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

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Abstract. The in-situ formed hydrazine Schiff base ligand (E)-N'-((2-hydroxy-3-methoxybenzylidene)benzohydrazide (H2L1) and nicotinamide (L2) give the copper(II) complex [CuL1L2] 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 [CuL1(µ-L2)CuL1L2]. The coordination polyhedra are a CuO2N2 square and a CuO3N2 square pyramid. Cyclic voltammetric experiments of the solution species [CuL1L2] in DMF reveal reduction of the L1 ligand at three potentials with a reduction at ~0.5 V resulting in decomposition of the complex.

Keywords: Copper; Hydrazine 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-tertbutylcatechol (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 hydrazine 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 [CuL1(µ-L2)CuL1L2] and the electrochemistry of the solution species [CuL1L2] with H2L1 = (E)-N’-(2-hydroxy-3-methoxybenzylidene)benzohydrazide and L2 = nicotinamide.

The hydrazine Schiff base dianion (L1)2− forms in-situ when equimolar quantities of 2-hydroxy-3-methoxybenzaldehyde and benzohydrazide are reacted with copper(II) acetate monohydrate and nicotinamide (L2) in methanol [18]. The complex [CuL1L2] 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 hydrazine Schiff base dianion (L1)2− to copper through the 2-hydroxy, hydrazine 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 CuII atoms connected through a nicotinamide bridge (µ-L2) is revealed (Fig. 1). Only the nicotinamide ligand on Cu1 acts as a bridge with

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O4···Cu2 = 2.781(3) Å, but not the nicotinamide on Cu2. The O8 distance to Cu1 (−1+x, y, z) is 3.784(3) Å. Thus, the geometry around Cu1 remains approximately square planar while the coordination around Cu2 becomes square-pyramidal (τ = 0.055) [19]. However, the amide-C=O···Cu contact is rather long and weak, hence, the dicopper(II) complex [CuL1(µ-L2)CuL1L2] may be regarded as pseudo-dinuclear. Most likely, this nicotinamide bridge is present in a DMF solution of [CuL1L2] or may form upon decomposition of [CuL1L2]. There is a linear relationship between the cathodic peak current (Ic3) and the square root of the scan rate (v 1/2) in the 5 to 400 mV s−1 range (Fig. 4). This behavior is diagnostic of an electron transfer process controlled by diffusion. The ΔEp = (Epa − Epc) value was 176 mV and the ipa/ipc = 0.28 relationship was far from unity. This finding shows the quasi-reversibility of this redox process.

The cyclic voltammogram of a solution containing presumably the fragment CuL1 (prepared by mixing Cu(NO3)2 and H2L1 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 Ic3 and Ia2 and Ic4, respectively, of [CuL1L2] in Fig. 2. This indicates that a CuL1 fragment is present in a DMF solution of [CuL1L2] or may form upon decomposition of [CuL1L2]. There is a linear relationship between the cathodic peak current (Ic3) and the square root of the scan rate (v 1/2) in the 5 to 400 mV s−1 range (Fig. 4). This behavior is diagnostic of an electron transfer process controlled by diffusion. The ΔEp = (Epa − Epc) value was 176 mV and the ipa/ipc = 0.28 relationship was far from unity. This finding shows the quasi-reversibility of this redox process.

Electrochemical cyclic voltammetry measurements were carried out to probe the redox stability of the [CuL1L2] complex in solution [25]. The cyclic voltammogram of the complex [CuL1L2] in dimethylformamide displays three cathodic potentials at about 0 (Ic3), −0.5 (Ic2) and −1.0 V (Ic1) (Fig. 2). They can be assigned to reduction of coordinated L1 from their similarity to a CV scan of H2L1 alone (not shown). The very sharp oxidation peak at about 0.3 V (Ia2) is assigned to the oxidation of liberated copper. CuII is initially reduced to CuI during the forward scan; the cathodic reduction at about 0 V is, however, covered by the 0 V reduction of L1. The sharpness of oxidation peak of copper is due to the stability of CuII 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 (Ia3) associated with the cathodic peak L3. An anodic wave associated with L2 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 [CuL1L2] occurs at −0.5 V by the reduction of L1.

Cyclic voltammetry between 1.5 and 0 V permits the study of the [CuL1L2] 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 (Ia3), 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 H2L1 alone (not shown).

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.
Nicotinamide-bridged Dinuclear Copper Complex

![Graph](image)

Fig. 4 Plot of cathodic current (i_\text{pa}) versus the square root of sweep rate (ν/2) for I_{13} 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^\{3\}-(2-hydroxy-3-methoxybenzylidene)benzohydrazido)(nicotinamide)-\{(µ-nicotinamide)dicopper(II), [CuL^1(µ-L^2)CuL^2]^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), benzohydrazide (0.045, 0.33 mmol) and nicotinamide (0.04 g, 0.33 mmol) by diffusion along a thermal gradient in methanol solution (‘branched tube method’ [26]) provided dark brown crystals within 5 d (yield 140 mg, 93%). Calc. for C_{42}H_{36}Cu_{2}N_{8}O_{8} (907.86) C 55.56, H 4.01, N 12.40, Cu 14.00%.

ν of (NH\textsubscript{2}), 2923 (w), 1700 (s, C=O). UV/Vis (in CH\textsubscript{3}CN, c = 2.21·10^{-3} mol/l, green solution, λ\textsubscript{max} [mm] with ε [l/mol·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^2]^2**

Crystal data: Molecular formula C_{42}H_{36}Cu_{2}N_{8}O_{8}, formular weight 907.86 g mol^{-1}, a = 12.694(2), b = 9.923(2), c = 15.119(4) Å, β = 95.661(6)°, V = 1895.2(7) Å\textsuperscript{3}, Z = 2, D\textsubscript{calc} = 1.591 g cm\textsuperscript{-3}, μ(Mo-Kα) = 3.710 mm\textsuperscript{-1}, crystallographic data (space group P2\textsubscript{1}, Data collection: Bruker APEX2 CCD, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, crystal size 0.40 x 0.20 x 0.20 mm\textsuperscript{3}, 100(2) K, θ- and ω-scan, 3.2° ≤ 2θ ≤ 56.5°, −16 ≤ h ≤ 16, −13 ≤ k ≤ 11, −20 ≤ l ≤ 20, 14396 reflections measured, 8926 independent (R\textsubscript{int} = 0.0421), μ(Mo-Kα) = 1.191 mm\textsuperscript{-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\textsuperscript{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\textsubscript{eq}(H) = 1.2 U\textsubscript{eq}(C, N), for CH\textsubscript{3}, NH\textsubscript{2} and 1.5 U\textsubscript{eq}(C) for CH\textsubscript{2}. 544 refined parameters, final R\textsubscript{1} = 0.0473, wR\textsubscript{2} = 0.0901 for 6869 reflections with I > 2σ(I), final R\textsubscript{1} = 0.0740, wR\textsubscript{2} = 0.1060 for all data, goodness-of-fit 0.990, largest difference peak and hole 0.495/-0.711 e Å\textsuperscript{-3}. Flack parameter [30] or batch scale factor (BASF) for unequal components in twin refinement 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 computrace voltammetric analyzer model 757 VA. A conventional three-electrode system was used with a polished glassy carbon electrode (area 3.14 mm\textsuperscript{2}) 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\textsubscript{2} saturated with solvent for ca. 15 min prior to taking measurements in order to remove dissolved O\textsubscript{2}. Voltammograms were recorded in the range from 1.5 to −2.0 V vs Ag/AgCl.

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