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Structural, magnetic and optical properties of two concomitant molecular crystals

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ARTICLE INFO

ABSTRACT

A new 1D complex has been prepared and characterized. X-ray single crystal structure confirms that the Cu(II) ions assemble in alternating chains with Cu … Cu distances of 2.5685(4) and 3.1760(4) Å. The temperature dependence of the magnetic susceptibility reveals an antiferromagnetic interaction between the paddle-wheel copper centers with an exchange of -300 cm^{-1}. The exchange integral was also determined by quantum chemical ab-initio calculations, using polarised and unpolarised basis sets reproducing well the experimental value. The second harmonic generation efficiency of a concomitantly crystallized material was evaluated and was found to be comparable to urea.

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1. Introduction

Zero and one-dimensional magnetism have attracted the attention of both solid state physicists and chemists. For the physicists, low dimensional magnetism offers the advantage of simplicity, providing systems where to test models that cannot be solved at higher dimensions. For chemists, it is an opportunity to design and control the synthesis of novel low-dimensional materials.

Back in 1976, Hatfield and Hodgson [1] found a linear correlation between the experimentally determined exchange coupling constant (2J) and the Cu—O—Cu bond angle in hydroxo-bridged Cu(II) dimers. Such magneto—structural correlation that was later on computationally studied by Ruiz et al. [2], who elucidated the role of the terminal ligands and of the counterions.

More recently, a Cu(II) chain was used by Mourigal et al. to confirm the existence of higher order spinon states in this simple quantum many-body system [3]. The existence of such higher order excitations had been theoretically predicted and could be confirmed using inelastic neutron scattering data. Moreover, Brukner et al. [4] showed the crucial role of quantum entanglement in bulk properties of solids by studying the structural and magnetic properties of an alternating one-dimensional antiferromagnetic Heisenberg spin chain. It is thought that quantum entanglement may allow for powerful communication and for computational tasks that are not classically possible.

Nevertheless, the primeval effect of the ligands on the nature and strength of the magnetic interaction within a chain is still under research. For instance, the group of Prof. Julve in Valencia (Spain) has been focussing in the magnetochemistry of copper(II) chain compounds: in last two decades, they have synthesized uniform and alternating chains, some of them with alternating antiferro/ferromagnetic interactions and, in some cases, they could account for the magnetic interaction with simple orbital analysis [5–33].

In this paper we describe the synthesis of a nitrophenylacetato bridged Cu(II) compound and report its structure and magnetic properties. An accurate evaluation of the exchange coupling

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between the two copper centers, calculated by *ab-initio* methods, is also presented. We also report the structure and non-linear optical properties of a concomitant organic crystal.

2. Experimental

2.1. Synthesis of catena-(bis(μ_3-4-nitrophenylacetato-O,O,O')-(bis(μ_2-4-nitrophenylacetato-O,O')-dicopper(II) and methyl 2-(4-nitrophenyl)acetate

0.362 g of 4-nitrophenylacetic acid (CAS No. 104-03-0, 99%, Sigma−Aldrich) were added to 0.170 g of copper(II) chloride dihydrate (CAS No. 10125-13-0, 99%, Sigma−Aldrich) in a 2:1 M ratio, in a methanol/water solution (10 mL). A copper wire was placed in the medium. After a few weeks in a vacuum desiccator at room temperature, small green/blue single crystals were grown, corresponding to the copper complex, together with other transparent crystals of the esterification of 4-nitrophenilacetic acid by methanol (catalysed by metal copper). The yield for the Cu(II) complex, under static condition, was ca. 30% in weight (vs. the original copper salt) over a 48 h period.

2.2. X-ray structure determination

A blue single crystal with dimensions $0.50 \times 0.10 \times 0.08$ mm^3 and a transparent prismatic crystal of dimensions $0.4 \times 0.2 \times 0.1$ mm^3 were used for structural determination at 293 K on an ApexII Bruker diffractometer using MoKα radiation. The structures were solved by direct methods using SHELXS97 [34,35] and refined on F^2 by full-matrix least-squares methods using SHELXL97 [34]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to ride on the respective parent atoms with an isotropic displacement parameter multiple of that of the parent atom using SHELXL97 defaults. Terminal nitro groups were found disordered, in the coordination compound structure, and refined isotropically in two alternative positions with occupancies close to 50%, the highest peak and the deepest hole of 0.65 and −0.60 e/Å^3, respectively, lie in those groups. An anisotropic disorder model was attempted but yielded unrealistic displacement factors. The C−N and N−O distances within the terminal nitro groups were fixed using DFIX. The second sample, although non-centrosymmetric, did not contain atoms with sufficient differences in anomalous scattering to yield a meaningful absolute structure result. PLATON [36] was used for figure plotting and structural analysis. Crystal data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

