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New Dimeric Copper(II) Complex $[Cu(5\text{-}MeOsal)_2(\mu\text{-}nia)(H_2O)]_2$ with Magnetic Exchange Interactions through H-Bonds

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The synthesis and characterization (elemental analysis, IR, electronic and EPR spectra as well as magnetization measurements over the temperature range 1.8 K–300 K) of solid complex $[Cu(5\text{-}MeOsal)_2(\mu\text{-}nia)(H_2O)]_2$ (**1**; 5-MeOsal = 5-methoxysalicylate, nia = nicotinamide) is reported together with the crystal structure. In blue–green complex **1**, two $Cu(5\text{-}MeOsal)_2(H_2O)$ units are held together by a pair of bidentate nonchelating nicotinamide ligands, which form a $(CuNC_3O)_2$ ring. Each Cu atom adopts a distorted square-pyramidal geometry. The oxygen atoms from two unidentate 5-MeOsal anions occupy the *trans* position, a water molecule and the pyridine N atom of nicotinamide build the basal plane and a carboxamide O atom occupies the apical position. The separation between two Cu atoms within the centrosymmetric dimer is 6.940(2) Å. The dimeric units are self-assembled across a centre of symmetry by the formation of two pairs of strong hydrogen bonds, which create a one-dimensional polymeric structure with the interdimer Cu···Cu separation 4.901(2) Å. It is believed that these hydrogen bonds between the copper(II) atoms are responsible for the unique magnetic properties of compound **1**. The magnetic susceptibility of complex **1** exhibits a maximum at 6 K. A satisfactory explanation was found with the Bleaney–Bowers equation for Cu–Cu interaction through carboxylato groups and H-bond bridges ($2J = -6.83$ cm^{-1}). An additional molecular field correction that was used to characterize the interaction across the nia bridges is assumed to be extremely weak ($zJ' = -0.28$ cm^{-1}).

Introduction

For quite some time, copper complexes with various organic ligands have been a subject of intense study because of their interesting properties which include biomedical activities. Nicotinamide (also known as a niacin derivative or vitamin B_3) is a nitrogen donor ligand that has been used in the treatment of various skin diseases (atopic eczema,[1,2] psoriasis and skin cancer[3–5]), and the biological activity of its copper complexes have also been studied.[6] In addition, the biological activity of different salicylic acid derivatives and their copper(II) complexes is well known.[7–10] Meanwhile, salicylatocopper(II) complexes that contain nicotinamide are rarely studied in spite of their possible structural diversities. There are only two examples (out of 26 known structures)[6,11] of polymeric copper(II) complexes where nicotinamide acts as a bridging ligand – $[Cu_2(CH_3COO)_4(\mu\text{-}nia)]_n$ and $\{[Cu(sacharinato)_2(\mu\text{-}nia)(H_2O)]\cdot H_2O\}_n$.

With the purpose to obtain and study the properties of all possible products that could be prepared by the reactions under study, we report the synthesis, structural characterisation and properties of the unusual dimeric complex $[Cu(5\text{-}MeOsal)_2(\mu\text{-}nia)(H_2O)]_2$ (**1**), which exhibits rare intradimer and/or interdimer interactions that result in magnetic properties that are of interest.

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Results and Discussion

The molecular structure of **1** (Figure 1) consists of dimeric $[Cu(5\text{-}MeOsal)_2(\mu\text{-}nia)(H_2O)]_2$ molecules that are located at a centre of symmetry. Two equivalent $Cu(5\text{-}MeOsal)_2(H_2O)$ moieties are connected by a pair of bidentate nonchelating nicotinamide ligands, which creates a twelve-membered metallocyclic $(CuNC_3O)_2$ ring. Each Cu atom adopts a distorted square-pyramidal geometry with the oxygen atoms of two unidentate 5-MeOsal anions in the *trans* position [Cu–O12 = 1.945(2) Å]. A water molecule [Cu–O1W = 1.989(2) Å] and the pyridine N atom of nicotinamide [Cu–N1 = 2.030(3) Å] build the basal plane; a carboxamide O atom of the bridging nicotinamide assumes the apical position [Cu–O1 = 2.267(2) Å]. The copper atom is displaced from the basal plane towards the carboxamide O atom by 0.047(1) Å. The τ value[12] of 0.066 implies an almost perfect square-pyramidal geometry. The separation between Cu···Cu^{i} ($1-x$, $1-y$, $1-z$) within the dimeric molecule is 6.940(2) Å(Figure 1). The amide H atoms of the apically coordinated carboxamide group are linked to the co-

