

# Synthesis, Structural Characterization and Electrochemical Studies of a Nicotinamide-bridged Dinuclear Copper Complex derived from a Tridentate Hydrazone Schiff Base Ligand

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Received May 9th, 2007.

**Abstract.** The in-situ formed hydrazone Schiff base ligand (*E*)-*N'*-(2-hydroxy-3-methoxybenzylidene)benzohydrazide ( $H_2L^1$ ) and nicotinamide ( $L^2$ ) give the copper(II) complex  $[CuL^1L^2]$  on reaction with copper(II) acetate. In the solid state two copper atoms are linked by nicotinamide through coordination with its pyridyl nitrogen atom and its amide-C=O group to the dicopper(II) complex  $[CuL^1(\mu-L^2)CuL^1L^2]$ . The coordination polyhedra

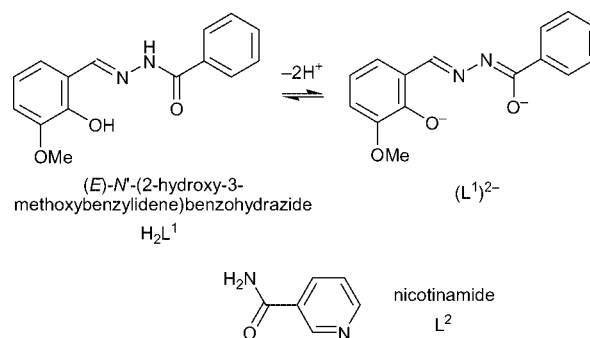
are a  $CuO_2N_2$  square and a  $CuO_3N_2$  square pyramid. Cyclic voltammetric experiments of the solution species  $[CuL^1L^2]$  in DMF reveal reduction of the  $L^1$  ligand at three potentials with a reduction at  $-0.5$  V resulting in decomposition of the complex.

**Keywords:** Copper; Hydrazone Schiff base; Dinuclear complex; pi-Stacking; Metalloaromaticity; Cyclic voltammetry

The chemistry of copper complexes is of interest owing to their importance in biological and industrial processes [1]. Biological activities may be related to the redox properties of complexes. For some copper(II) compounds a lower reduction potential seems to be related to an increased antifungal activity [2]. Copper and dicopper complexes can exhibit the abilities of superoxide dismutase (SOD), catechol oxidase and chemical nucleases [3]. Complexes of copper(II) with Schiff base ligands [4] are frequently studied, e.g. for their antibacterial properties [5]. Dicopper(II) Schiff base and related complexes have been probed electrochemically [6] magnetically [7] and by EPR [8] for their electronic situation. A number of neutral dicopper(II) complexes of reduced Schiff base show catalytic activity on the oxidation of 3,5-di-tert-butylcatechol (3,5-DTBC) to the 3,5-di-tert-butylquinone (3,5-DTBQ) [9] and interesting magnetic properties [10].

Hydrazones,  $RR'C=N-NR''R'''$ , are used as intermediates in synthesis [11], as functional groups in metal carbonyls [12], in organic compounds [13] and particular in hydrazone Schiff base ligands [14, 15], e.g. employed in dinuclear catalysts [16]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis which is attributed to the formation of stable chelate complexes with transition metals which catalyze physiological processes [17]. We describe here the solid-state

structure of the dicopper(II) complex  $[CuL^1(\mu-L^2)CuL^1L^2]$  and the electrochemistry of the solution species  $[CuL^1L^2]$  with  $H_2L^1 =$  (*E*)-*N'*-(2-hydroxy-3-methoxybenzylidene)benzohydrazide and  $L^2 =$  nicotinamide.



