

Synthesis, Characterization, Crystal Structure and Magnetic Properties of $[(\text{en})\text{Cu}^{\text{II}}(\text{ImH})_2](\text{ClO}_4)_2$ (en = Ethylenediamine, ImH = Imidazole): A Metalloligand as a Building Block for Heterometal Chains

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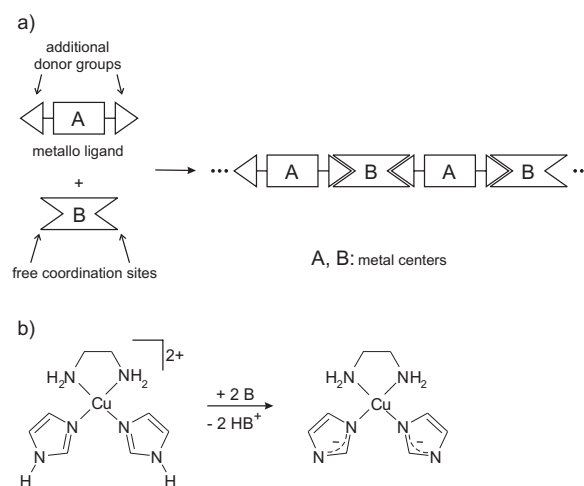
The reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, imidazole (ImH), and ethylenediamine (en) in a 1 : 2 : 1 ratio afforded in high yield dark-blue single-crystals of $[(\text{en})\text{Cu}^{\text{II}}(\text{ImH})_2](\text{ClO}_4)_2$, **1**, which can be used after deprotonation as a building block for heterometallic ferrimagnetic chains. The structural and electronic properties of **1** were examined by X-ray crystallography, FTIR, ESI-MS, electrochemistry, UV/vis/NIR, EPR, and magnetic susceptibility measurements. The structure of **1** exhibits intermolecular π - π interactions and hydrogen bonds but the magnetic data exclude the presence of intermolecular exchange interactions.

Key words: Cu Complexes, Magnetic Properties, N Ligands

Introduction

The design of molecular compounds exhibiting a spontaneous magnetization below a certain critical temperature is probably the most active area of molecular magnetism [1]. One strategy is the synthesis of one-dimensional chains with two different spin-carriers A and B. Even in the case of antiferromagnetic interactions between nearest neighbors, there is a noncompensation of the local spins $|S_A - S_B|$ leading to ferrimagnetic chains. The archetype of ferrimagnetic chains is the system $\text{MnCu}(\text{pba})$ (pba = 1,3-propylenebis(oxamato)) [2]. Mn^{II} ($S_{\text{Mn}} = 5/2$) and Cu^{II} ($S_{\text{Cu}} = 1/2$) are antiferromagnetically coupled in $\text{Mn}^{\text{II}}(\text{OH}_2)[\text{Cu}^{\text{II}}(\text{pba})\text{OH}_2] \cdot 2\text{H}_2\text{O}$ (intra-chain coupling), and a weak antiferromagnetic coupling between the chains (inter-chain coupling) results in a long-range antiferromagnetic ordering at 2.4 K. The introduction of a hydroxy group into the ligand results in $\text{Mn}^{\text{II}}(\text{OH}_2)[\text{Cu}^{\text{II}}(\text{pbaOH})\text{OH}_2] \cdot 2\text{H}_2\text{O}$ (pbaOH = 2-hydroxy-1,3-propylenbis(oxamato)) and an inter-chain ferromagnetic coupling leads to a ferromagnetic long-range ordering at 4.6 K. Dehydration by thermal treatment increases the Curie-temperature to 30 K due to a proposed decrease of inter-chain distances. The prerequisite for the rational design of hetero-metallic ferrimagnetic chains is the use of a metallo-ligand, *i. e.*

a metal complex with additional donor groups, as a supramolecular building block. For the construction of one-dimensional chains, such a metallo-ligand needs two additional donor sites (Scheme 1a). Addition of a suitable metal complex fragment with two free coordination sites or a metal complex with two labile ligands leads to the formation of a one-dimensional heterometallic chain. Because the crystallization of such chains appears to be difficult due to their polymeric nature, the exact structural and spectroscopic charac-



Scheme 1.

terization of the parent molecular building blocks is mandatory for the characterization of the one-dimensional chains.

