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Facile synthesis of Cu(II) complexes of mono- and bicondensed N donor Schiff base 1*H*-pyrazolate ligands: Crystal structures, spectroscopic and magnetic properties

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ABSTRACT

Two [2 × 2] grid-like complexes, $[Cu_4(\mathbf{L^1})_4]\cdot 2MeOH\cdot 2H_2O\cdot dmf$ (**1**) and $[Cu_4(\mathbf{L^2})_4]\cdot 2NaClO_4\cdot 2MeOH$ (**2**) based on new substituted pyrazole ligands 5-(1-((2-aminoethyl)imino)ethyl)-4-methyl-1*H*-pyrazole-3-carboxylic ($H_2\mathbf{L^1}$) acid and 5-(1-((3-aminopropyl)imino)ethyl)-4-methyl-1*H*-pyrazole-3-carboxylic acid ($H_2\mathbf{L^2}$) have been synthesized and characterized spectroscopically and crystallographically. It was found that the ligand $H_2\mathbf{L^2}$ condenses with 3-acetyl-4-methyl-pyrazole-5 carbonic acid ($H_2\mathbf{L}$) to produce a new dinuclear Cu(II) complex upon reaction with $Cu(ClO_4)_2\cdot 6H_2O$ and $CuAc_2\cdot 2H_2O$. In the grid complexes the four Cu(II) atoms are in square-pyramidal environment formed by two pyrazole, imine and amine N atoms, and the carboxylate O atom and occupy the corners of a [2 × 2] grid with the Cu···Cu separations, varying from 3.998(1) to 4.2049(9) and 4.794(1) to 5.091(1) Å for the adjacent and diagonal atoms, respectively. In the dinuclear complex **3** the metal ions are found in square planar environment with their coordination planes lying roughly within the plane of the pyrazolate heterocycle. The separation between Cu(II) centers is 3.921(1) Å. Magnetic susceptibility measurements of **3** revealed the presence of strong antiferromagnetic interaction, with a *J* value of −207.5 cm^{-1}. This is larger than the *J* values found for the **1** and **2** grid complexes, which are −20.2 and −18.3 cm^{-1}, respectively.

1. Introduction

Pyrazolate-based binucleating ligands have proven very useful for nesting several metal ions. The scope of modulating electronic and geometric characteristics of the bimetallic core by varying the ligand side arms attached to the 3- and 5-positions of the heterocycle is an attractive option for this class of ligands [1].

The pyrazolate-derived bimetallic entities can be assembled in various ways, from tetranuclear species to alternating 1D chain systems [2]. On the other hand self-assembly strategies open ways to numerous nanosized molecular architectures displaying functional (catalytic, electrochemical, photoactive, magnetic, etc.) or multifunctional properties [3]. Molecular grid-type systems seem to be especially interesting for molecular magnetic applications. Among a variety of ligands used for the synthesis of self-assembled complexes, pyrazole derivatives were studied poorly, although some work devoted to grid-like complexes was recently reported [4–9]. As the pyrazolate has some inherent similarities to previously employed pyridine, triazolate and pyridazine moieties, [10–12] and moreover is able to bridge metal centers thus providing a magnetic and/or electronic exchange pathway, we have decided to use 3,5-disubstituted pyrazolates as self-assembling scaffolds. Initially we have focused our interest on copper(II) coordination chemistry of Schiff-base ligands derived from 3,5-dicarbonylpyrazole [4,13]. Although some studies with 3,5-diformylpyrazole derivatives have been reported, [14], to the best of our knowledge, no paper was dealing with the asymmetric pyrazoles bearing a keto-function that reacts with amines to produce Schiff bases.

Herein, we describe the results of our studies on copper(II) complexes derived from the pyrazolate-based dinucleating ligands (Scheme 1). The synthesis, characterization and X-ray crystal structures of the resulting di- and tetranuclear pyrazolate-bridged copper(II) complexes are reported, along with their magnetic behavior.

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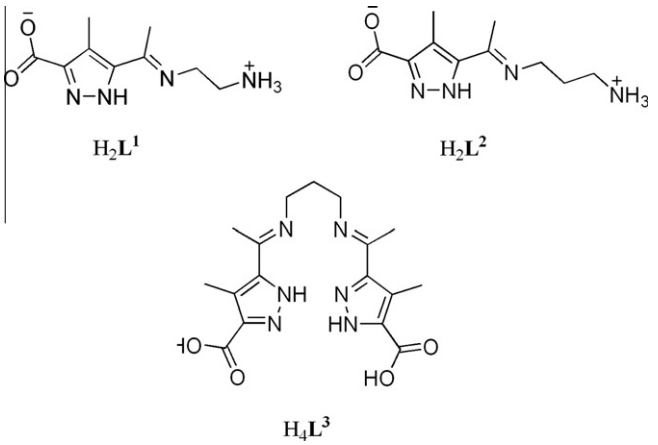

Scheme 1. Schematic representation of ligands discussed in the present work.

