.1068	0.1308	0.1483
R_1 (based on all I_{hkl})	0.0420	0.0433	0.0545	0.0734
wR_2	0.1105	0.1095	0.1365	0.1605

* Number of measured/independent reflections.

** Number of parameters in the refinement.

based on transition metal coordination compounds with polyfunctional nitroxides, whose structures allow alternative modes of coordination of the paramagnetic ligand, one should take into account the possibility of formation of bis-chelates with seven-membered metallocycles.

Experimental

Nitroxide HL was synthesized according to a known procedure.[2] Single crystals of the complexes were grown from a 1 : 1 benzene—heptane mixture.

Bis[2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxylato 3-oxide]ethylacetatecopper(II), CuL$_2$(AcOEt). A solution of KOH (11.2 mg, 0.20 mmol) in MeOH and then $CuCl_2 \cdot 2H_2O$ (17.1 mg, 0.10 mmol) were added to a solution of HL (58.8 mg, 0.20 mmol) in MeOH (20 mL). The reaction mixture was stirred and concentrated to dryness. The residue was treated with a 1 : 1 AcOEt—heptane mixture (20 mL) and filtered. The filtrate was kept in an open flask at ~20 °C for several days to prepare dark-brown crystals suitable for X-ray diffraction analysis, which were separated by filtration. The yield was 60%. IR (KBr), ν/cm^{-1}: 2984, 1721, 1706, 1600, 1544, 1523, 1448, 1426, 1395, 1371, 1331, 1264, 1215, 1136, 1081, 1041, 867, 755, 606, 547, 447. Found (%): C, 48.9; H, 5.2; N, 11.5. $C_{30}H_{38}CuN_6O_{12}$. Calculated (%): C, 48.8; H, 5.2; N, 11.4. The mother liquor was concentrated to dryness and then MeCN (5 mL) was added to the residue. The resulting solution was filtered and the filtrate was kept at ~20 °C over a long period. Once the solvent was almost completely evaporated, black crystals of **bis[2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxylato]copper(II), solvate with MeCN (1 : 1), CuL′$_2$ · MeCN** were obtained. The yield was 15%. IR (KBr), ν/cm^{-1}: 2981, 2919, 1607, 1542, 1516, 1429, 1392, 1371, 1336, 1304, 1264, 1221, 1147, 1085, 871, 754, 672, 617, 566. Found (%): C, 50.9; H, 5.0; N, 14.8. $C_{28}H_{33}CuN_7O_8$. Calculated (%): C, 51.0; H, 5.1; N, 14.9.

Acetonitrilebis[2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxylate 3-oxide]copper(II), CuL$_2$(MeCN). A solution of KOH (11.2 mg, 0.20 mmol) in MeOH and then $CuCl_2 \cdot 2H_2O$ (17.1 mg, 0.10 mmol) were added to a solution of HL (58.8 mg, 0.20 mmol) in MeCN (20 mL). The reaction mixture was stirred and concentrated to dryness. The residue was treated with MeCN (5 mL). The resulting solution was filtered and the filtrate was kept at ~20 °C for 10 day to prepare dark-brown crystals suitable for X-ray diffraction analysis. The crystals were separated by filtration. The yield was 55%. IR (KBr), ν/cm^{-1}: 2986, 1600, 1525, 1445, 1423, 1392, 1367, 1335, 1264, 1213, 1173, 1135, 1080, 867, 814, 756, 685, 604, 548, 455. Found (%): C, 48.3; H, 5.0; N, 14.1. $C_{28}H_{33}CuN_7O_{10}$. Calculated (%): C, 48.7; H, 4.8; N, 14.2.

X-ray diffraction analysis. The X-ray diffraction data sets were collected on a Smart Apex diffractometer (Bruker AXS). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms (SHELX97 program package[3]). The positions of some H atoms were revealed from the difference electron density synthesis. The positions of the remaining atoms were calculated geometrically and refined with isotropic thermal parameters in the rigid-body approximation. The crystallographic characteristics and details of X-ray diffraction study are given in Table 2.

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