The imidazolate (Im) ligand is well-known for its ability to serve as a bridging ligand between two different metal complex fragments. The strategy for the rational synthesis of a hetero-dinuclear unit implies the preparation of a metal complex with a mono-dentately bound ImH ([A-ImH]ⁿ) followed by base-induced proton abstraction (frequently termed ‘pH-switch for a self-assembly process’) giving ([A-Im]⁽ⁿ⁻¹⁾) which reacts in a subsequent step with a second metal center resulting in a hetero-metallic unit ([A-Im-B]^m). Some hetero-metallic compounds were synthesized by this synthetic route [3]. Using only copper as metal ion, several homo-metallic chains and supramolecular complexes were obtained [4]. The magnetic properties of these compounds were investigated in detail. In most cases, the bridging imidazolate ligand acts as a strong antiferromagnetic coupler between the metal ions. Several studies were performed to rationalize the nature of the antiferromagnetic coupling identifying a σ -pathway for antiferromagnetic exchange interactions as the most effective one [5]. However, two ferromagnetically coupled heterometallic compounds were reported and the origin of the ferromagnetic exchange interactions was rationalized by the orthogonality of a σ - π -pathway [3a,b]. The three-dimensional compound [Fe₃(Im)₆(ImH)₂]_x is a ferromagnet with a Curie temperature of 17 K [6]. Here, we report on the synthesis and detailed characterization of the bis-imidazol copper complex [(en)Cu^{II}(ImH)₂](ClO₄)₂, **1**, (en = ethylenediamine) which is obtained from inexpensive, easily available starting materials. This thorough characterization is the basis for our ongoing studies on the ability of **1** to act after deprotonation (Scheme 1b) as a building block for hetero-metal one-dimensional ferromagnetic chains. To the best of our knowledge, no such hetero-metal chains using imidazolate have been reported so far.

Results and Discussion

Synthesis and characterization

The reaction of Cu(ClO₄)₂·6H₂O, imidazole, and ethylenediamine in a 1 : 2 : 1 ratio in a EtOH/H₂O mixture (3 : 1) yielded a dark-blue solution from which after slow evaporation of the solvent large single-crystals of [(en)Cu^{II}(ImH)₂](ClO₄)₂, **1**, separated. ESI-mass spectra and elemental analysis corroborate this formu-

Table 1. Selected bond lengths [Å] and bond angles [°] for **1**.

| | | | |
|------------|------------|-----------|------------|
| Cu-N1a | 1.9870(18) | N3-Cu-N3a | 84.41(11) |
| Cu-N1 | 1.9870(18) | N1a-Cu-O1 | 90.23(7) |
| Cu-N3 | 2.0119(19) | N1-Cu-O1 | 91.59(7) |
| Cu-N3a | 2.0119(19) | N3-Cu-O1 | 91.77(7) |
| Cu-O1 | 2.5803(17) | N3a-Cu-O1 | 86.33(7) |
| C1-C2 | 1.353(3) | C2-C1-N1 | 109.1(2) |
| C1-N1 | 1.376(3) | C1-C2-N2 | 106.0(2) |
| C2-N2 | 1.360(3) | N1-C3-N2 | 110.3(2) |
| C3-N1 | 1.326(3) | N3-C4-C4a | 107.30(14) |
| C3-N2 | 1.328(3) | C3-N1-C1 | 105.96(19) |
| C4-N3 | 1.484(3) | C3-N1-Cu | 123.70(15) |
| C4-C4a | 1.512(4) | C1-N1-Cu | 129.89(16) |
| Cl-O4 | 1.4276(18) | C3-N2-C2 | 108.6(2) |
| Cl-O2 | 1.4339(18) | C4-N3-Cu | 109.01(13) |
| Cl-O1 | 1.4354(18) | O4-Cl-O2 | 111.57(13) |
| Cl-O3 | 1.439(2) | O4-Cl-O1 | 110.36(12) |
| N1a-Cu-N1 | 89.70(11) | O2-Cl-O1 | 110.18(11) |
| N1a-Cu-N3 | 176.61(7) | O4-Cl-O3 | 108.15(15) |
| N1-Cu-N3 | 92.98(8) | O2-Cl-O3 | 108.03(14) |
| N1a-Cu-N3a | 92.98(8) | O1-Cl-O3 | 108.45(14) |
| N1-Cu-N3a | 176.61(7) | Cl-O1-Cu | 133.19(11) |

