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Crystal structure, magnetic and optical properties of (2-picoloylcarbonyl) thiosemicarbazonatocopper(II) ($[Cu_3L_2(H_2O)_2]\cdot 2ClO_4\cdot 3H_2O$, and $L=[C_7H_8N_4OS]^{2-}$)

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Abstract

Trinuclear copper(II) complex of $[Cu_3L_2(H_2O)_2]\cdot 2ClO_4\cdot 3H_2O$ was prepared by the reaction of (2-picoloylcarbonyl)thiosemicarbazone(H_2L) and copper perchlorate hydrate, and the magnetic properties and absorption spectra were measured for the title compound, and the origin of third-order optical response was identified in terms of calculated results using density functional theory combined with sum-over-states methods.

Keywords: Trinuclear copper(II) complex; Thiosemicarbazone; Magnetic properties; Chromium; Third-order optical response; Crystal structure

Polynuclear metal complexes with multiatom bridging ligands have been the subject of growing interest due to their widespread applications in bioinorganic chemistry, materials science and catalysis [1–3]. For trinuclear copper(II) complexes, reseachers are mostly interested in their magnetic properties [4–6], and rarely reports their linear and nonlinear optical properties. In this paper, a novel diazine nitrogen-bridged trinuclear copper complex formulated as $[Cu_3L_2(H_2O)_2]\cdot 2ClO_4\cdot 3H_2O$, where L stands for (2-picoloylcarbonyl)thiosemicarbazone dideprotonate $[(C_7H_8N_4OS)^{2-}]$, has been synthesized and its crystal structure has been characterized by using single-crystal X-ray diffractometer. The magnetic susceptibility of the title compound has been measured in the temperature range 5–300 K to investigate the electronic spin multiplicities at ground state, and the electronic absorption spectrum has been obtained from UV–Vis diffuse reflection integral spectrum (UV–Vis DRIS) (see Fig. S1 in supplementation) in order to determine the excitation energies at lower excitation states, and the electronic origin of third-order nonlinear optical response has been assigned for the title compound.

The title compound was prepared by the reactions of the (2-picoloylcarbonyl)thiosemicarbazone (H_2L) [7] dissolved in methanol solution and copper perchlorate hydrate dissolved in water solution, and the dark blue rectangular crystals were obtained after the filtrate stood for 7 days

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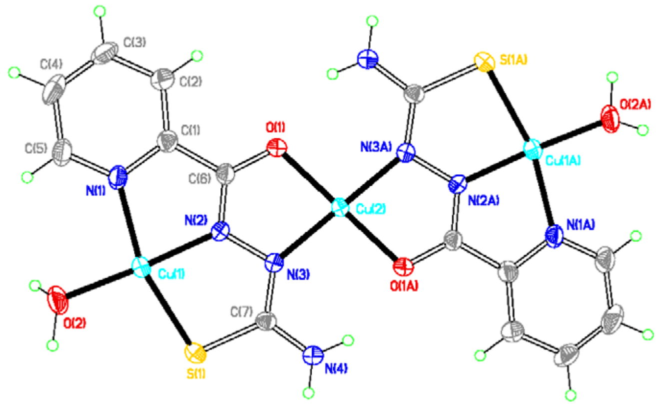

Fig. 1. ORTEP diagram of the title complex (30% probability ellipsoids, solvent molecules and perchlorate anions have been omitted for clarity). Selected bond distances (Å) and angles (°): Cu(1)–N(2), 1.914(3); Cu(1)–O(2), 1.954(3); Cu(1)–N(1), 2.056(4); Cu(1)–S(1), 2.304(1); Cu(2)–N(3), 1.942(3); Cu(2)–O(1), 1.962(3); N(2)–Cu(1)–O(2), 176.8(1); N(2)–Cu(1)–N(1), 79.8(1); O(2)–Cu(1)–N(1), 97.0(1); N(2)–Cu(1)–S(1), 83.4(1); O(2)–Cu(1)–S(1), 99.8(11); N(1)–Cu(1)–S(1), 161.9(1); N(3)–Cu(2)–O(1a), 96.7(1); N(3a)–Cu(2)–O(1), 96.7(1); N(3)–Cu(2)–O(1), 83.3(1) (Symmetry code: a, $-x+1,-y+1,-z+1$).

in the room temperature. Single-crystal X-ray analysis of the title compound (Fig. 1)[1] (http://pubs.rsc.org/images/entities/char_2020.gif) showed that a unit consists of two complex ions and four perchlorate anions.

