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Inorganic Chemistry Communications 8 (2005) 235–238
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

Ferromagnetic exchange in μ-alkoxo-μ-dicarboxylato double bridged tetranuclear copper(II) complexes: $[Cu_4(L\text{-}X)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (L = 1,3-bis(5-X-salicylideneamino)-2-propanol, X = Br, Cl)

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Received 9 September 2004; accepted 29 November 2004
Available online 5 January 2005

Abstract

Two new μ-alkoxo-μ-dicarboxylato double bridged tetranuclear copper(II) complexes $[Cu_4(L\text{-}Br)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (**1**) and $[Cu_4(L\text{-}Cl)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (**2**) (H_3L-Br = 1,3-bis(5-bromo-salicylideneamino)-2-propanol; H_3L-Cl = 1,3-bis(5-chloro-salicylideneamino)-2-propanol; dmf = *N,N*-dimethylformamide) have been prepared and structurally characterized. Temperature dependence of magnetic susceptibility measurements show a ferromagnetic coupling between two copper(II) ions in complex **1** with $J = 54$ cm^{-1}, and in **2** with $J = 56$ cm^{-1}.

Keywords: μ-alkoxo-μ-dicarboxylato double bridges; Tetranuclear copper(II) complex; Crystal structure; Magnetic property

To predict the sign and magnitude of magnetic exchange integrals as functional parameters and vice versa as well as the design of new exchange-coupled systems are some of the major challenges in magnetochemistry [1–9]. Heterobridged ligands, μ-hydroxo/alkoxo-μ-X and [10–19] ($X = N_3^-, NO_2^-$, pyrazolate, carboxylate, etc.) and their metallic compounds can be considered as a special class of exchange-coupled systems where the magnetic properties are more dependent on the second bridging ligand (X); e.g., they are strongly antiferromagnetic for $X = N_3^-$, moderately antiferromagnetic for $X = NO_2^-$, weakly to strongly antiferromagnetic for X = pyrazolate and weakly antiferromagnetic to weakly ferromagnetic for $X = RCO_2^-$. Evidently, most of the μ-hydroxo/alkoxo-μ-X systems, exception of $X = RCO_2^-$, are antiferromagnetically coupled, in which their structural feature shown that the dihedral angles between two coordination planes of copper(II) ions are nearly planar.

The structures and magnetism of binuclear Cu(II) complexes with both μ-alkoxo-μ-carboxylato/μ-halogens bridges have been system studied to reveal the orbital counter-complementary effect [17,20–23]. These Cu(II) complexes are usually antiferromagnetic with the Cu–O–Cu angle greater than 130°. However, the antiferromagnetic interaction is suppressed to present ferromagnetic coupling by the so-called roof-shaped distortion [10,12,17,20–24], which is measured by the dihedral angle (δ) between two copper coordination planes.

Recently, we have reported two new ferromagnetic coupled ($2J = 33.4$ and 52 cm^{-1}) μ-alkoxo-μ-7-azaindolato double bridged dicopper(II) complexes which also show a roof-shaped coordination site of two copper(II) coordination planes with dihedral angle of 112.8° and 118.6° [24]. In order to develop new types of μ-alkoxo-μ-dicarboxylato heterobridged tetranuclear copper(II)

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doi:10.1016/j.inoche.2004.11.031

complexes, we have used dicarboxylato as the second bridging ligand and isolate two tetracopper(II) complexes, $[Cu_4(L\text{-}Br)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (**1**) and $[Cu_4(L\text{-}Cl)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (**2**) (H_3L-Br = 1,3-bis (3-bromo-salicylideneamino)-2-propanol; H_3L-Cl = 1,3-bis(3-chloro-salicylideneamino)-2-propanol). We have been particularly interested to use dicarboxylato as a double bridging moiety because it was anticipated that its introduction will induce considerable twist in the complex molecules to bring about significant change in their magnetic exchange interactions.