Symmetry operations used to generate equivalent atoms: $-x, y, -z + 1/2$.

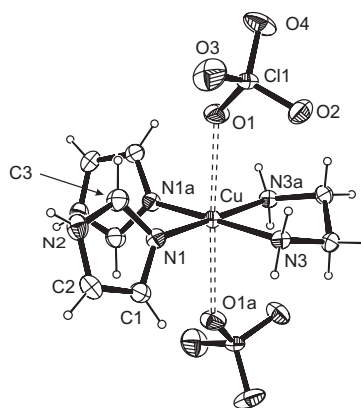


Fig. 1. Molecular structure of [(en)Cu^{II}(ImH)₂](ClO₄)₂, **1**. Displacement ellipsoids represent the 50% probability surfaces.

lation. The elemental analysis indicates the absence of solvent molecules. The FTIR spectrum shows characteristic vibrations due to en, ImH, and ClO₄⁻. Since the preparation of heterometallic chains by use of **1** as a building block could give non-crystalline materials, a rigorous assignment of the IR-bands was performed (see Experimental Section) based on the FTIR spectra of the starting materials and of [Cu(en)₂](BF₄)₂ (prepared from Cu(BF₄)₂·3H₂O and en in EtOH) as well on the assignment for [Cu(Im)₂]_n phases by Masciocchi *et al.* [7].

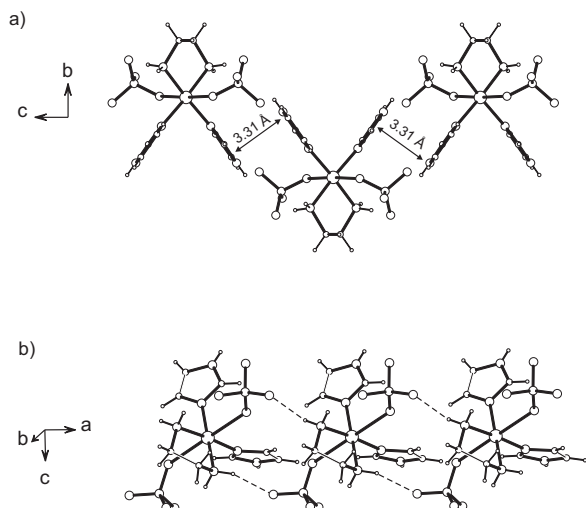


Fig. 2. Intermolecular interactions in the solid state: a) π - π stacking along the c -direction; b) hydrogen-bonding along the a -direction.

Solid state structure

Fig. 1 shows the molecular structure of **1** with the labeling scheme used. Selected bond distances and angles are given in Table 1. The asymmetric unit consists of one half of the molecule with the other half generated by a crystallographically imposed twofold axis passing through Cu and the center of the C-C bond of the en ligand. The copper center is coordinated by the nitrogen atoms of the en ligand with Cu-N bond distances of 2.01 Å and by the nitrogen atoms of two ImH ligands with Cu-N bond distances of 1.99 Å. The two ClO₄⁻ anions form weak Cu-O bonds at 2.58 Å distance. Thus, the coordination environment may be described as an elongated octahedron. Due to the twofold symmetry, the copper atom and the four nitrogen donor atoms form a perfect plane. The en ligand forms a five-membered chelate ring Cu-N3-C4-C4a-N3a with a gauche conformation, C4 and C4a being located 0.35 Å below and above the plane defined by Cu, N3, and N3a, respectively. The plane defined by Cu and the four coordinated nitrogen atoms (N1, N1a, N3, N3a) forms an angle of 65.4° with the plane of the ImH ring. The coordinated ClO₄⁻ anions form intramolecular hydrogen-bonds with the amine group of the coordinated en ligand (O2-N3 = 3.10 Å, N3-H3N = 0.90 Å, O2-H3N = 2.29 Å, N3-H3N-O2 = 149°).

