CRYSTAL STRUCTURES AND PHYSICAL PROPERTIES OF THREE COPPER-BASED COMPLEXES WITH N,O- OR N,O,N- CHELATING LIGANDS AND SiF_6^-, ClO_4^- AS COUNTERIONS

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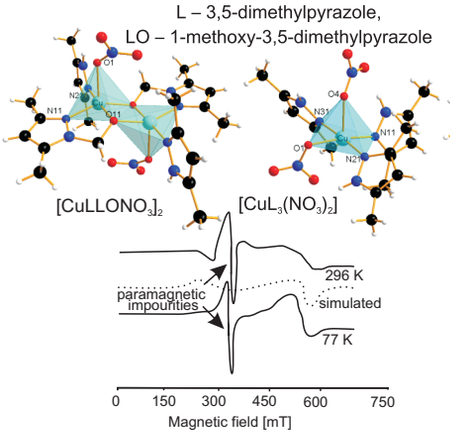
INTRODUCTION

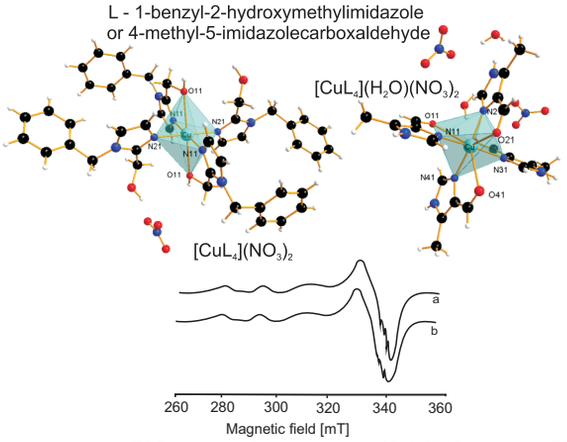
Copper is an essential metal that is required for cellular respiration, iron oxidation, pigment formation, neurotransmitter biosynthesis, antioxidant defense, peptide amidation, central nervous system development, and connective tissue formation [1]. Copper exists mainly in two redox states with many known enzymes requiring it. Copper is found complexed to proteins in its ionic form. Free Cu ions, like free Fe ions, catalyze the formation of free radicals, resulting in Fenton chemistry [2]. On the other hand, under physiological conditions, copper serves as an important cofactor for proteins participating for example with SOD in the free radical detoxification. This study display model complexes of Cu(II) ions which were synthesized in our lab and characterized by means of analytical and spectroscopic techniques for their future investigation of the SOD or catalase mimics catalytic activity.

L – 3,5-dimethylpyrazole,
LO – 1-methoxy-3,5-dimethylpyrazole



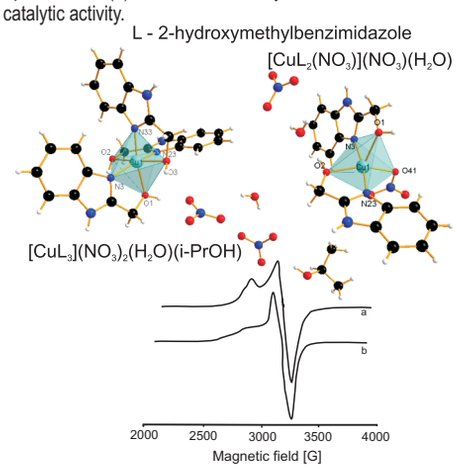
EPR spectra of polycrystalline $[CuLLONO_3]$.

L - 1-benzyl-2-hydroxymethylimidazole
or 4-methyl-5-imidazolecarboxaldehyde



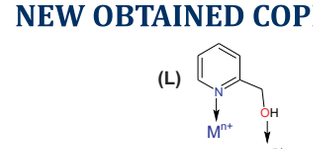
EPR spectra of polycrystalline $[CuL_4](NO_3)_2$ or $[CuL_4](H_2O)(NO_3)_2$ (a) and its ethanolic solution (b).

