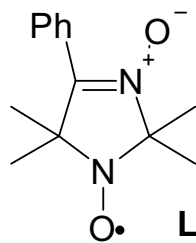


s9.m1.p19 Investigation of crystal structure of $M(\text{hfac})_2$ with 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl-3-oxide ($M=\text{Cu}(\text{II}), \text{Co}(\text{II})$). N.V. Pervukhina, A.B. Burdukov. *Institute of Inorganic Chemistry, Novosibirsk, Russia*.
Keywords: complex, nitroxide.

Design of heterospin exchange-coupled systems based on nitroxide complexes demands for deep understanding of coordination ability and bonding modes of the nitroxide function. We develop systematic structural study of the complexes with nitroxides containing diamagnetic functions similar to the nitroxide one, the radical L being an example of such ligand. The structures of 3 complexes of L are reported:



$\text{Cu}(\text{hfac})_2\text{L}$ (**I**): space gr. $P1(-)$, $a=9.430(2)$, $b=9.578(2)$, $c=16.047(3)$ Å, $\alpha=91.53(3)$, $\beta=93.61(3)$, $\gamma=98.55(3)^\circ$, $z=2$, $R=0.0583$;
 $\text{Co}(\text{hfac})_2\text{L}$ (**II**): space gr. $Pna2_1$, $a=14.127(1)$, $b=11.081(3)$, $c=18.108(5)$ Å, $z=4$, $R=0.0308$;
 $\text{Co}(\text{hfac})_2\text{L}_2$ (**III**): space gr. Cc , $a=21.777(4)$, $b=9.763(2)$, $c=21.705(4)$ Å, $\beta=115.23(3)^\circ$, $z=4$, $R=0.0334$. Complex **III** has molecular structure, the cobalt atom is octahedrally coordinated with four hfac oxygens in the equatorial plane (Co-O 2.03(1)-2.12(1) Å) and two N-oxide oxygens in the axial positions ((Co-O(5) 2.09(1) Å, (Co-O(7) 2.15(1) Å). The complexes **I** and **II** have chain structure with bridging L. Two independent copper atoms are bound to hfac oxygens in the equatorial plane (Cu-O 1.933(4)-1.956(4) Å), the axial positions of Cu(1) are occupied with nitroxide oxygens of L (Cu(1)-O(5) 2.613(4) Å) while Cu(2) is axially coordinated with the N-oxide oxygens (Cu(2)-O(6) 2.369(5) Å). In **II** the nitroxide is coordinated in the head-to-tail fashion, the nitroxide and N-oxide oxygens being in the cis-position ((Co-O(5) 2.082(7) Å, (Co-O(6') 2.103(6) Å). The other four coordination sites are occupied with hfac oxygens (Co-O 2.033(6)-2.102(7) Å). The imidazoline heterocycles are planar, N-O bond lengths varying within 1.24(2)-1.32(2) Å. The structural results indicate that the nitroxide and N-oxide functions have comparable ability to make bonds with Co(II) and Cu(II) ions.

s9.m1.p20 Synthesis, Crystal Structure and Magnetic Properties of Binuclear (μ -Hydroxo)(μ -acetato) Dicopper(II) Complexes. E. Kavlakoglu¹, A. Elmali¹, I. Svoboda², H. Fuess². ¹Department of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Besevler-Ankara, Turkey. ²Materials Science Department, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany.

Keywords: dinuclear copper(II) complex; super-exchange interactions; antiferromagnetic coupling.

$[\text{Cu}_2(\text{L1})(\text{O}_2\text{CMe})] \cdot \text{H}_2\text{O}$ (L1 = 1,3 - Bis(2-Hydroxy-1-naphthylideneamino)propan-2-ol) (**1**) and $[\text{Cu}_2(\text{L2})(\text{O}_2\text{CMe})] \cdot \text{H}_2\text{O}$ (L2=1,3- Bis(2-Hydroxy-5-chlorosalicylideneamino)propan-2-ol) (**2**) were synthesized and their crystal structures determined. $(\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_5\text{Cu}_2) \cdot \text{H}_2\text{O}$ (**1**), monoclinic, space group $P2_1/c$, $a = 11.795(3)$, $b = 17.988(5)$, $c = 12.005(6)$ Å, $\beta=109.99(3)^\circ$, $V=2393(2)$ Å³, $Z = 4$. $(\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_5\text{Cl}_2\text{Cu}_2) \cdot 1/2\text{H}_2\text{O}$ (**2**), monoclinic, space group $P2_1/c$, $a = 20.660(10)$, $b = 9.618(2)$, $c = 21.810(10)$ Å, $\beta=109.3(8)^\circ$, $V=4090(2)$ Å³, $Z=8$. In both compounds, two copper(II) ions in a square-planar coordination are bridged by alkoxide and acetate oxygen atoms to form a dinuclear unit. Each metal coordination sphere is four-coordinate, planar with an NO_3 donor set. In the compound (**1**) and (**2**), the copper(II) centers are separated by 3.492(2) Å and 3.490(2) Å, respectively. In both compounds, the copper(II) ions are weakly antiferromagnetically coupled $2J = -163.6$ cm⁻¹ for (**1**) and $2J = -146.6$ cm⁻¹ for (**2**), which follows from temperature-dependent magnetic susceptibility measurements in the temperature range 4.6 to 310 K. The Cu-O-Cu angles are $133.59(1)^\circ$ and $132.97(1)^\circ$, respectively in the super-exchange pathway. The weak antiferromagnetic coupling of the complexes is interpreted in terms of countercomplementary effect of the different bridging ligands which participate in the super-exchange interaction by using Hoffmann's theory¹. In the compound (**1**), the magnetic moment at 310 K is ca. 2.7 B. M. , and 0.2 B. M. at 4.6 K. The magnetic susceptibility is at a maximum near 140 K and decreases rapidly as the temperature is lowered to liquid helium temperature. In the compound (**2**), the magnetic moment decreases with temperature and in the $\chi(T)$ curve a characteristic maximum was observed near 150 K.

[1] Hay, P. J., Thibault, J. C., Hoffmann, R., J. Am. Chem. Soc. (1975), 97, 4887.