Intermolecular interactions in the crystal structure of **1** are based on π - π stacking interactions between the planes of the coordinated ImH ligands in

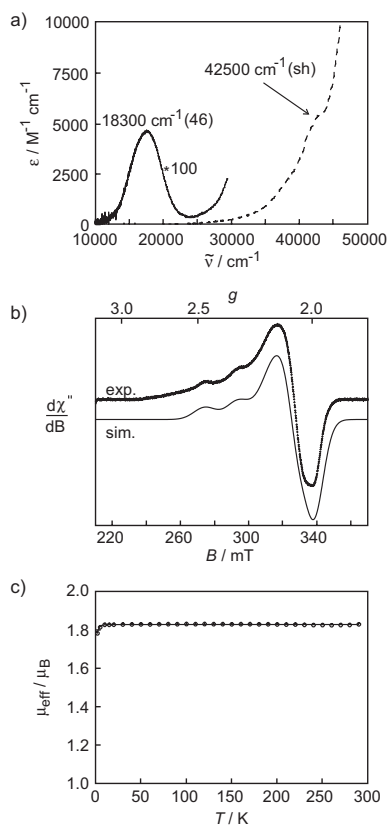


Fig. 3. a) Electronic spectrum of **1** in CH₃CN; b) X-band EPR spectra of **1** at 20 K in frozen CH₃CN, conditions: frequency: 9.4521 GHz, power: 50.4 μW, modulation: 10.0 G; c) Temperature dependence of the effective magnetic moment, μ_{eff} , of **1** at 1 T. The solid line is a fit to the experimental data using the spin-Hamiltonian for $S_{\text{I}} = 1/2$ including saturation effects at low temperatures.

the c -direction of the unit cell with a distance of 3.31 Å (Fig. 2a). Additionally, there are two hydrogen bonds between neighboring molecules along the a -direction of the unit cell which are stronger than the intramolecular hydrogen bonds (Fig. 2b; O4'-N3 = 3.01 Å, N3-H3M = 0.92 Å, O4'-H3M = 2.13 Å, N3-H3M-O4' = 161°).

Electronic properties

The UV/vis/NIR absorption spectrum of **1** in CH₃CN solution is shown in Fig. 3a. The spectrum consists of CT- and intra-ligand transitions above 35000 cm⁻¹ and a d-d transition at 18300 cm⁻¹. The high energy of this d-d absorption band without further transitions at lower energy is in accordance with a pure square-planar geometry of **1** in CH₃CN solution [8],

i. e. without even weakly coordinated ClO₄[−] anions. The ground state is d_{x²−y²} (*b*_{1g} in *D*_{4h} symmetry).

The X-band EPR spectrum of **1** in a frozen CH₃CN solution at 20 K displays a relatively broad *S* = 1/2 spectrum with hyperfine coupling in the *g*_{||} region (Fig. 3b). The line width does not change by increasing or decreasing the concentration. This indicates an association of the molecules in solution to larger aggregates which leads to a concentration-independent line-broadening by dipolar interactions. The spectrum was simulated with parameters *g*_x = 2.066, *g*_y = 2.084, *g*_z = 2.230 and hyperfine coupling to the ^{63/65}Cu (*I* = 3/2) nucleus of *A*_x = 20, *A*_y = 20, *A*_z = 200 · 10^{−4} cm^{−1}. These parameters corroborate with a d_{x²−y²} ground state in a square planar Cu^{II} complex [8a]. The small splitting of *g*_{xy} accounts for the C₂ distortion due to different ligands.

