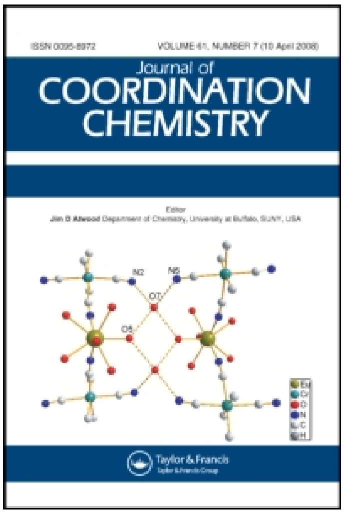

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Synthesis and structure of a trimeric copper(II) complex of N'-[(1Z)-1H-1,2,4-triazol-3-ylmethylene]-1H-1,2,4-triazole-3-carbohydrazide

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The complex $[Cu_3L_2Cl_4](H_2O)_6$ (HL = N'-[(1Z)-1H-1,2,4-triazol-3-ylmethylene]-1H-1,2,4-triazole-3-carbohydrazide) has been synthesized and characterized by IR, elemental analysis and X-ray crystal structure analysis. Crystal data: triclinic, $P\bar{1}$, $a = 7.8591(12)$, $b = 9.6745(14)$, $c = 9.8798(15)$ Å, $\alpha = 83.301(3)$, $\beta = 71.602(3)$, $\gamma = 80.531(3)^\circ$, $V = 701.40(18)$ Å^3, $Z = 1$, $D_c = 2.014$ Mg m^{-3}, $\mu = 2.706$ mm^{-1}, $F(000) = 425$, $R_1 = 0.0447$, $wR_2 = 0.1133$ ($I \geq 2\sigma(I)$), $S = 1.001$. The crystal structure contains $[Cu_3L_2Cl_4]$ trimers combining coordination and hydrogen bonding interactions. The geometries of the Cu(II) ions differ. The terminal Cu(II) ions have distorted square pyramidal geometry and are surrounded by two chloride anions and one deprotonated ligand. The central Cu(II) is square planar, bonded to one imino nitrogen atom and one carbonyl oxygen atom of each ligand.

Keywords: Copper(II); Trimer; 1,2,4-Triazole; Crystal structure

1. Introduction

1H-1,2,4-triazole and its derivatives have attracted broad interest because of their antimicrobial, antifungal, anticonvulsant and root growth regulating activities [1]. They have been widely used as ligands in coordination chemistry due to their versatility [2] in terms of the arrangement of the three nitrogen atoms in the triazole ring and varying subtituents [3]. The tiazole ring often binds as a monodentate, together with a donor atom in the substituent [4]; otherwise the rings bridge to form polynuclear complexes [3, 5] with interesting magenetic properties [6]. Such diversity in structure and properties has prompted our further research. To obtain more information about the interactions of triazole ligands with transition metals, we have prepared a number of 3-substituted-1H-1,2,4-triazoles and their complexes. Here we report the synthesis

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and X-ray structure of a trinuclear copper(II) complex **1**, containing *N′*-[(1Z)-1H-1,2,4-triazol-3-ylmethylene]-1*H*-1,2,4-triazole-3-carbohydrazide.

2. Experimental

All chemicals were used as purchased without further purification. Solvents were of analytical grade. IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400/II instrument.

2.1. *Synthesis of* $[Cu_3L_2Cl_4](H_2O)_6$ *(1)*

A mixture of $CuAc_2 \cdot H_2O$ (1 mmol, 0.1996 g), (1,2,4-triazole-3-yl)hydrazide (1 mmol, 0.1270 g) and DMF (40 cm^3) was stirred for 7 h. The dark green precipitate (yield about 80%) was filtered off, washed with ethanol and dried over P_2O_5 for 24 h. The solid was dissolved in 2 M HCl (15 cm^3) to give, with slow evaporation over one month at room temperature, green blocky crystals adequate for X-ray analysis. Yield: 31% based on Cu. Anal. Calcd for $C_{12}H_{22}Cl_4Cu_3N_{16}O_8$ (%): C, 17.00; H, 2.62; N, 26.46. Found: C, 22.89; H, 2.30; N, 9.02. IR (cm^{-1}): 3367, 3419 (m, ν(N–H)), 1653 (m, ν(C=O)), 1635 (m, ν(C=N)), 1623 (m), 1587 (s), 1558.4 (m), 1472.5 (s), 1313.4 (m, ν(C=N)), 836 (m, δ(N–H)).