The ligands H_3L-Br and H_3L-Cl were isolated as yellow crystalline compounds through the condensation of 1,3-diamino-2-propanol with 5-bromosalicylaldehyde and 5-chlorosalicylaldehyde, respectively. Complexes **1** and **2** were obtained [1] by reacting H_3L-Br or H_3L-Cl with $Cu(ClO_4)_2 \cdot 6H_2O$ (*Caution*: Perchlorate salts are potentially explosive and should only be handled in small quantities), fumaric acid, and triethylamine. The X-ray crystal structures [2] of the two complexes are found to be similar. The structure of **1** (Fig. 1) shows that the two bimetal centers are central symmetry doubly bridged by the alkoxo oxygen and dicarboxylato oxygen atoms of fumarate anion. Each of the metal centers is coordinated to one imine nitrogen, one alkoxo oxygen (Cu(1)–O(2) 1.927(4) Å and Cu(2)–O(2) 1.925(4) Å), one phenolate oxygen (Cu(1)–O(1) 1.886(5) Å and Cu(2)–O(3) 1.925(4) Å) provided by the $[L\text{-}Br]^{3-}$, and one oxygen atom (Cu(1)–O(5) 1.949(4) Å and Cu(2)–O(4) 1.946(4) Å) from fumarato, essentially to form a four-coordination sphere, in addition, the axial apical position of Cu(2) is occupied by oxygen atom of dmf molecule (Cu(2)–O(6) 2.202(7) Å) thus to form a square-pyramidal symmetry. The deviations of the metal centers (0.132 Å for Cu(1) and 0.001 Å for Cu(2)) from the coordination planes and also the range of the *cisoid* (85.3(2)–94.4(2)° for Cu(1) and 84.7(2)–93.5(2)° for Cu(2)) and *transoid* (177.7(2)° and 178.2(2)° for Cu(1), and 162.7(2)–177.2(2)° for Cu(2)) angles indicate that the basal coordination geometry of the metal ions can be approximated as square planar. It should be noted that the bridging moiety in **1** is appreciably twisted forming roof-type of two copper(II) coordination planes; the dihedral angle (δ) between the best coordination planes is 107.63(7)° (δ = 180° for coplanarity). The twisting is further indicated by the smaller Cu(2)–O(2)–Cu(1) bridge angle (107.6(2)°) and the shorter Cu(1)···Cu(2) separation (3.109(3) Å).

The crystal structure of **2** is essentially similar to that of **1** and having structural parameters that are almost the same. As in **1**, the bridging moieties significantly twisted are reflected by the dihedral angles of 107.78(6)° between the two coordination planes. The