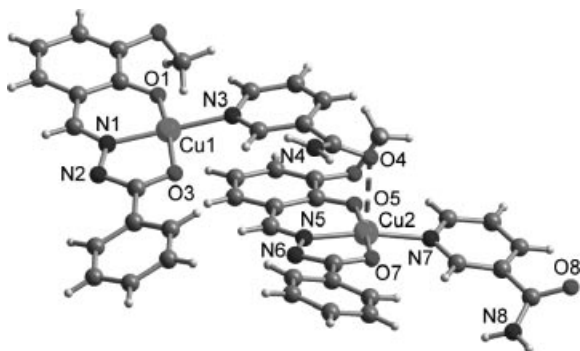
The hydrazone Schiff base dianion  $(L^1)^{2-}$  forms *in-situ* when equimolar quantities of 2-hydroxy-3-methoxybenzaldehyde and benzhydrazide are reacted with copper(II) acetate monohydrate and nicotinamide ( $L^2$ ) in methanol [18]. The complex  $[CuL^1L^2]$  is moderately soluble in common organic solvent. The infrared spectrum of the complex shows a very broad N–H band for the nicotinamide and so does not allow for any conclusion on Schiff base N–H deprotonation.

The X-ray structural analysis of the complex shows coordination of the doubly deprotonated hydrazone Schiff base dianion  $(L^1)^{2-}$  to copper through the 2-hydroxy, hydrazone nitrogen and benzo-carboxide group (Fig. 1), thereby acting as a tridentate ONO-donor. The nicotinamide ligand completes the copper coordination in the square plane with its pyridine nitrogen atom. Furthermore, a dinuclear structure with two symmetry-independent  $Cu^{II}$  atoms connected through a nicotinamide bridge ( $\mu-L^2$ ) is revealed (Fig. 1). Only the nicotinamide ligand on  $CuI$  acts as a bridge with

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$O4 \cdots Cu2 = 2.781(3) \text{ \AA}$ , but not the nicotinamide on Cu2. The O8 distance to Cu1 ( $-1+x, y, z$ ) is  $3.784(3) \text{ \AA}$ . Thus, the geometry around Cu1 remains approximately square planar while the coordination around Cu2 becomes square-pyramidal ( $\tau = 0.055$ ) [19]. However, the amide- $C=O \cdots Cu$  contact is rather long and weak, hence, the dicopper(II) complex  $[CuL^1(\mu-L^2)CuL^1L^2]$  may be regarded as pseudo-dinuclear. Most likely, this nicotinamide bridge is not retained in solution. In addition, there is substantial intramolecular  $\pi$ -stacking between the pyridyl ring plane of N3 and both the six-membered chelate ring built from Cu2–N5–O5 and the adjacent benzylidene ring with short centroid-centroid distances ( $3.572$  and  $3.621 \text{ \AA}$ ) and slip angles ( $\sim 22^\circ$  and  $\sim 21^\circ$ , respectively) [20, 21, 22]. Masui had suggested an active electron delocalization within a metal-N-heterocyclic chelate ring in such a way that it could exhibit some degree of “metalloaromaticity” [23, 24].



**Fig. 1** Structure of the asymmetric unit of  $[CuL^1(\mu-L^2)CuL^1L^2]$ .

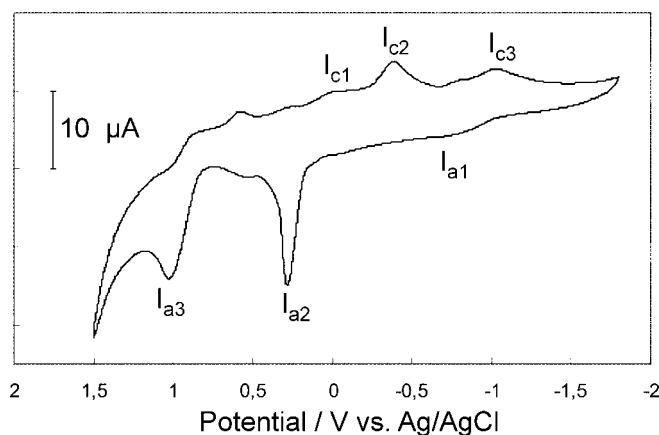
Selected distances / $\text{\AA}$  and angles / $^\circ$ : Cu1–O1 1.893(3), Cu1–O3 1.943(3), Cu1–N1 1.917(3), Cu1–N3 1.990(4), Cu2–O5 1.902(3), Cu2–O7 1.927(3), Cu2–N5 1.928(3), Cu2–N7 2.006(4), Cu2–O4 2.781(3), O1–Cu1–N1 93.6(2), O1–Cu1–O3 170.7(2), N1–Cu1–O3 81.6(2), O1–Cu1–N3 92.2(2), N1–Cu1–N3 172.8(2), O3–Cu1–N3 93.3(2), O5–Cu2–N5 93.2(2), O5–Cu2–O7 173.9(2), N5–Cu2–O7 81.5(2), O5–Cu2–N7 92.0(2), N5–Cu2–N7 170.6(2), O7–Cu2–N7 93.7(2).