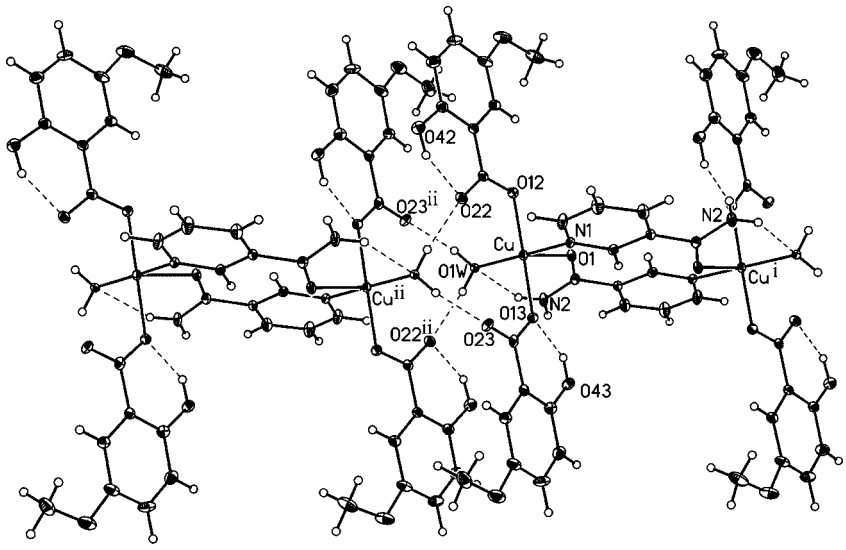

Figure 1. Perspective view of $[Cu(5\text{-}MeOsal)_2(\mu\text{-nia})(H_2O)]_2$, with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Cu–O13 = 1.945(2), Cu–O12 = 1.952(2), Cu–N1 = 2.030(3), Cu–O1W = 1.989(2), Cu–O1 = 2.267(2), O13–Cu–O12 = 177.05(9), O1W–Cu–N1 = 173.09(10), O13–Cu–O1W = 87.35(9), O13–Cu–O1 = 86.67(9), O12–Cu–O1W = 90.27(9), O12–Cu–O1 = 91.73(9), O13–Cu–N1 = 92.14(10), O1W–Cu–O1 = 93.32(9), O12–Cu–N1 = 90.42(10), N1–Cu–O1 = 93.52(9), symmetry codes: (i) $1-x$, $1-y$, $1-z$, (ii) $1-x$, $-y$, $1-z$.

ordinated (in the equatorial position) water O atoms (O1W) by hydrogen bonds N2–H2A···O1W^{i} ($1-x$, $1-y$, $1-z$) with interatomic distances N2···O1W^{i} of 3.129(4) Å. These hydrogen bonds create six-membered metallocyclic rings (CuO_2NCH) and stabilize the molecular structure of the dimeric unit of **1**. The other short intramolecular hydrogen bonds are formed by the salicylato hydroxy H atoms (H43O and H42O) to the carboxylate O atoms (O13 and O22) and create six-membered cyclic rings (O_2C_3H) that stabilize the molecular structure as well.

The unusual dimeric structure of **1** prompted the study of its magnetic properties within the temperature range 1.8–300 K and the measurement of its EPR spectrum. The EPR spectrum (Figure 2) at room temperature is of axial symmetry and simulation of its shape[13] gave $g_{\perp}$ = 2.061 and $g_{\parallel}$ = 2.345 (g_{av} = 2.156). When the temperature is decreased to –196 °C (liquid nitrogen), the spectrum becomes pseudo-isotropic in shape with g = 2.133, and no information concerning the mutual interaction between the paramagnetic centres within the dimer could be drawn from these spectra (Figures 2 and 3).