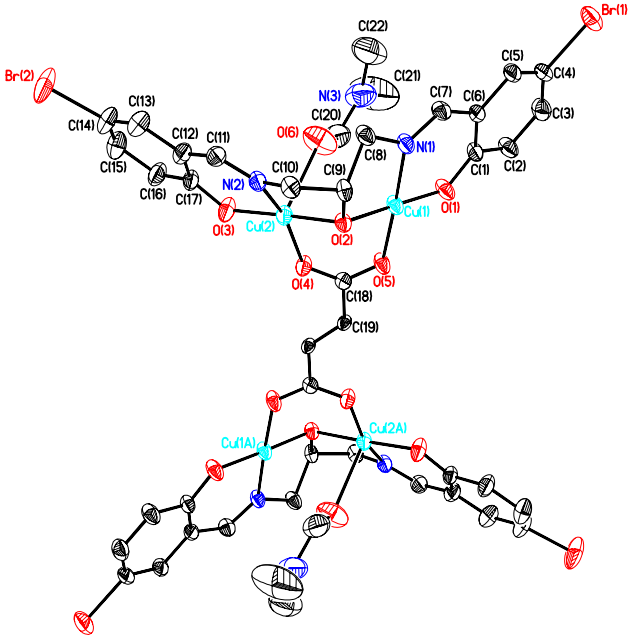

Fig. 1. ORTEP representation (50% thermal ellipsoids) of **1** with atom level schemes. Selected bond distances (Å): Cu(1)–O(1) 1.886(5), Cu(1)–N(1) 1.920(5), Cu(1)–O(2) 1.927(4), Cu(1)–O(5) 1.949(4), Cu(2)–O(3) 1.885(4), Cu(2)–O(2) 1.925(4), Cu(2)–N(2) 1.931(6), Cu(2)–O(4) 1.946(4), Cu(2)–O(6) 2.456(4) Å. Selected bond angles (°): O(1)–Cu(1)–N(1) 94.4(2), O(1)–Cu(1)–O(2) 178.2(2), N(1)–Cu(1)–O(2) 85.3(2), O(1)–Cu(1)–O(5) 86.96(18), N(1)–Cu(1)–O(5) 177.7(2), O(2)–Cu(1)–O(5) 93.35(18), O(3)–Cu(2)–O(2) 177.2(2), O(3)–Cu(2)–N(2) 93.5(2), O(2)–Cu(2)–N(2) 84.7(2), O(3)–Cu(2)–O(4) 87.62(19), O(2)–Cu(2)–O(4) 93.43(18), N(2)–Cu(2)–O(4) 162.7(2).

[1] To a stirred methanol solution (60 ml) containing H_3L-Br (0.456 g, 1 mmol), (H_3L-Br = 1,3-bis(5-bromo-salicylideneamino)-2-propanol), fumaric acid (0.66 g, 0.5 mmol), and triethylamine (0.52 g, 5 mmol), was dropwise added methanol solution (20 ml) of copper(II) perchlorate hexahydrate (0.74 g, 2 mmol). After a few minutes, a greenish precipitate was appeared. The stirring was continued for 30 min and the filtrate was concentrated in a rotary evaporator to ~15 ml. Recrystallization from a dimethyl-formamide (dmf)–methanol mixture afforded the green crystalline compound, $[Cu_4(L\text{-}Br)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (**1**). Yield: 89%. Anal. Calcd. for $C_{44}H_{42}Br_4Cu_4N_6O_{12}$: C, 37.20; H, 2.98; N, 5.92; Br, 22.50; Cu, 17.89%. Found: C, 37.08; H, 2.92; N, 5.79; Br, 22. 35; Cu, 18.05%. Single crystals of **1** were prepared by diffusion a methanol into a dmf solution of the green crystalline compound. The compound $[Cu_4(L\text{-}Cl)_2(\mu\text{-}C_4H_4O_4)(dmf)_2]$ (**2**) was synthesized following the similar method as described for **1**, except using H_3L-Cl, H_3L-Cl = 1,3-bis(3-chloro-salicylideneamino)-2-propanol), instead of H_3L-Br. Yield: 86%. Anal. Calcd. for $C_{44}H_{42}Cl_4Cu_4N_6O_{12}$: C, 42.52; H, 3.41; N, 6.76; Cl, 11.41; Cu, 20.45%. Found: C, 42.48; H, 3.52; N, 6.79; Cl, 11.36; Cu, 20.25%.

[2] Crystal data determinate at 293 K for **1**: $C_{44}H_{42}Br_4Cu_4N_6O_{12}$, $M = 1420.66$ monoclinic, space group $P2_1/n$, $a = 14.3109(9)$ Å, $b = 13.1137(8)$ Å, $c = 14.9312(10)$ Å, $\beta = 110.714(4)°$, $V = 2602.3(3)$ Å^3, $Z = 4$, $D_c = 1.813$ (g cm^{-3}), R_1 ($I > 2\sigma(I)$, 4606 unique reflections) = 0.0613, $wR_2 = 0.0983$. Crystallographic data for **2**: $C_{44}H_{42}Cl_4Cu_4N_6O_{12}$, $M = 1242.85$, monoclinic, space group $P2_1/n$, $a = 14.033(3)$ Å, $b = 13.078(3)$ Å, $c = 14.738(3)$ Å, $\beta = 111.769(1)$, $V = 2530.0(8)$ Å^3, $Z = 4$, $D_c = 1.631$ (g cm^{-3}), $R_1(I > 2\sigma I)$, 6265 unique reflections) = 0.0527 and $wR_2 = 0.1011$. Data were collected on a Siemens Smart CCD diffractometer for both compounds. The structure was solved by direct and Fourier methods, and refined by full-matrix least-squares on F^2 using SHELXL-93 (G.M. Shelderick, University of Gottingen, 1993). All non-hydrogen atoms were readily located and refined anisotropic thermal parameters.