The magnetic susceptibility of **1** was measured in the temperature range 2–300 K. The raw data were corrected for underlying diamagnetism by using tabulated Pascal constants and for temperature-independent paramagnetism, *χ*_{TIP}, which was obtained as a fit parameter. A fit to the spin Hamiltonian for an *S*_t = 1/2 system is in good agreement with the EPR spectrum (*g* = 2.11 and *χ*_{TIP} = 17 · 10⁶ cm³ mol^{−1}) [9]. The effective magnetic moment, *μ*_{eff}, has a temperature-independent value of 1.83 *μ*_B in the range 300–30 K and decreases below 30 K to a value of 1.78 *μ*_B at 2 K. A decrease of *μ*_{eff} at low temperature can be assigned to three reasons: (*i*) saturation effects, (*ii*) zero-field splitting, and (*iii*) intermolecular antiferromagnetic exchange interactions. Zero-field splitting can be discarded due to the spin doublet. The crystal structure of **1** exhibits two possible pathways for an intermolecular interaction, *i. e.* *π*–*π* stacking along the *c*-direction and hydrogen-bonding along the *a*-direction. However, the fit shown in Fig. 3c includes saturation effects and reproduces the experimental data at low temperatures perfectly. Thus, the analysis of the magnetic data shows that despite of available pathways there are no intermolecular exchange interactions in **1**.

The cyclic voltammogram of **1** in CH₃CN exhibits several irreversible electron-transfer waves. There are three irreversible reductions at −0.65, −0.96, and −1.64 V vs. Fc⁺/Fc. The latter reduction leads to an adsorption on the surface of the working electrode (glassy carbon or Pt). An oxidative current starts at +1.24 V vs. Fc⁺/Fc. These observations are typical for Cu^{II} complexes in a non-rigid coordination environment including mono-dentate ligands. The reduc-

Table 2. Crystallographic data for **1**.

| | |
|--|---|
| Habit | blue transparent prism |
| Crystal size [mm] | 0.14 × 0.12 × 0.06 |
| Formula | C ₈ H ₁₆ Cl ₂ N ₆ O ₈ Cu |
| fw [amu] | 458.70 |
| <i>a</i> [Å] | 7.4196(5) |
| <i>b</i> [Å] | 15.7272(10) |
| <i>c</i> [Å] | 14.4480(9) |
| <i>α</i> [deg] | 90 |
| <i>β</i> [deg] | 98.1170(10) |
| <i>γ</i> [deg] | 90 |
| <i>V</i> [Å ³] | 1669.04(19) |
| Calculated density [g cm ^{−3}] | 1.825 |
| Crystal system | monoclinic |
| Space group | <i>C</i> 2/ <i>c</i> |
| <i>Z</i> | 4 |
| <i>λ</i> [Å] | 0.71073 |
| Monochromator | graphite |
| Temperature [K] | 153(2) |
| Scan type | omega and phi scans |
| 2 <i>θ</i> Range [deg] | 5–45 |
| <i>hkl</i> Limits | −9 ≤ <i>h</i> ≤ 9, −20 ≤ <i>k</i> ≤ 16, −18 ≤ <i>l</i> ≤ 17 |
| <i>μ</i> [mm ^{−1}] | 1.681 |
| Reflections measured | 5619 |
| Independent reflections | 1909 |
| Observed (<i>I</i> > 2σ(<i>I</i>)) | 1802 |
| <i>R</i> (observed) | <i>R</i> 1 = 0.0357, <i>R</i> _w = 0.0910 |
| <i>R</i> (all) | <i>R</i> 1 = 0.0374, <i>R</i> _w = 0.0921 |
| GOF | 1.083 |
| No. of variables | 146 |
| Res. el. dens. [e/Å ³] | 1.246 / −0.522 |

tion to Cu^I leads to a rearrangement and/or loss of ligands resulting in irreversible electron-transfer waves with additional waves for the chemically generated new species (ECE mechanism).