2.3. X-ray powder diffraction

Prior to magnetic characterisation, blue crystals were handpicked from the crystallization flask and grinded, and a powder diffractogram was collected to confirm that the sample to be tested only contained crystals of complex **1**. A small amount of powder was glued to the outside of a glass capillary using Vaseline. The sample was mounted on an ENRAF-NONIUS powder diffractometer (equipped with a CPS120 detector by INEL) in a Debye-Scherrer geometry. Cu Kα_1 radiation was used ($\lambda = 1.540598$ Å). Silicon was used as an external calibrant.

2.4. Magnetic measurements

Blue crystals were hand-picked from the crystallization flask and grinded and inserted in a gelatine capsule sample holder. Magnetic data on that crystalline powder were then collected using a 7T S700X superconducting quantum interference device (SQUID) magnetometer (Cryogenic Ltd). The temperature dependence of the magnetic susceptibility curves were measured over the temperature range 2−300 K, after zero field cooling under a magnetic field of 10 kOe. The paramagnetic susceptibility was obtained from the experimental magnetization data after a diamagnetism correction was estimated from the tabulated Pascal constants as −169.4 × 10^{-6} emu/mol.

2.5. Electronic structure calculations for complex 1

All theoretical calculations were performed with the Orca electronic structure package version 2.9.1 [37].

The system chosen for study is shown in Fig. 1 and contained two Cu^{2+} ions in the configuration giving the shortest inter-copper separation observed in the crystal structure. The axial ligands from the crystal structure were replaced by protonated acetic acid molecules in order to truncate the system and also approximate the charge environment in the experimental system. The geometry of this model system was optimized at the DFT level using the hybrid meta-GGA TPSSh functional (10% Hartree-Fock exchange) with the double-ζ Def2-SVP basis set on all main group atoms and the larger triple-ζ Def2-TZVP basis set on Cu [38–40].

The exchange coupling between the two copper centers was evaluated using the broken-symmetry approach [41,42]. Initial calculations used the TPSSh functional as this had previously been shown to perform quite well in calculations of this type [43]. However, in the present case it was found to overestimate the value of -2J considerably (Fig. 2). The related TPSS0 functional (also based on the TPSS meta-GGA functional [38] but with 25% Hartree-Fock exchange) was tested and found to provide much better agreement with experiment for this system. A range of SV and TZV double- and triple-ζ basis sets with varying numbers of polarization functions were employed in order to evaluate the convergence of the calculated values and dense integration grids were also used in order to increase accuracy (Orca keyword 'Grid5').

2.6. Kurtz-Perry powder method for compound 2

The Second-Harmonic Generation (SHG) efficiency of methyl 2-(4-nitrophenyl)acetate, compound **2**, was measured using the Kurtz and Perry powder method [44]. The measurements were performed at a wavelength of 1064 nm produced by a Nd:YAG laser operating at 10 Hz and producing 10 ns pulses with a pulse energy of 11 mJ. The sample preparation procedure was as follows: the transparent material (compound **2**) was mulled to a fine powder and compacted in a mount and then installed in the sample holder. Sample grain sizes were not standardized. Signals between individual measurements were seen to vary in some cases by as much as ±10%. For a proper comparison with the urea reference material the measurements were averaged over several laser thermal cycles.

3. Results and discussion

3.1. Crystal structures

In complex **1**, the metallic atoms are assembled in infinite chains of dimers running along the *a*-axis. Each dimeric unit contains two crystalographically related Cu(II) ions bridged by the carboxylic groups of four organic moieties in a paddle-wheel configuration with an intradimer Cu … Cu distance of 2.5678(6) Å (Fig. 3). A pair of such adjacent, inversely related Cu(II) dimers are bridged by a pair of μ-carboxylato-O bridges (Cu−O−Cu 98.07°, interdimer Cu … Cu distance 3.1770(6) Å, Fig. 4).

The metallic ions have a square-pyramidal geometry (the τ