Electrochemical cyclic voltammetry measurements were carried out to probe the redox stability of the  $[CuL^1L^2]$  complex in solution [25]. The cyclic voltammogram of the complex  $[CuL^1L^2]$  in dimethylformamide displays three cathodic potentials at about 0 ( $I_{c1}$ ),  $-0.5$  ( $I_{c2}$ ) and  $-1.0$  V ( $I_{c3}$ ) (Fig. 2). They can be assigned to reduction of coordinated  $L^1$  from their similarity to a CV scan of  $H_2L^1$  alone (not shown). The very sharp oxidation peak at about 0.3 V ( $I_{a2}$ ) is assigned to the oxidation of liberated copper.  $Cu^{II}$  is initially reduced to  $Cu^0$  during the forward scan; the cathodic reduction at about 0 V is, however, covered by the 0 V reduction of  $L^1$ . The sharpness of oxidation peak of copper is due to the stability of  $Cu^{II}$  in the medium as this peak is also seen in a cyclic voltammogram with copper(II) acetate in DMF (not shown). During the reverse scan a poorly defined oxidation wave ( $I_{a1}$ ) appears at  $-0.86$  V, which is associated with the cathodic peak  $I_{c3}$ . An anodic wave associated with  $I_{c2}$  is not found. The sharp oxidation peak assigned to copper is also seen in a separate CV scan ranging from 1.5 to  $-0.67$  V but not in a scan from 1.5 to 0 V (not shown). Thus, it is concluded that the decomposition of  $[CuL^1L^2]$  occurs at  $-0.5$  V by the reduction of  $L^1$ .

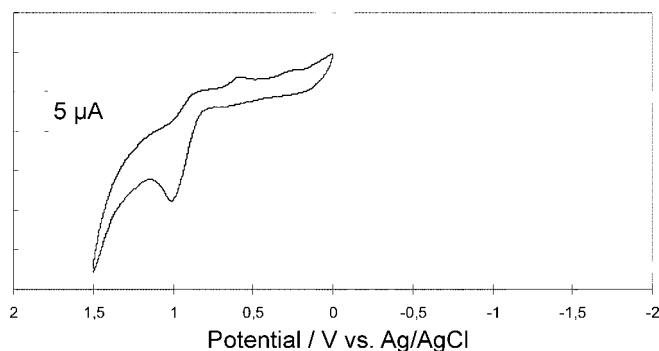
Cyclic voltammetry between 1.5 and 0 V permits the study of the  $[CuL^1L^2]$  complex without decomposition. The sharp oxidation peak of copper is absent in this potential range (Fig. 3). The oxidation peak of the complex occurs at about 1.0 V ( $I_{a3}$ ), and in the reverse scan it shows a small reduction peak about 0.9 V as was

also seen in Fig. 2. This oxidation peak at 1.0 V is also seen in the CV scan of  $H_2L^1$  alone (not shown).