Magnetization measurements showed that **1** exhibits maximum magnetic susceptibility at 6 K (Figure 3). The magnetic data of the complex were fit with the Bleaney–Bowers equation,[14] to characterize the intradimer interaction,

$$\chi_m = \frac{N\beta^2 g^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}$$

(where N is Avogadro's number, g is the spectroscopic splitting factor, β is the Bohr magneton, k is Boltzmann's con-

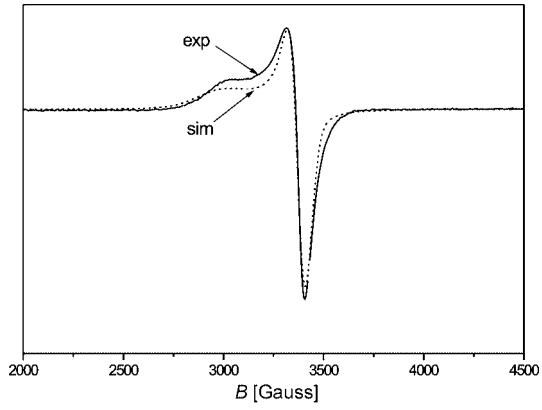

Figure 2. EPR spectrum of **1** at room temperature.

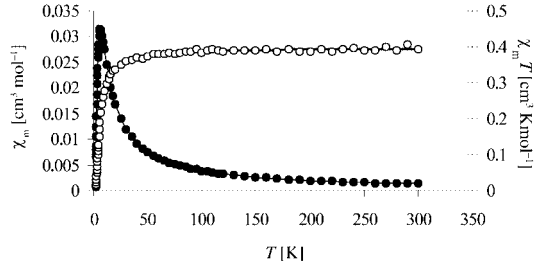

Figure 3. The plot of the χ_m and $\chi_m T$ product versus temperature [χ_m – the molar magnetic susceptibility calculated per one copper(II) centre]. The solid line was generated from the best-fit magnetic parameters.

stant and J is the exchange parameter) together with the application of a molecular field model to the calculation of the present magnetic data of complex **1** to obtain characteristics of interdimer magnetic interactions.[15]

$$\chi_m^{corr} = \frac{\chi_m}{1 - \frac{2zJ'\chi_m}{Ng^2\beta^2}}$$

where χ_m is the molar susceptibility given by the Bleaney–Bowers equation, zJ' is the molecular exchange parameter, z is number of the nearest neighbours and R is the agreement factor defined as

$$R = \sum_{i=1}^{n} \frac{(\chi_i^{exp}T - \chi_i^{calc}T)^2}{(\chi_i^{exp}T)^2}$$

Satisfactory least-squares fit to the experimental results was obtained for g = 2.06, $2J$ = –6.83 cm^{-1}, zJ' = –0.28 cm^{-1}, and R = 9.99·10^{-5}. The small differences between the g values obtained from the least-squares fit procedure and g_{av} from the EPR spectra is often observed and can be attributed to the unresolved axial anisotropy of the EPR spectra and the fact that the g values obtained from the magnetic data are only refined isotropically.[16]

This magnetic behaviour of **1** is surprising because the magnetic centres are bridged by a nicotinamide ligand (the shortest pathway covers a five-atom bridge) which includes the aromatic pyridine ring and the carboxamide side chain. The π-system of the pyridine ring is probably not the actual mode of interaction [the C31–C71 bond length of 1.506(4) Å is much longer than the average bond length of 1.385(4) Å within the pyridine ring]. The pyridine ring and the carboxamide group are not coplanar (ring plane to carboxamide group plane angle is 14.2°); thus, the structural data support the notion that there is no possibility for the π-system to be involved in the magnetic interaction. The σ-bonds involved in the intradimer magnetic interaction by nicotinamide ligands can be ruled out on the basis of our recently published results.[17] The 3-pyridylmethanol bridging ligand shows[17] the same number of σ-bonds and a very weak ferromagnetic interaction (Weiss constant Θ = +1.1 K). Consequently, the model for the magnetic interaction between the Cu^{2+} ions within the dimeric molecule can be ruled out as well, and another interaction that is responsible for the magnetic properties of **1** should be found.