L - 2-hydroxymethylbenzimidazole

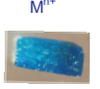


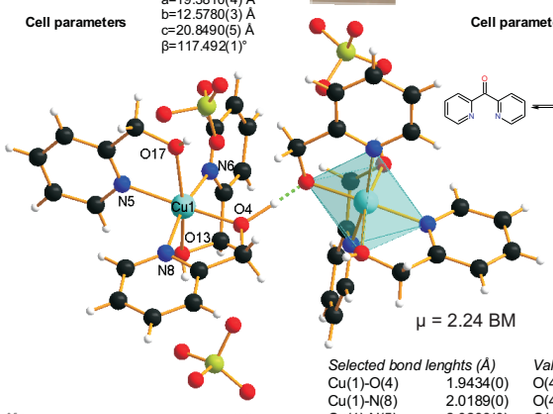
EPR spectra of the powdered $[CuL_2(NO_3)](NO_3)(H_2O)$ (a) and $[CuL_3](NO_3)_2(H_2O)(i\text{-}PrOH)$ (b) at 77 K.

NEW OBTAINED COPPER COMPLEXES

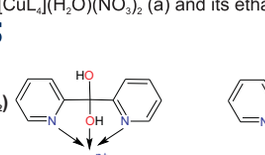


Crystal system	Monoclinic
Space group	C 2/c
Cell parameters	a=19.3810(4) Å b=12.5780(3) Å c=20.8490(5) Å β=117.492(1)°

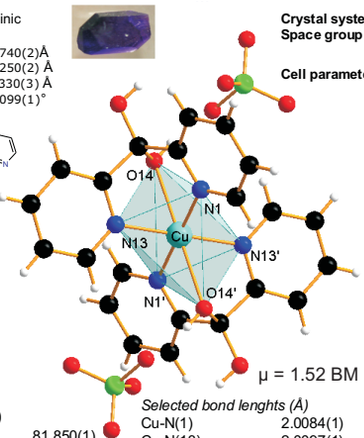




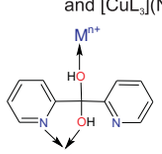
μ = 2.24 BM



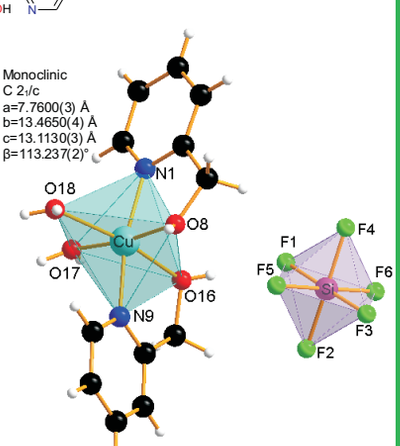
Crystal system	Monoclinic
Space group	P 21/c
Cell parameters	a=10.2740(2)Å b=10.1250(2) Å c=16.7330(3) Å β=104.099(1)°



μ = 1.52 BM



Crystal system	Monoclinic
Space group	C 2/c
Cell parameters	a=7.7600(3) Å b=13.4650(4) Å c=13.1130(3) Å β=113.237(2)°



Selected bond lenghts (Å)

Cu(1)-O(4)	1.9434(0)
Cu(1)-N(8)	2.0189(0)
Cu(1)-N(5)	2.0296(0)
Cu(1)-N(6)	2.0377(0)
Cu(1)-O(17)	2.3061(0)
Cu(1)-O(13)	2.4401(0)

Valence angles (°)

O(4)-Cu(1)-N(8)	81.850(1)
O(4)-Cu(1)-N(5)	173.074(1)
O(4)-Cu(1)-N(6)	89.441(1)
O(4)-Cu(1)-O(17)	99.196(1)
O(4)-Cu(1)-O(13)	93.375(1)
N(8)-Cu(1)-N(5)	95.500(1)
N(8)-Cu(1)-N(6)	165.761(1)
N(8)-Cu(1)-O(17)	98.472(1)
N(8)-Cu(1)-O(13)	94.690(1)
N(5)-Cu(1)-N(6)	94.361(1)
N(5)-Cu(1)-O(17)	74.791(1)
N(5)-Cu(1)-O(13)	93.219(1)
N(6)-Cu(1)-O(17)	94.009(1)
N(6)-Cu(1)-O(13)	74.502(1)
O(17)-Cu(1)-O(13)	162.927(1)

Selected bond lenghts (Å)

Cu-N(1)	2.0084(1)
Cu-N(13)	2.0097(1)
Cu-O(14)	2.4429(1)

Valence angles (°)