The cyclic voltammogram of a solution containing presumably the fragment  $CuL^1$  (prepared by mixing  $Cu(NO_3)_2$  and  $H_2L^1$  in DMF) in the potential range 1.5 to  $-1.8$  V (not shown) exhibits reduction peaks at about 0 and  $-0.5$  and oxidation peaks at about 0.3 and 1.0 V which strongly resemble  $I_{c1}$  and  $I_{c2}$  and  $I_{a2}$  and  $I_{a3}$ , respectively, of  $[CuL^1L^2]$  in Fig. 2. This indicates that a  $CuL^1$  fragment is present in a DMF solution of  $[CuL^1L^2]$  or may form upon decomposition of  $[CuL^1L^2]$ . There is a linear relationship between the cathodic peak current ( $I_{c3}$ ) and the square root of the scan rate ( $v^{1/2}$ ) in the 5 to  $400 \text{ mV s}^{-1}$  range (Fig. 4). This behavior is diagnostic of an electron transfer process controlled by diffusion. The  $\Delta E_p = (E_{pa} - E_{pc})$  value was 176 mV and the  $i_{pa}/i_{pc} = 0.28$  relationship was far from unity. This finding shows the quasi-reversibility of this redox process.



**Fig. 2** Cyclic voltammogram of  $10^{-3} \text{ mol/l}$   $[CuL^1L^2]$  in DMF and TBAP (0.1 mol/l); scan rate  $100 \text{ mV s}^{-1}$ .



**Fig. 3** Cyclic voltammogram of  $10^{-3} \text{ mol/l}$   $[CuL^1L^2]$  in DMF and TBAP (0.1 mol/l); scan rate  $100 \text{ mV s}^{-1}$  in the potential range 1.5 to 0 V.

## Experimental Section

Benzhydrazide, nicotinamide, 2-hydroxy-3-methoxybenzaldehyde, copper(II) acetate monohydrate, and solvents with high purity were purchased from Merck and used as received. IR spectra were recorded in KBr disks with a Matson 1000 FT-IR spectrophotometer, solution UV-VIS spectra on a Shimadzu 160 spectrometer.

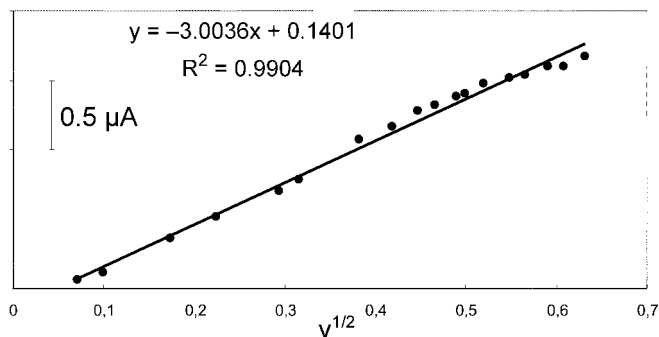


Fig. 4 Plot of cathodic current ( $i_{pc}$ ) versus the square root of sweep rate ( $v^{1/2}$ ) for  $I_{c3}$  of the  $[CuL^1L^2]$  complex.

Microanalytical (CHN) data were obtained with a Carlo ERBA Model EA-1108 analyzer. Molar conductivities were determined with a Metrohm 644 conductometer. Copper percentage was measured by a Varian spectrometer AAS-110.

### Synthesis of bis{(E)-N'-(2-hydroxy-3-methoxybenzylidene)benzohydrazido}(nicotinamide)-(μ-nicotinamide)dicopper(II), $[CuL^1(μ-L^2)CuL^1L^2]$

Reaction between 2-hydroxy-3-methoxybenzaldehyde (0.05 g, 0.33 mmol) and an equimolar mixture of copper(II) acetate monohydrate (0.066 g, 0.33 mmol), benzhydrazide (0.045, 0.33 mmol) and nicotinamide (0.04 g, 0.33 mmol) by diffusion along a thermal gradient in methanol solution (‘branched tuber method’ [26]) provided dark brown crystals within 5 d (yield 140 mg, 93 %). Calc. for  $C_{42}H_{36}Cu_2N_8O_8$  (907.86) C 55.56, H 4.01, N 12.35, Cu 14.00. Found C 55.40, H 3.99, N 12.40, Cu 14.00 %.