The strongest interdimer interactions are illustrated Figure 1 as a system of O–H···O hydrogen bonds between dimeric units of **1** that create a supramolecular chain of dimers along the b axis with an interdimer copper-to-copper distance [distance Cu···Cu^{ii} (1 – x, –y, 1 – z) of 4.901(2) Å] shorter than the distance Cu···Cu^{i} within the dimeric units. The H atoms of the water molecules are linked to uncoordinated carboxyl O atoms (O12^{ii} and O22^{ii}) of the neighbouring 5-methoxysalicylate anions by hydrogen bonds O1W–H1W···O22^{ii} and O1W–H2W···O23^{ii} (1 – x, –y, 1 – z) with interatomic distances O1W···O22^{ii} of 2.695(3) Å and O1W···O23^{ii} of 2.658(3) Å, respectively. The interdimer interactions could cause magnetic interactions because the pairs of Cu^{2+} ions are, in this case, bridged by four carboxylato groups [similar to "paddle-wheel" copper(II) acetate structures], but one water molecule is inserted into each pair of carboxylato groups (Figure 4). This water molecule insertion into the bis-carboxylato bridge induces a greater distance between the polyhedra basal planes, a greater Cu···Cu distance and a longer path for the magnetic interaction compared with regular carboxylato dimers. This explanation needs further evidence based either on similar structures or the analysis of magnetic orbital interactions to be validated. Both of these topics are currently under investigation in our lab. Data which show that hydrogen bonds could cause antiferromagnetic interactions between copper(II) centres were found in literature,[18–22] but unfortunately most of the examples involve a completely different types of ligand.

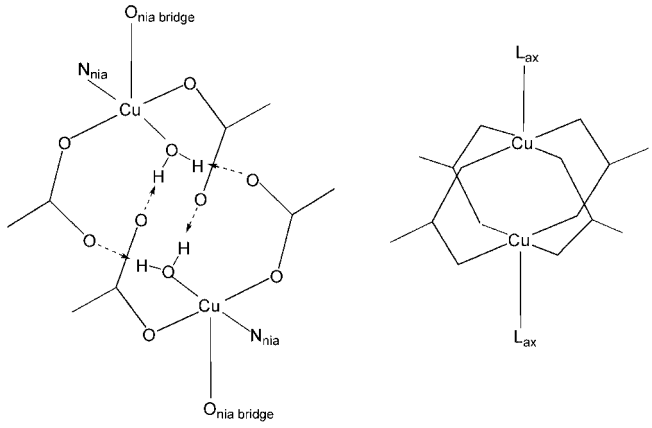

Figure 4. Schematic comparison of interdimer Cu···Cu interactions in **1** and in regular "paddle-wheel" carboxylatocopper(II) structures.

As mentioned above, the crystal structure of **1** can be compared with polymeric complexes[6,11] $[Cu_2(CH_3COO)_4(\mu\text{-nia})]_n$ and $\{[Cu(sacharinato)_2(\mu\text{-nia})(H_2O)]\cdot H_2O\}_n$ where each Cu atom has a square-pyramidal environment. In the former complex, the $Cu_2(CH_3COO)_4$ moieties form dimer units, and in the latter complex, the Cu(sacharinato)$_2$(H_2O) units are connected by bidentate nonchelating nicotinamide ligands by N and O donor sites. The Cu–N (N atom of nia pyridine ring), Cu–O (O atom of carboxamide group of nia ligand) and finally Cu···Cu (neighbouring Cu atoms bridged by nia ligands) distances are 2.002, 2.315 and 7.547 Å, respectively, for $[Cu_2(CH_3COO)_4(\mu\text{-nia})]_n$, 2.158, 2.146 and 7.056 Å, respectively, for $\{[Cu(sacharinato)_2(\mu\text{-nia})(H_2O)]\cdot H_2O\}_n$ and 2.030(3), 2.268(2) and 6.939(2) Å, respectively, for complex **1**. The shorter Cu···Cu separation could be explained by a pair of nia bridging ligands and probably by additional hydrogen bond interaction with N–H···O (see above).

In $[CuCl_2(\mu\text{-denia})(denia)]_2$,[23] where a pair of denia ligands also serve as a bridge between two equivalent $CuCl_2$(denia) moieties, the Cu···Cu separation is about 0.762 Å longer than that found in **1**. The Cu–N (N atom of the pyridine ring of the bridging *N*,*N*-diethylnicotinamide molecule) of 2.012(3) Å compares well with the bond length Cu–N1 of complex $[Cu(5\text{-MeOsal})_2(\mu\text{-nia})(H_2O)]_2$, but Cu–

O (O atom from amide group of bridging *N*,*N*-diethylnicotinamide molecule) of 2.475(2) Å is about 0.207 Å longer than that found in **1**. These complexes, however, were not magnetically characterized.