2.2. *X-ray crystallography*

Crystallographic data for **1** were collected with a Bruker APEX area-detector diffractometer equipped with a graphite-monochromatized Mo-Kα X-ray radiation ($\lambda = 0.71073$ Å) using the ω–θ scan mode in the range $2.14 \le \theta \le 27.00°$ at 293 K. Raw frame data were integrated with the SAINT [7] program. The structure was solved by direct methods (SHELXS97) and refined by full-matrix least-squares techniques (SHELXL97) on F^2 [8]. An empirical absorption correction was applied with the program SADABS [9]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter.

2.2.1. Crystallographic data. $C_{12}H_{22}Cl_4Cu_3N_{16}O_8$, $M = 850.88$, triclinic, $P\bar{1}$, $a = 7.8591(12)$, $b = 9.6745(14)$, $c = 9.8798(15)$ Å, $\alpha = 83.301(3)$, $\beta = 71.602(3)$, $\gamma = 80.531(3)°$, $V = 701.40(18)$ Å^3, $Z = 1$, $D_c = 2.014\ Mg\,m^{-3}$, crystal dimensions $0.347 \times 0.261 \times 0.203\ mm^3$, $\mu = 2.706\ mm^{-1}$, $R_1 = 0.0447$, $wR_2 = 0.1133$ ($I \ge 2\sigma(I)$), goodness-of-fit is 1.001. A total of 2997 reflections were collected (2499 independent reflections with $R_{int} = 0.0514$). The largest peak and hole on the final difference Fourier map were 1.515 and −0.445 e Å^{-3}, respectively.

3. Results and discussion

An ORTEP drawing of **1**, a diagram showing its 1D chain structure and a packing view are shown in figures 1–3, respectively. The complex is constructed from

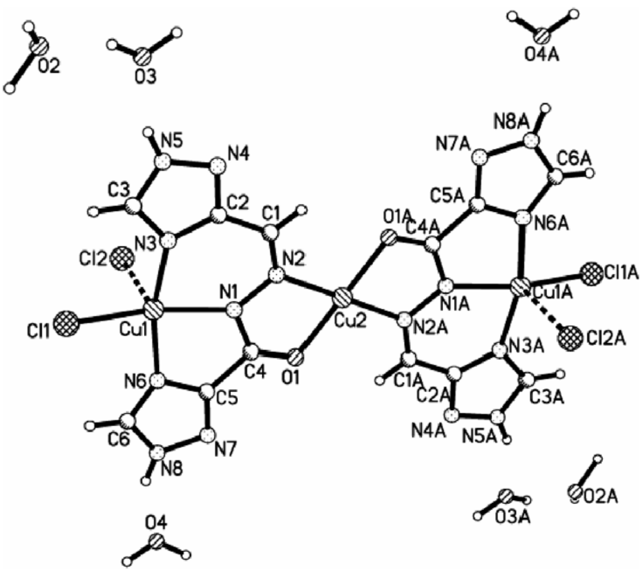

Figure 1. ORTEP diagram of **1**. Selected bond distances (Å) and angles (°): Cu(1)–N(3) 1.965(3), Cu(1)–N(6) 1.973(3), Cu(1)–N(1) 2.018(3), Cu1–Cl(1) 2.2411(10), Cu(1)–Cl(2) 2.8589(12), Cu(2)–O(1) 1.946(3), Cu(2)–N(2) 1.979(3), O(1)–Cu(2)–N(2) 82.54(13), Cl(1)–Cu(1)–Cl(2) 98.56(4), N(3)–Cu(1)–N(1) 86.24(12), N(6)–Cu(1)–Cl(1) 95.89(10), N(6)–Cu(1)–N(1) 81.13(12), N(3)–Cu(1)–Cl(1) 94.96(9), O(1)–Cu(2)–N(2) 82.54(13), O(1)–Cu(2)–N(2) 97.46(13).

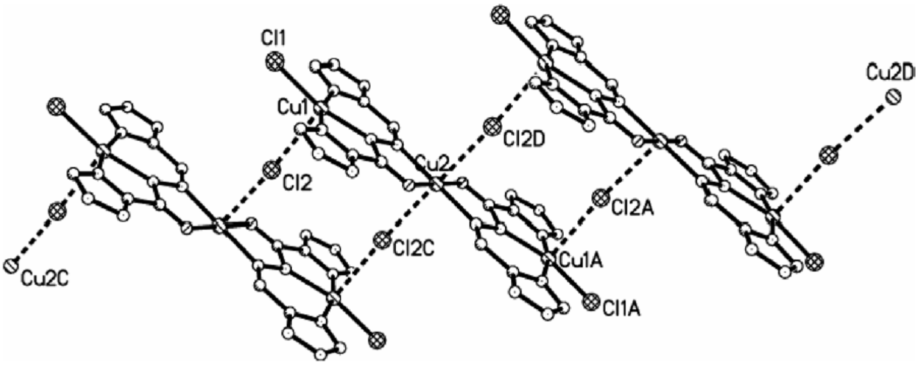

Figure 2. 1D chain formed by the weak Cu–Cl bond in **1**. Water molecules and hydrogen atoms are omitted for clarity.