IR (KBr,  $cm^{-1}$ ): 3446 (vs, br,  $\nu(NH_2)$ ), 2923 (w), 1700 (s,  $\nu(C=O)$ ), 1638 (s,  $\nu(C=N)$  [27]), 1500 (s), 1438 (m), 1200 (m), 1123 (m), 746 (m), 654 (m). UV/Vis (in  $CH_3CN$ ,  $c = 2.21 \cdot 10^{-5}$  mol/l, green solution,  $\lambda_{max}$  [nm] with  $\epsilon$  [ $l \cdot mol^{-1} \cdot cm^{-1}$ ]): 206 (13 940), 247 (11 100), 313 (9 420), 408 (2 800, d-d transition).

### Crystal structure determination of $[CuL^1(μ-L^2)CuL^1L^2]$

*Crystal data*: Molecular formula  $C_{42}H_{36}Cu_2N_8O_8$ , formula weight 907.86  $g \cdot mol^{-1}$ ,  $a = 12.694(2)$ ,  $b = 9.923(2)$ ,  $c = 15.119(4)$  Å,  $\beta = 95.661(6)^\circ$ ,  $V = 1895.2(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 1.591$   $g \cdot cm^{-3}$ , monoclinic, space group  $P2_1$ . *Data collection*: Bruker APEX2 CCD, Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), graphite monochromator, crystal size 0.40 x 0.20 x 0.20 mm<sup>3</sup>, 100(2) K,  $\phi$ - and  $\omega$ -scan,  $3.2^\circ \leq 2\theta \leq 56.5^\circ$ ,  $-16 \leq h \leq 16$ ,  $-13 \leq k \leq 11$ ,  $-20 \leq l \leq 20$ , 14396 reflections measured, 8926 independent ( $R_{int} = 0.0421$ ),  $\mu(Mo-K\alpha)$  1.191  $mm^{-1}$ , experimental absorption correction with SADABS [28]. *Structural Analysis and Refinement*: The structure was solved by direct methods (SHELXS-97), refinement was done by full-matrix least squares on  $F^2$  using the SHELXL-97 program suite [29]; all non-hydrogen positions were found and refined with anisotropic temperature factors; hydrogen atoms were calculated using appropriate riding models (AFIX 43, 33, 23) and isotropic temperature factors of  $U_{eq}(H) = 1.2 U_{eq}(C, N)$  for CH, NH<sub>2</sub> and  $1.5 U_{eq}(C)$  for CH<sub>3</sub>. 544 refined parameters, final  $RI = 0.0473$ ,  $wR2 = 0.0901$  for 6869 reflections with  $I > 2\sigma(I)$ , final  $RI = 0.0740$ ,  $wR2 = 0.1006$  for all data, goodness-of-fit 0.990, largest difference peak and hole 0.945/−0.711  $e \cdot \text{Å}^{-3}$ . Flack parameter [30] or batch scale factor (BASF) for unequal components in twin re-

finement 0.306(13); BASF = 0.5 corresponds to racemic twinning. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. 636946).

### Electrochemistry

Voltammetric experiments were performed using a Metrohm computerized voltammetric analyzer model 757 VA. A conventional three-electrode system was used with a polished glassy carbon electrode (area 3.14 mm<sup>2</sup>) as working electrode and a platinum wire counter electrode. The reference was an aqueous Ag/AgCl saturated electrode, separated from the bulk of the solution by a bridge with solvent and supporting electrolyte. The solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the Ag/AgCl electrode. Before each experiment the working electrode was cleaned by polishing with alumina 0.05 mm and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 mol/l tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in dimethylformamide (DMF) and all experiments were carried out at room temperature. The solutions were freshly prepared before use, and were purged with N<sub>2</sub> saturated with solvent for ca. 15 min prior to taking measurements in order to remove dissolved O<sub>2</sub>. Voltammograms were recorded in the range from 1.5 to −2.0 V vs Ag/AgCl.

*Acknowledgments*. We thank Zanjan University for the financial support of this study.

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