Conclusions

In conclusion, we have prepared and characterized a novel dimeric molecular complex that contains nicotinamide as a bridging ligand. These dimers are linked into a chain structure by strong hydrogen bonds that give interdimer copper-to-copper distances that are shorter than those found in intradimers. The nature of the bridging ligands (four carboxylic groups of salicylato anions) that are involved in the formation of the interdimer hydrogen bonds are probably the reason for the unusual magnetic behaviour of this dimeric substance.

Experimental Section

Materials: All used chemicals were of analytical grade (Aldrich, or Sigma) and used without further purification.

Physical Measurements: Carbon, hydrogen and nitrogen elemental analyses were carried out with a CHNSO FlashEA 1112 (Thermo-Finnigan) elemental analyzer. The copper content of the complex was determined by the electrolysis of a water solution obtained by the mineralization of the sample in a mixture of sulfuric acid and potassium peroxodisulfate. Infrared spectra were measured with a Nicolet MAGNA 750 IR spectrometer with both KBr pellet and nujol suspension techniques for the 4000–400 cm^{-1} region and a polyethylene pellet for the 400–100 cm^{-1} region. Electronic spectra (190–1100 nm) of the complexes were measured in Nujol suspensions with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer. Magnetization measurements in the temperature range of 1.8–300 K were carried out on powdered samples of the complexes with a magnetic field strength of 0.5 T and with a Quantum Design SQUID Magnetometer (type MPMS-XL5). Corrections for the diamagnetism of the constituting atoms were calculated with Pascal constants,[24] the value of $60 \cdot 10^{-6}$ $cm^3 mol^{-1}$ was used as the temperature-independent paramagnetism of the copper(II) ion. EPR spectra of the powdered samples were recorded at room temperature with a spectrometer Bruker ESP 300 operating at X-band equipped with an ER 035M Bruker NMR gaussmeter and a HP 5350B Hewlett Packard microwave frequency counter.

Synthesis of 1: Nicotinamide (122 mg, 1.0 mmol) was added to an ethanol solution (30 mL) of copper(II) acetate (200 mg, 1 mmol) while stirring. After several minutes, 5-methoxysalicylic acid (336 mg, 2 mmol) was added to the dark blue solution. The reaction mixture was stirred for a few days at ambient temperature. The blue–green powder product which precipitated from the solution was filtered off (150 mg, 56%), and the mother liquid was left to crystallize at ambient temperature. The dark blue–green crystals were separated and dried at ambient temperature. $C_{44}H_{44}Cu_2N_4O_{20}$ (1075.93): calcd C 49.03, H 4.30, Cu 11.79, N 5.19; found C 48.63, H 4.21, Cu 12.19, N 5.49. IR (KBr): $\tilde{\nu}$ = 1635 $\nu_{as}(COO^-)$, 1432 $\nu_s(COO^-)$ cm^{-1}. ES (Nujol): 244 (CT band), 323 (CT band), 671 (*d*←*d* band) nm.

X-ray Structural Studies: Data collection and cell refinement of complex **1** were carried out with a Kuma KM4-CCD difractometer with graphite monochromated Mo *Kα* radiation and the use of the *CrysAlis* software package.[25] Intensity data were corrected for Lorenz and polarization factors; absorption correction was applied as well. The structures of the complexes were solved by direct methods with *SHELXS-97*[26] and refined by the full-matrix least-squares procedure with *SHELXL-97*. Geometrical analyses were performed with *SHELXL-97*.[27] The structures were drawn with *XP* in *SHELXTL*.[28] Crystallographic data for $C_{44}H_{44}Cu_2N_4O_{20}$ (**1**): M_r = 1075.93, dark green plate, 0.09 × 0.20 × 0.20 mm, monoclinic, *C*2/*c*, *a* = 21.805 (6), *b* = 11.735 (3), *c* = 17.585 (5) Å, *β* = 104.72 (3)°, *V* = 4352 (2) $Å^3$, *Z* = 4, D_c = 1.642 $Mg \cdot m^{-3}$, μ = 1.07 mm^{-1}, *F*(000) = 2216, *T* = 100(2) K. Of the 15711 reflections, 5122 were unique (R_{int} = 0.066), 3248 observed [$F_2 > 2.0\sigma(F^2)$], which refined to *R* = 0.058, *wR* = 0.091.

CCDC-603094 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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