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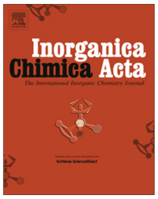

What happens when (1H-benzimidazol-2-ylmethyl)-N-phenyl amine is added to copper(II) acetate? Spectroscopic, magnetic, and DFT studies

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ABSTRACT

On performing a reaction between (1H-benzimidazol-2-ylmethyl)-N-phenyl amine (H_2L) and copper(II) acetate in methanol, a green "paddle-wheel" copper(II) complex, $[Cu_2(CH_3COO)_4(H_2L)_2]$ (**1**), was separated after about 5 min. The two Cu atoms are separated by 2.852 Å and bridged by four bidentate acetate groups with Cu–O distance of 2.012–2.043 Å as calculated by DFT/B3LYP method. As the reflux continues, the reaction mixture was rapidly turned brown, and a polymeric complex, $\{[Cu_2(CH_3COO)_3(H_2O)_2(HL)]\}_n$ (**2**), was separated. In complex **2**, the benzimidazole ligand serves as a bridge between dimeric $Cu_2(CH_3COO)_3(H_2O)_2$ units *via* the benzimidazole moiety. The anionic effect was established by comparing complexes (**1**) and (**2**) with $[Cu(H_2L)_2(OH_2)_2Cl]\cdot Cl$ (**3**). Variable temperature magnetic susceptibility measurements of compound **2** showed occurrence of large anti-ferromagnetic interactions caused by the presence of *syn–syn* conformation of bridged acetate groups in terms of direct interaction, and π–π super exchange pathway of the benzimidazolate moiety.

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1. Introduction

Recently, coordination polymers, created by self assembly of the metal complex, have received considerable attention owing to their diverse potential applications in catalysis, separation, gas storage, and molecular recognition [1], as well as magnetic, and optical materials [2,3]. The carboxylate group is one of the most widely used bridging ligands for designing polynuclear metal complexes with interesting magnetic properties and sometimes surprising molecular architectures [4–6]. Furthermore, the increasing interest in the coordination chemistry of the $RCOO^-$ group is due the catalytic activity of its coordination compounds, and its occurrence in several metalloenzymes [7]. Normally, each of the two oxygen atoms of a bridged carboxylate group is bonded to a different copper atom to form Cu–O–C–O-Cu bridge in one of the *syn-syn*, *syn-anti* or *anti-anti* modes (Fig. 1a). As reported, copper(II) acetate, $Cu_2(CH_3COO)_4\cdot 2H_2O$, (Fig. 1b) can act as a prototype of a rapidly expanding class of polynuclear molecules with metal–metal bonds and especially the "paddle wheel" dimeric unit [8]. Water molecules in the apical positions are usually replaced either by oxygen or nitrogen containing ligands (L), preserving the paddle wheel structure, $Cu_2(CH_3COO)_4\cdot 2L$ [8]. However, the use of donor molecules having bifunctional properties, also allows the extension of the dimer into chain polymers, $\{[Cu_2(CH_3COO)_4(L)]\}_n$ (Fig. 1c). The investigation of the magnetic properties of binuclear and polynuclear compounds in terms of magneto-structural correlation is still a challenging area of research for synthetic inorganic chemists. For example, in the paddle wheel copper complexes, whose structures are ideally suited for a direct Cu–Cu interaction, a weak covalent bond exists and the ground state is a diamagnetic singlet. However, the paramagnetic triplet state is thermally accessible resulting in temperature dependent magnetic moments and antiferromagnetic behavior. Several structural parameters such as Cu···Cu, and Cu–O distances, Cu–C–O angle, nature of the bridge, coordinating ligand, and their steric exchange interaction.

Imidazole is another important bridging ligand that occurs in biological systems and constitutes most of the binding sites of metalloenzymes. In addition, the conjugate base imidazolate ion plays a biologically significant role in constructing an active centre in metalloproteins, such as superoxide dismutase (Cu–Zn–SOD) [9], which catalyses the disproportionation of the harmful superoxide radical anion. Benzimidazole derivatives are also of wide interest because of their diverse biological activity and clinical applications such as anti-helmintic [10], antitumor [11], and antimicrobial [12]. Besides, benzimidazoles were used in liquid crystals [13], OLED's [14], switch's devices [15], DNA intercalator [11] and corrosion inhibitors [16]. Moreover, benzimidazoles can act as monodentate ligands *via* the pyridine-type nitrogen [17–19] or as bridges forming polynuclear complexes [20] of intriguing structural research applications.

Although the benzimidazole scaffold is a useful structural motif for displaying chemical functionality in biologically active molecules and industrial applications, their derivatives were rarely

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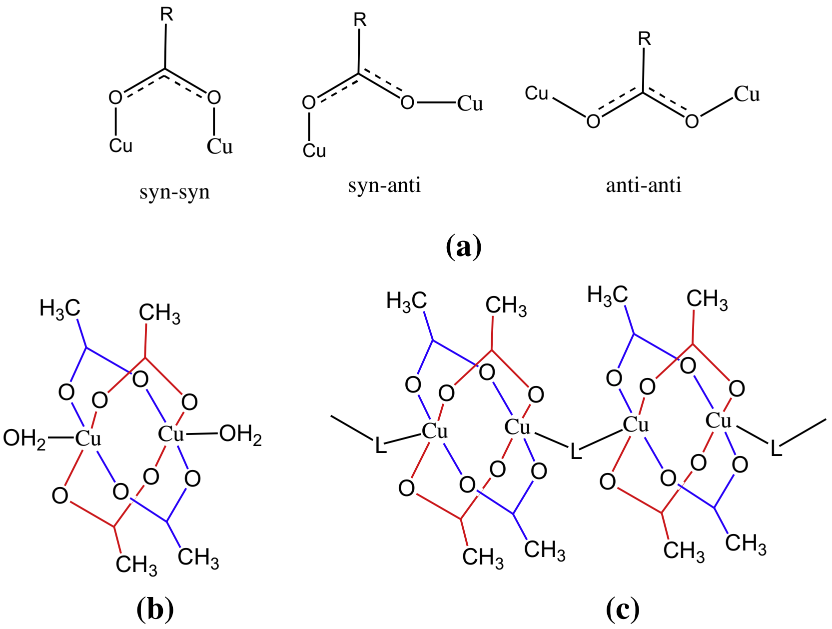