2. Experimental

All chemicals were purchased from commercial sources and used as received.

Caution! Although no problems were encountered in this work, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

2.1. Preparations

2.1.1. Preparation of ligands (H_2**L**^{1}, H_2**L**^{2})

3-Acetyl-4-methyl-pyrazole-5 carboxylic acid [13a] (H_2**L**) (1.25 g, 7.5 mmol) was dissolved in 35 ml MeOH and 1,2-diaminoethane (0.62 g, 7.9 mmol) or 1,3-diaminopropane (0.59 g, 7.9 mmol) in 35 ml of MeOH was added dropwise. Small amount of acetic acid (40 μl) was added as a catalyst. Within few minutes a white precipitate formed, and the reaction mixture was refluxed for 1 h. The product was filtered off, washed with hot methanol and dried in air.

For H_2**L**^{1}: Yield: 1.11 g, 70%; white solid, 250 °C.

IR (KBr pellets): $\nu_s(NH_3^+)$ 3200 $\nu_{as}(NH_3^+)$ 3415 $\delta(NH_3^+)$ 1632, 1614 $\nu_{as}(CO_2^-)$ 1555 $\nu_s(CO_2^-)$ 1439, 1332, 1301, 1224, 1082, 812 cm^{-1}. (^{1}H NMR) CF_3COOH: δ = 2.841 (s, 3H, CH_3), 2.918 (s, 3H, CH_3), 4.187 (t, 2H, CH_2, J = 5.2 Hz), 4.436 (t, 2H, CH_2, J = 5.2 Hz). EI MS: m/z (%) = 211.1 (100) [H_2**L**^{1}+H^+]$^+$. *Anal.* Calc. for $C_9H_{14}N_4O_2$ (210.11): C, 51.42; H, 6.71; N, 26.65. Found: C, 51.10; H, 6.53; N, 26.35%.

For H_2**L**^{2}: Yield: 1.05 g, 75%; white solid, 235 °C. IR (KBr pellets): $\nu_s(NH_3^+)$ 3257 $\nu_{as}(NH_3^+)$ 3455 $\delta(NH_3^+)$ 1636 $\nu_{as}(CO_2^-)$ 1590 $\nu_s(CO_2^-)$ 1401, 1327, 1257, 1176, 1058, 812 cm^{-1}. (^{1}H NMR) DMSOd_6: δ(ppm) = 2.594 (dd, $^2J_1$ = 7.6, $^2J_3$ = 7.2 Hz, 2H), 2.765 (s, 3H), 3.046 (s, 3H), 3.566 (t, $^2J_2$ = 7.2 Hz, 2H), 4.223 (t, $^2J_2$ = 7.6 Hz, 2H). EI MS: m/z (%) = 225.2 (100) [H_2**L**^{2}+H^+]$^+$. *Anal.* Calc. for $C_{10}H_{16}N_4O_2$ (224.13): C, 53.56; H, 7.19; N, 24.98. Found: C, 52.95; H, 7.12; N, 24.50%.

2.1.2. Preparation of [Cu_4(**L**^{1})$_4$]·2MeOH·2H_2O·dmf (**1**) and [Cu_4(**L**^{2})$_4$]·2$NaClO_4$·2MeOH (**2**)

The ligand H_2**L**^{1} (0.245 g, 1.16 mmol) or H_2**L**^{2} (0.259 g, 1.16 mmol) was suspended in methanol (40 ml) and a solution of $Cu(ClO_4)_2$·H_2O (0.438 g, 1.16 mmol) was added. Within 5 min two equivalents of NaOH (2.32 ml, 1 M) was added dropwise while stirring. After that the reaction mixture was stirred for 1 h at room temperature. X-ray-quality crystals of **1** or **2** were grown by slow diffusion of diethyl ether into the resulting dark blue methanolic solutions.

For **1**: Yield: 0.32 g (88%). *Anal.* Calc. for $C_{41}H_{67}Cu_4N_{17}O_{13}$ (1260.3): C, 39.07; H, 5.36; N, 18.89. Found: C, 38.72; H, 6.10; N, 19.05%. IR (KBr): ν(C—N) 1634 $\nu_{as}(CO_2^-)$ 1570 br, $\nu_s(CO_2^-)$ 1434, 1384, 1321 ν(Cl—O) 1093, 816, 621 cm^{-1}. ESI MS: 1087.1, {[Cu_4(**L**^{1})$_4$]+H^+}$^+$. UV–Vis (MeOH), λ_{max} (ε): 595 (326) nm; (DR) λ_{max}: 618 nm.