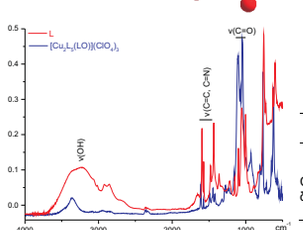
N(1)-Cu-N(1)'	180.00
N(1)-Cu-N(13)'	88.501(1)
N(1)-Cu-N(13)	91.499(1)
N(1)-Cu-O(14)	74.821(1)
N(1)-Cu-O(14)'	105.179(1)
N(13)-Cu-N(13)'	180.00
N(13)-Cu-O(14)	72.458(1)
N(13)-Cu-O(14)'	107.542(1)
O(14)-Cu-O(14)	180.00

Selected bond lenghts (Å)

Cu-N(1)	1.9898
Cu-N(9)	1.9972
Cu-O(17)	2.0007
Cu-O(8)	2.0145
Cu-O(16)	2.2396
Cu-O(18)	2.3128
Si-F(1)	1.7088
Si-F(2)	1.6616
Si-F(3)	1.6796
Si-F(4)	1.6803
Si-F(5)	1.696
Si-F(6)	1.6817

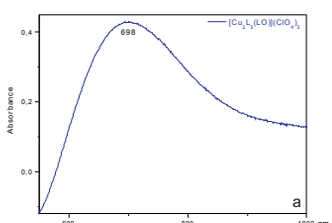
Valence angles (°)

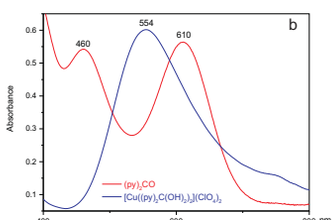
N(1)-Cu-N(9)	168.797(1)
N(1)-Cu-O(17)	93.977(1)
N(1)-Cu-O(8)	80.912(1)
N(1)-Cu-O(16)	93.863(1)
N(1)-Cu-O(18)	91.253(1)
N(9)-Cu-O(17)	93.292(1)
N(9)-Cu-O(8)	92.419(1)
N(9)-Cu-O(16)	78.135(1)
N(9)-Cu-O(18)	97.888(1)
O(17)-Cu-O(8)	173.308(1)
O(17)-Cu-O(16)	86.121(1)
O(17)-Cu-O(18)	84.806(1)



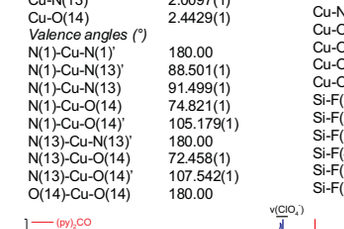
Infrared spectra for free ligand and copper(II) complex

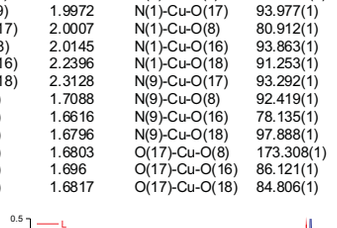
Vibration bands	L	$[Cu_2L_5(LO)](ClO_4)_3$
(OH)	3228	3363
(C=C, C=N)	1595, 1435	1608, 1444
δ(C=O)	1053	1049
(ClO_4^-)	-	1101, 929





The UV-VIS spectra of $[Cu_2L_5(LO)](ClO_4)_3$ ($C = 4.82 \cdot 10^{-3}$ M, cm^{-1} (a) and $[Cu((py)_2C(OH)_2)_2](ClO_4)_2$ ($C = 5.02 \cdot 10^{-3}$ M, cm^{-1} (b) recorded in methanol solution





Infrared spectra for free ligands and copper(II) complexes

Vibration bands	$(py)_2CO$	$[Cu((py)_2C(OH)_2)_2](ClO_4)_2$
(OH)	-	3484
(C=C, C=N)	1567, 1428	1607, 1445
δ(C=O)	1044	-
(ClO_4^-)	-	1091

Vibration bands	L	$[CuL_2(H_2O)_2]SiF_6$
(OH)	3228	3186
(C=C, C=N)	1595, 1435	1612, 1444
δ(C=O)	1053	1054

REFERENCES

[1] Madsen E., Gitlin J.D. (2007) Annu. Rev. Neurosci., 30, 317–337.
[2] DeBie P., Muller P., Wijmenga C., Klomp, L.W.J. (2009) J. Med.Genet., 44, 673–688.