centrosymmetric trinuclear entities [$Cu_3L_2Cl_4$] with six uncoordinated water molecules in the lattice. As shown in figure 1, there are two types of copper(II) ions in the complex. The terminal copper(II) ion (Cu(1)) has distorted square pyramidal geometry, with the apical site of the coordination sphere occupied by a chloride anion (Cl(2)) and the basal plane comprised of three nitrogen atoms (N(1) (deprotoned –NH– group), N(3) and N(6) (triazole)) of a ligand and another chloride anion (Cl(1)). The metal atom is located 0.1564 Å above the plane. As in most complexes of 1*H*-1,2,4-triazole with 3-substituents containing donor atoms, the triazole ring is coordinated through one N atom. The average Cu–N (triazole) distance of 1.969(3) Å falls in the range (1.932 to

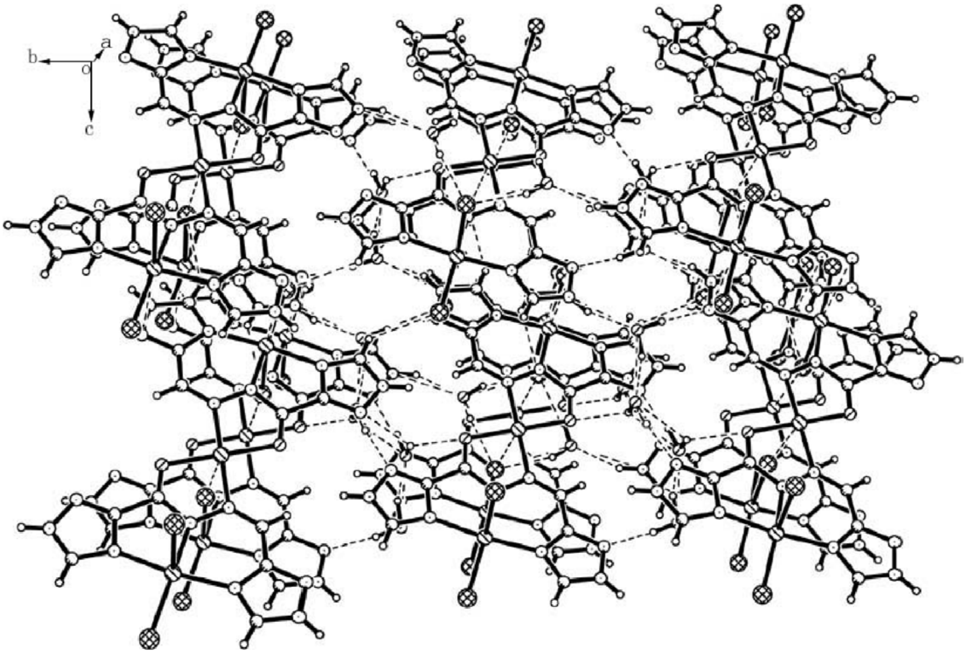

Figure 3. Packing view along *b*.

2.018 Å) found in related complexes [10]. The Cu–N(N$^-$) distance of 2.018(3) Å is slightly longer than those observed in related complexes [11]. The coordination geometry of the central copper(II) ion (Cu(2)) is square planar, involving an imino nitrogen atom and a carbonyl oxygen atom of two ligands, with Cu–O and Cu–N bond lengths of 1.946(3) and 1.979(3) Å, respectively. Thus the two different types of copper(II) ions are bridged by the ligand to give a trinuclear entity. It is worth noting that the two terminal Cl anions (Cl(2) and Cl(2A)) are weakly coordinated to Cu(2) of neighboring molecules at a distance of 3.009 Å; the Cu $\cdots$ Cu separation is 5.848 Å. The Cu $\cdots$ Cl interactions link the trimers to form a one-dimensional infinite chain parallel to the *a* axis (figure 2). Futhermore, adjacent chains are connected along the *b* axis *via* weak coordination between Cu(1) and N(3) (3.346 Å). In addition, hydrongen bonds between the weakly coordinated chloride atom and −NH groups of the triazole rings stabilise the crystal packing (figure 3).

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 284662. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

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