For **2**: Yield: 0.36 g (85%). *Anal.* Calc. for $C_{42}H_{64}Cl_2Cu_4N_{16}Na_2O_{18}$ (1452.2): C, 34.74; H, 4.44; N, 15.43. Found: C, 34.35; H, 4.82; N, 15.25%. IR (KBr): $\nu_{as}(CO_2^-)$/$\delta(NH_3^+)$/ν(C—N) 1603 br, $\nu_s(CO_2^-)$ 1432, 1325, ν(Cl—O) 1088, 814, 624 cm^{-1}. ESI MS: 1143.1, {[Cu_4(**L**^{2})$_4$]+H^+}$^+$. UV–Vis (MeOH), λ_{max} (ε): 582 nm (226), (DR) λ_{max}: 603 nm.

2.1.3. Preparation of [Cu_2(**L**^{3})]·3H_2O (**3**)

$Cu(ClO_4)_2$·6H_2O (0.464 g, 1.24 mmol) was mixed with H_2**L** (0.210 g, 1.24 mmol) and 1,3-diaminopropane (0.046 g, 0.62 mmol) in methanol (20 ml). After that two equivalents of NaOH (0.099 g) was added and the reaction mixture was boiled for 3 h. The resulting brown-green solution was filtered. After few days of slow solvent evaporation at room temperature the brown needles of **3** formed.

Yield: 0.274 g (80%). *Anal.* Calc. for $C_{17}H_{24}Cu_2N_6O_7$ (551.5): C, 37.02; H, 4.39; N, 15.24. Found: C, 36.95; H, 4.82; N, 15.15%. IR (KBr): $\nu_{as}(CO_2^-)$ 1645, ν(C—N) 1599, $\nu_s(CO_2^-)$ 1430, 1362, 1246, 1224, 1090, 836, 816, 801 cm^{-1}. ESI MS: 496.8, {[Cu_2(**L**^{3})]+H^+}$^+$; 518.9, {[Cu_2(**L**^{3})]+Na^+}$^+$. UV–Vis (MeOH), λ_{max} (ε): 456 (263), 603 (183) nm, (DR) λ_{max}: 470, 595 nm.

2.2. Physical measurements

Melting points/decomposition temperatures were determined with an OptiMelt system (Stanford Research Systems, Inc.). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 or Bruker Avance 400 spectrometers. ^{13}C resonances were obtained with broad-band proton decoupling, spectra were recorded at 298 K. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced internally to solvent signals (DMSO-d_6 δ_H = 2.49, δ_C = 39.7). Mass spectra were recorded with a Finnigan MAT 95 (EI) or Bruker APEX IV (HRMS, ESI). IR spectra from KBr pellets were recorded on a Perkin Elmer FT-IR Spectrum BX II spectrometer. Elemental analyses were performed on an Elementar vario EL III instrument. UV–Vis spectra were recorded with a Cary 50 spectrometer. Variable-temperature magnetic susceptibility data (2–300 K) were acquired on a powdered sample using a Quantum Design MPMS-5S SQUID magnetometer. Corrections for the diamagnetism of the ligand were applied using Pascal's constants. X-B and EPR spectra were recorded on a Bruker ESP 300E spectrometer equipped with a Bruker NMR gaussmeter ER 035M and a Hewlett Packard microwave frequency counter HP 5350B.

2.3. X-ray crystallography

Image frames datasets from single crystals **1**, **2** and **3** were collected on a Bruker APEX2 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation and an Oxford Cryosystems low-temperature device. All structures were solved by direct methods using SHELXS-97 program and refined in anisotropic approximation for all non hydrogen atoms by least squares method on F^2 using SHELXL-97 [15]. The semi-empirical absorption correction was applied to all datasets utilizing SADABS [16]. All methyl and methylene hydrogens were calculated geometrically regarding the hybridization of the parent atom and refined using "riding" model with $U_{iso}(H) = 1.5U_{iso}(C)$ for methyl groups and $U_{iso}(H) = 1.2U_{iso}(C)$ for methylene groups. Hydrogen atoms located on nitrogens and oxygens were determined from the difference Fourier map and refined with constrained thermal parameters $U_{iso}(H) = 1.2U_{iso}(N)$