Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Stabilisation of true π-electron–π-electron interactions in an inorganic cocrystal

Nirmal K. Shee [a], Jnan P. Naskar [b], Michael G.B. Drew [c], Nuria Aliaga-Alcalde [d], Dipankar Datta [a,*]

[a] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India
[b] Department of Chemistry, Jadavpur University, Calcutta 700 032, India
[c] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK
[d] Institut de Ciència de Materials, Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

ABSTRACT

Using the 1:2 condensate of hydrazine and 4-methylimidazole-5-carboxaldehyde as an N-donor ligand (L), two green copper(II) dinuclear complexes $[Cu_2L_4](PF_6)_4 \cdot 2H_2O$ (**1**) and $[Cu_2L_3](NO_3)_4 \cdot H_2O$ (**2**) are synthesised. In the X-ray crystal structures, both the compounds contain the centrosymmetric cation $[Cu_2L_3]^{4+}$ where the metal is pentaco-ordinated with a square pyramidal geometry. The solid state X-band EPR at 4 K is axial with $g_{||}$ = 2.20 and $g_\perp$ = 2.06 for **1**, and, $g_{||}$ = 2.19 and $g_\perp$ = 2.05 for **2**, indicating a $d_{x^2-y^2}$ ground state. Variable temperature (2–300 K) magnetic susceptibility measurements on **1** reveal that the exchange coupling constant between the two copper(II) centres is negligible. In **1**, the cation is sandwiched between two unco-ordinated ligands. The free ligand stacks at distances of ∼3.6 Å more or less parallel to the co-ordinated ligand, with several interatomic distances less than 3.50 Å indicating π–π stacking. Currently, by π–π stacking, interactions between solely arenes are implicated. But here is a case of hetero-olefin–hetero-olefin interactions. Thus complex **1** represents interactions among π electrons in the true sense. These observations are backed by DFT calculations, which show that the stacking energy is −19.5 kcal mol^{-1} in the gas phase. The DFT calculations also indicate that the observed stacking in **1** is not a result of tolerated short contacts. Since this stacking does not occur in **2**, the counter anions seem to play a definite role in the formation of the cocrystal obtained in **1**.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

A cocrystal is a crystalline conglomerate of at least two different molecules [1,2]. The components individually may not be crystalline but become so in presence of other component(s). Water is not crystalline at room temperature but as a solvate it may be found in a crystal. A case in point is anhydrous Na_2SO_4, which takes up water to yield crystals. The properties/structures of the individual components may change upon formation of a cocrystal. For example, iodine vapourises at room temperature but becomes thermally stable up to 100 °C in a cocrystal with Ru(2,2′-bipyridine)$_2$Cl$_2$ [3]. Ferrocenyl groups in some molecules adopt the high energy eclipsed configuration upon cocrystallisation [4]. Even the property of the conglomerate may be different from those of the constituent molecules. For example, neither urea [5] nor KCl is hygroscopic under ordinary conditions, but the cocrystal of KCl and urea is hygroscopic [6].

Cocrystals are known from at least the late 19th century [7]. But only in the last two decades they have assumed great importance because of the scope they offer to obtain a variety of materials for myriad applications. They are having a tremendous impact in non-linear optics [8], organo-electrics [9] and ferroelectrics [10]. Pharmaceutical co-crystals provide a new path to improved medicines [11–13].

H-bonding or other weak intermolecular forces like π–π stacking bind the components in a cocrystal. Herein we report for the first time stacking of hetero-olefins stabilised in a cocrystal of a dinuclear copper(II) complex with an unco-ordinated bare ligand.