There are two dideprotonate ligands $[(C_7H_8N_4OS)^{2-}]$ and three copper(II) ion in a complex. Three copper(II) ions are in a straight line in the complex and the atomic distance of Cu $\cdots$ Cu is 4.6284(6) Å. One copper(II) ion (Cu(2)) in the complex is coordinated with two diazine nitrogen atoms and two carbonyl oxygen atoms from two tridentate ligands, forming a distorted square pyramidal arrangement of N_2O_2. The lengths of Cu(2)–O bonds (1.962(3) Å) are longer than the corresponding bond (1.946(2) Å) in the complex $[Cu_2(sphz)(DMF)_3H_2O]\cdot(ClO_4)_2$ [8]. The lengths of Cu(2)–N bonds (1.942(3) Å) are longer than the one (1.928(2) Å) in the complex $[Cu_2(sphz)(DMF)_3H_2O]\cdot(ClO_4)_2$. The environments of other two copper(II) ions are in the same and the copper(II) ion is coordinated with a pyridine nitrogen atom, a diazine nitrogen atom, a sulphur atom and a water oxygen atom, forming a distorted square arrangement of N_2OS. The lengths of Cu(1)–N(1) bonds (2.056(4) Å) are longer than that (2.017(2) Å) in the complex $[Cu_2(sphz)(DMF)_3H_2O]\cdot(ClO_4)_2$. The lengths of Cu(1)–N(2) bonds (1.914(3) Å) are shorter than that (1.985(2) Å) in the complex $[Cu_2(sphz)(DMF)_3H_2O]\cdot(ClO_4)_2$. The lengths of Cu(1)–S bonds (2.304(1) Å) are in good agreement with the corresponding bond (2.295(5) Å) in the complex $[CuBr_2(C_7H_8N_4S)]\cdot H_2O$ [9].

There is a plane containing 29 non-hydrogen atoms in the title compound, and the structural feature of coplane is rarely reported in three nuclear copper complexes. It is notable that the aromatic face-to-face distance of 3.192(4) Å between the neighborplanic reveals a strong π–π stacking interaction on the complexes [10]. In addition, these aromatic π–π stacks show offset or slipped packing rather than a perfect face-to-face array of the atoms, which are available for increasing stability in the interaction of π–π framework stacking due to the contribution of π-σ attraction (i.e., aromatic CH$\cdots$π interaction). There is a one-dimensional chain structure through the N(amino-group)–H$\cdots$O(perchlorate anion) and O(coordinate water)–H$\cdots$O(perchlorate anion) intermolecular hydrogen bonds in the crystal (Fig. 2).

The temperature dependence of the molar susceptibility χ_m and the product $\chi_m T$, measured at a magnetic field of 500 Oe, for the title compound is shown in Fig. 3. At room temperature the value of the effective magnetic moment defined as $\mu_{eff} = 2.828(\chi T)^{1/2}$ is 2.458 μ_B (μ_B is the Bohr magneton) per $[Cu_3]$ formula unit, which is much larger than the expected value for divalent copper, namely 1.73 μ_B for spin $S = 1/2$ and a spin-only g-value of 2.0. The magnetic moment 2.458 μ_B at room temperature is in

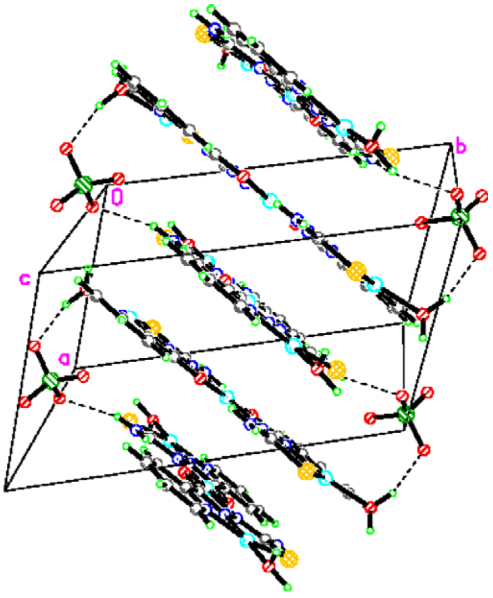

Fig. 2. Packing diagram of the title complex, viewed along the c axis.

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[1] Crystal data for the title complex: $C_{14}H_{22}Cl_2Cu_3N_8O_{15}S_2$. $M = 868.04$, crystal dimensions $0.80 \times 0.06 \times 0.03$ mm^3, triclinic, space group $\bar{P}$, $a = 8.2157(6)$ Å, $b = 13.470(2)$ Å, $c = 14.963(1)$ Å, $\alpha = 107.485(5)°$, $\beta = 105.864(4)°$, $\gamma = 100.872(3)°$, $V = 1451.6(3)$ Å^3, $Z = 2$, $D_a = 1.986$ g cm^{-3}, $\mu = 2.587$ mm^{-1}, λ (Mo Kα) = 0.71073 Å, at room temperature, unique reflections 6388, observed $[I > 2\sigma(I)]$ 4267, parameters 404. The data were corrected for Lorentz and polarization effects and processed using the SAINT, SADABS and XPREP processing packages. The structure was solved by direct methods (SHELXTL 5.1) and refined by full-matrix least squares techniques against F^2. In the final cycles of each refinement, the non-hydrogen atoms were refined anisotropically. No attempt was made to locate the hydrogen atoms of solvent water; the other hydrogen atoms were added in the riding model. For the observed reflections, $R = 0.0444$, $wR2 = 0.1017$. The goodness-of-fit indicator for all data is 0.999. Peaks on the final difference map ranged from 0.629 to -0.680 e Å^{-3}.