Fig. 1. (a) Different coordination conformations of the bridging carboxylate group, (b) Paddle-wheel copper(II) acetate structure, and (c) Polymeric copper(II) acetate complex bridged by bifunctional ligand (L) and acetate groups.

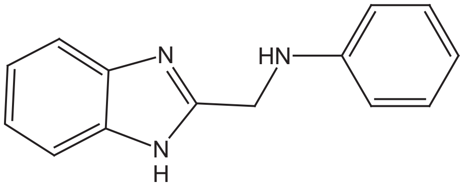

Fig. 2. Structure of ligand H_2L utilized in this work.

explored in regarding of binuclear and polymeric copper(II) acetate complexes, especially those closely related to the proposed complexes [21]. In the present study, synthesis, spectroscopic characterization, and magnetic studies of $[Cu_2(CH_3COO)_4(H_2L)_2]$ (**1**), $\{[Cu_2(CH_3COO)_3(H_2O)_2(HL)]\}_n$ (**2**), and $[Cu(H_2L)_2(OH_2)_2Cl]\cdot Cl$ (**3**) complexes of (1H-benzimidazol-2-ylmethyl)-N-phenyl amine (**H_2L**) (Fig. 2) are reported both experimentally, and theoretically. In addition, it is essential to explore what happens for the magnetic properties when the two paramagnetic Cu^{II} atoms are bridged by two different groups, namely benzimidazolate and acetate. The two bridges may either enforce or cancel their magnetic effects.

2. Experimental

2.1. Synthesis and characterization

The proposed benzimidazole **H_2L** was synthesized as previously described [22]. Complex **1** was prepared by adding a solid $Cu_2(CH_3COO)_4\cdot 2H_2O$ (200 mg, 0.5 mmol) to a hot methanolic solution of **H_2L** (223 mg, 1 mmol), where a green precipitate was isolated after 5 min. by washing several times with methanol/water mixture. Complex **2** was prepared on the same manner as compound **1**, where it was quantitatively separated after 30 min. The low molar conductance value (4.32 $\Omega^{-1}cm^2\ mole^{-1}$) of compound **1** ($10^{-3}$ M, DMF) indicates its non-electrolytic nature, while complex **2** is found to be insoluble in most common solvents such as DMSO and DMF, indicating its polymeric nature. Complex **3** was synthesized by refluxing **H_2L** (223 mg, 1 mmol) with $CuCl_2\cdot 2H_2O$ (85 mg, 0.5 mmol) together in methanol (30 mL) for 4 h, where the complex was precipitated as a dirty green solid. High conductance value (78.30 $\Omega^{-1}cm^2\ mole^{-1}$) of complex **3** reveals its 1:1 ionic character [23]. The observed and calculated elemental analysis percentages for (**1**) C, 53.44 (53.39); H, 4.69 (4.73); Cu, 15.55 (15.69); N, 10.30 (10.38); (**2**) C, 42.58 (42.70); H, 4.42 (4.48); Cu, 22.46 (22.59); N, 7.41 (7.47); (**3**) C, 54.43 (54.50); H, 4.84 (4.90); Cu, 10.25 (10.30); N, 13.53 (13.62).

2.2. Physical measurements

FT IR spectra were recorded as potassium bromide pellets using a Jasco FTIR 460 plus in the range of 4000 to 200 cm^{-1}. EIMS were recorded at 70 eV using SHIMADZU QP-2010 plus. UV–Vis spectra were scanned on a Shimdazu Lambda 4B spectrophotometer. X-band EPR measurements were performed on solid samples at 298 K using a Bruker EMX spectrometer. The magnetic modulation frequency was 100 kHz and the microwave power was set to 0.201 mW. The g-values were obtained by referencing to a diphenylpicrylhyrdazyl (DPPH) sample with $g = 2.0036$. The modulation amplitude was suited at 4 Gauss, while the microwave frequency was determined as 9.775 GHz. Elemental microanalysis was performed using Elementer Vario EL III. TG/DTA analysis was performed in a dinitrogen atmosphere (20 mL min^{-1}) in a platinum crucible with a heating rate of 10 °C min^{-1} using a Shimadzu DTG-60H simultaneous DTG/TG apparatus. A digital Jenway 4330 conductivity/pH meter with a cell constant of 1.02 was used for the pH and molar conductance measurements. DC magnetic measurements of samples **1** and **2** were performed by LakeShore 7410 in 77–298 K temperature range at a magnetic field H = 2 kG. Magnetic measurement of compound **3** was carried out on a Sherwood scientific magnetic balance using Gouy method [12]. Diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)4] was used as a calibrant.

2.3. Computational details

Geometry optimization of complex **1** was carried out without any symmetry restriction in the singlet state, whereas doublet state was assigned to compound **3**. All calculations were carried

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