2. Results and discussion

The ligand (L) employed here is 1,2-bis((4-methyl-1H-imidazol-5-yl)methylene)-hydrazine, the 1:2 condensate of hydrazine and 4-methylimidazole-5-carboxaldehyde. Its synthesis, X-ray crystal structure and annular tautomerism has been described earlier [14]. The 1:2 Schiff bases of hydrazine are known to be versatile ligands for copper(II) [15,16]. Reaction of L with copper(II)acetate
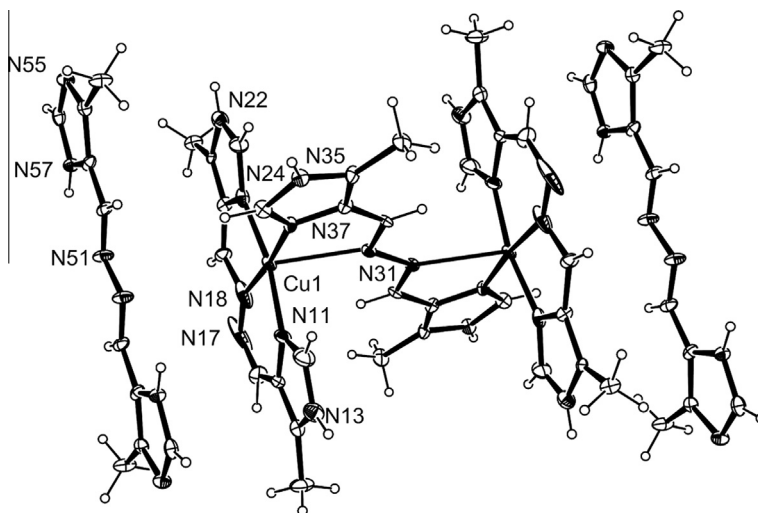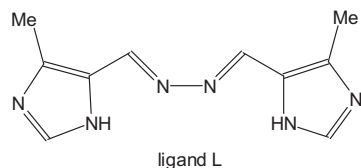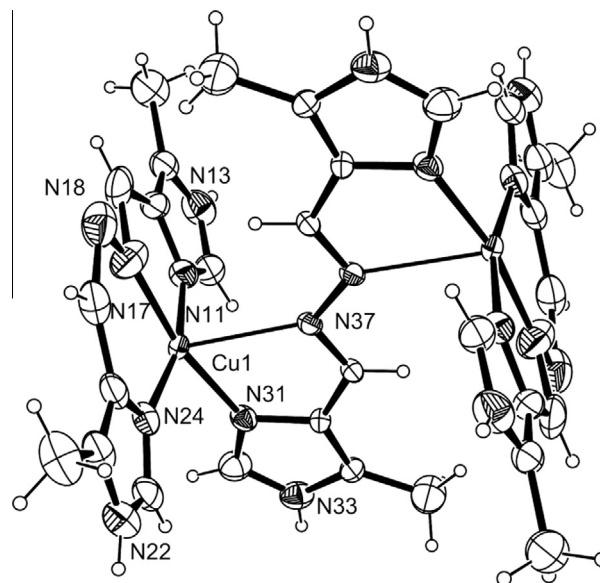

Fig. 1. The centrosymmetric structure of **1** with ellipsoids at 25% probability. Selected bond distances (Å) and angles (°): Cu(1)–N(11) 1.945(10), Cu(1)–N(24) 1.971(10), Cu(1)–N(37) 2.002(8), Cu(1)–N(18) 2.066(11), Cu(1)–N(31) 2.488(9), N(11)–Cu(1)–N(24) 168.7(4), N(11)–Cu(1)–N(37) 94.5(4), N(24)–Cu(1)–N(37) 93.5(3), N(11)–Cu(1)–N(18) 90.8(5), N(24)–Cu(1)–N(18) 80.9(5), N(37)–Cu(1)–N(18) 174.2(5), N(11)–Cu(1)–N(31) 88.6(3), N(24)–Cu(1)–N(31) 101.2(3), N(37)–Cu(1)–N(31) 75.6(3), N(18)–Cu(1)–N(31) 107.1(4).

monohydrate in 2:1 molar proportion in methanol at room temperature and subsequent addition of stoichiometric amount of NH_4PF_6 gives shining green crystals of $[CuL_2](PF_6)_2 \cdot H_2O$ (**1**). When L is reacted with $Cu(NO_3)_2 \cdot 3H_2O$, the resulting complex is green $[Cu_2L_3](NO_3)_4 \cdot H_2O$ (**2**). The X-ray crystal structures of both the complexes have been determined. It is found that in both the copper(II) complexes the 1,3-tautomer of the ligand binds to the metal.