In conclusion, we have synthesized a readily available building block for heterometallic ferrimagnetic chains and performed a detailed analysis of the structural and spectroscopic properties. Despite the presence of *π*–*π* stacking along the *c*-direction and hydrogen-bonding along the *a*-direction, no intermolecular exchange interactions are observed in the magnetic data.

Experimental Section

Physical techniques

Infrared spectra (400–4000 cm^{−1}) of solid samples were recorded on a Bruker Vector 22 spectrometer as KBr disks. UV/vis/NIR-absorption spectra of solutions were measured on a Varian Cary 50 spectrophotometer in the range 190–1100 nm at ambient temperature. Cyclic voltammetric measurements were performed with Eco-Chemie/Metrohm equipment (potentiostat/galvanostat model PGSTAT 30)

on Ar-flushed acetonitrile solutions of samples containing 0.1 M [N(*n*-butyl)₄][PF₆] as supporting electrolyte under an argon blanketing atmosphere. ESI mass spectra were recorded on a Micromass Quattro LC mass spectrometer. Temperature-dependent magnetic susceptibilities of powdered samples were measured by using a SQUID magnetometer (Quantum Design) at 1.0 T (2.0–300 K). For calculations of the molar magnetic susceptibility, χ_M , the measured susceptibilities were corrected for the underlying diamagnetism of the sample by using tabulated Pascal constants. X-band EPR spectra were measured on a Bruker ESP 300 spectrometer equipped with an Oxford Instruments ESR 910 helium-flow cryostat.

X-ray diffraction

Data of **1** were collected at –120 °C on a Bruker AXS APEX diffractometer equipped with a rotating anode using Mo-K α radiation (λ = 0.71073 Å). Empirical absorption correction with SADABS [10a] was applied to the raw data. Structure solution and refinement were done with the SHELXS [10b] and SHELXL [10c] programs using anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located by difference Fourier map techniques and were refined with isotropic displacement parameters. ORTEP [10d] was used for all drawings. Additional data collection and refinement details are listed in Table 2 [11].

[(en)Cu^{II}(ImH)₂](ClO₄)₂ (**1**)

To a solution of 1.11 g (3.00 mmol) Cu(ClO₄)₂ · 6H₂O in distilled water (5 ml) and EtOH (15 ml) was added 0.409 g (6.00 mmol) of solid imidazole. After stirring for 15 min, the solution was treated with 0.181 g (3.00 mmol) of ethylenediamine leading to a dark-blue color. The mixture was heated under reflux for 30 min. Slow evaporation of the solvent gave large dark-blue crystals. Yield: 1.13 g, 82%. UV/vis/NIR (CH₃CN): λ_{max} (ϵ_{max}) = 569 nm (46), 235 nm (sh). – IR (KBr): ν = 3389, 3335, 3303, 3280, 3237 (all N-H en), 3165, 3142 (both N-H imH), 3125 (N-H en), 3064 (N-H imH), 2959, 2904, 2867 (all C-H en), 1594, 1583 (both δ NH₂ en), 1541, 1513, 1499 (all imH), 1465 (δ CH₂ en), 1436, 1332 (δ CH), 1264 (all imH), 1093 ((ClO₄)[–]), 988 (C-N en), 948, 921, 848 (all imH), 770, 759 (both γ C-H imH), 714 (en), 663, 652 (both imH), 625 ((ClO₄)[–]), 522 (en) cm^{–1}. – MS (ESI in MeOH, positive ion mode): m/z = 358 [(en)Cu(imH)₂](ClO₄)⁺, 190 [(en)Cu(im)]⁺, 69 [imH₂]⁺. – C₈H₁₆Cl₂N₆O₈Cu (458.70): calcd. C 20.95, H 3.52, N 18.32; found C 20.96, H 3.26, N 18.12.

Acknowledgements

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- [11] Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC 192925. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).