ligand L

The structure of **1** contains centrosymmetric dinuclear units of $[Cu_2L_3]^{4+}$ together with unco-ordinated centrosymmetric L and PF_6^- anions. The cation is sandwiched between two unco-ordinated ligands as shown in Fig. 1. In the dimer the copper atoms have a slightly distorted square pyramidal five-co-ordinate environment as evidenced by the angular structural parameter τ defined by Addison et al. [17] which is 0.09 (for an ideal square pyramid, $\tau = 0$ and for an ideal trigonal bipyramid, $\tau = 1$). Each copper atom is bonded to three nitrogen atoms of one ligand [N(11) at 1.945(10) Å, N(18) at 2.066(11) Å and N(24) at 1.971(10) Å] in the equatorial plane together with two nitrogen atoms of the bridging ligand; N(37) in an equatorial site at 2.002(8) Å and N(31) at 2.488(9) Å in an axial position at a much longer distance. Thus one ligand is tridentate to one metal, while the bridging ligand is tetradentate, with pairs of two nitrogen atoms bound to two copper atoms. The tridentate ligand adopts a cis conformation with both five-membered rings on the same side of the C–N–N–C acyclic chain, while the bridging ligands are in the trans conformation which is also observed in the free ligand in **1**. As is apparent from Fig. 1, N(51) is in an approximately axial position to Cu(1) but at a distance of 3.666(16) Å which precludes any significant interaction. The positions of the hydrogen atoms on the nitrogen atoms are easily identified in the ligand that are bound to the metal. However for the centrosymmetric unco-ordinated ligand, the hydrogen atom can be positioned on either

N(55) or N(57). A difference Fourier map indicated that the hydrogen atom was bound to N(57) and this was confirmed by test refinements of the two possible positions. There is a close contact between N(22) and N(57)$(x, 1.5 - y, z - 0.5)$ of 3.014 Å, which is consistent with the placement of the hydrogen atom on N(57) as N(22) will be the hydrogen donor and N(57) the acceptor. This assignment of the hydrogen atom is consistent with the lowest

Fig. 2. The structure of the one centrosymmetric dinuclear cation in **2** with ellipsoids at 30% probability. The second cation, also centrosymmetric, has a similar structure. Selected bond distances (Å) and angles (°) are given here. Molecule 1: Cu(1)–N(24) 1.977(9), Cu(1)–N(11) 1.944(11), Cu(1)–N(31) 2.020(9), Cu(1)–N(17) 2.044(14), Cu(1)–N(37) 2.530(7), N(24)–Cu(1)–N(11) 165.2(4), N(24)–Cu(1)–N(31) 96.3(4), N(11)–Cu(1)–N(31) 94.4(4), N(24)–Cu(1)–N(17) 90.4(6), N(11)–Cu(1)–N(17) 80.6(6), N(31)–Cu(1)–N(17) 169.5(4), N(24)–Cu(1)–N(37) 95.0(4), N(11)–Cu(1)–N(37) 97.5(4), N(31)–Cu(1)–N(37) 75.9(4), N(17)–Cu(1)–N(37) 95.5(4). Molecule 2: Cu(2)–N(51) 1.985(9), Cu(2)–N(71) 2.008(8), Cu(2)–N(64) 2.009(8), Cu(2)–N(57) 2.083(12), Cu(2)–N(77) 2.583(8), N(51)–Cu(2)–N(71) 95.6(4), N(51)–Cu(2)–N(64) 165.9(4), N(71)–Cu(2)–N(64) 94.7(4), N(51)–Cu(2)–N(57) 79.6(4), N(71)–Cu(2)–N(57) 171.8(5), N(64)–Cu(2)–N(57) 91.2(5), N(64)–Cu(2)–N(77) 95.3(5), N(51)–Cu(2)–N(77) 96.7(5), N(71)–Cu(2)–N(77) 75.0(5), N(57)–Cu(2)–N(77) 98.8(3).