

Synthesis and Magnetic Properties of a Copper Cube: [Cu₄(OH)₄(C₁₆H₁₈N₂)₄]⁴⁺ (ClO₄)₄ C₃H₆O [C₁₆H₁₈N₂ = (*E*)-1,6-[Di (pyridin-4-yl)hex-3-ene]

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The synthesis of a Cu₄(OH)₄ cube which is coordinated by four molecules of the dipyridyl ligand 1,6-[di(pyridin-4-yl)hex-3-ene] is reported. This compound has a *trans* double bond which restricts the conformational freedom of the ligand and favours coordination within a unique copper cube. The structure was solved by an X-Ray single crystal structure determination and low temperature magnetic susceptibility measurements examined its magnetic properties. The cube classification corre-

sponds to the type I classification of Mergehenn and Haase and the short/long distribution of Cu...Cu separations in the cube as defined by Ruiz. The magnetic susceptibility measurements show paramagnetic behaviour down to 50 K but below this the copper cube shows weak ferromagnetic exchange interactions. The low temperature magnetic susceptibility characteristics are examined in detail then modelled and compared to other similar Cu₄O₄ copper cubes.

1. Introduction

Clusters of transition metal-ions have potential applications in transistors, magnetic memory, molecular wires, logic gates and other molecular devices.^[1] Multi-nuclear copper (II) complexes are of interest for molecular devices and in the active sites of copper oxidases.^[2–4] A common arrangement corresponds to cubane like structures which contain a Cu₄O₄ core. The oxygen bridges are hydroxo or alkoxo groups. Two different classifications have been proposed which are either based on the distribution of long Cu–O bond lengths in the cube, by Mergehenn and Haase (type I, II and III),^[5] or on the number of short and long Cu–Cu distances by Ruiz (2 + 4, 4 + 2 or 6 + 0 classes)^[6–7] (Figure 1). Compounds of type I or class 2 + 4 contain 2 short and 4 long Cu–Cu distances. Complexes of type II or class 4 + 2 have 4 short and 2 long Cu–Cu distances. The third class are 6 + 0 compounds which contain six similar Cu–Cu distances.

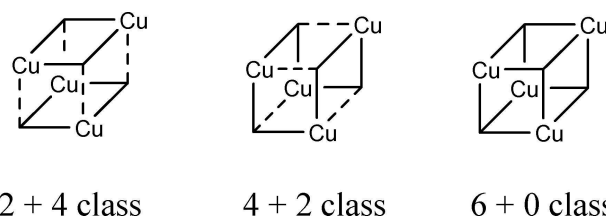


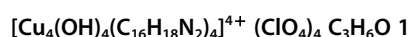
Figure 1. The classification of Cu₄O₄ cubanes. The bold lines are short Cu–Cu bond lengths and the dashed lines are long Cu–O bond lengths.^[5–7]

The specific geometry of the Cu₄O₄ core can lead to ferromagnetic as well as antiferromagnetic interactions.^[8] Small variations in their structure leads to tunable magnetic behaviour.^[9–11] Much effort has been made to understand the magnetic properties with the Cu₄O₄ structure and bond lengths.^[12–14] Other interesting Cu cubane clusters are also known.^[15–19] In this paper a new Cu₄(OH)₄ cube is described and analysed.

Experimental Section

General

IR spectra were recorded on a diamond anvil spectrophotometer. UV/Vis spectra were recorded using a Perkin-Elmer Lambda spectrometer with EtOH as the solvent. The crystal field stabilisation energy (CFSE) parameter in KJ mol⁻¹ = 0.119/λ_{max} (meters). 0.119 = Na × h × c (Avogadro's number × Planck's constant × speed of light).



(*E*)-1,6-[di(pyridin-4-yl)hex-3-ene] 2 (Figure 2)^[20–21] (50 mg, 0.21 mmol) was dissolved in EtOH (3 ml) and acetone (3 ml) then layered onto CuClO₄ · 6H₂O (78 mg, 0.21 mmol) in water (7 ml) in an

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/open.201900260>

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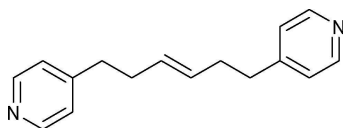


Figure 2. Drawing of (*E*)-1,6-[di(pyridin-4-yl)hex-3-ene] 2.

8×2.5 cm sample vial. After 24 h nucleation of blue crystals had started around the sides and the layers were gently mixed. Deep blue crystals were carefully collected (43 mg, 47.4%) after two days and briefly air dried. The crystals were collected from the sides of the sample vial after pouring off the supernatant solvent into a beaker and washing the sample vial with fresh solvent of the same composition used in the synthesis. The crystals were also collected from the supernatant solvent by decanting off the solvent from the beaker and adding more fresh solvent to decant. IR (Diamond anvil): $\tilde{\nu}$ = 3502 (w), 2934 (w), 1710 (w), 1619 (s), 1559 (w), 1506 (w), 1431 (s), 1229 (w), 1062 (s), 975 (s), 930 (w), 828 (s), 621 (s), 589 (s) and 528 (s) cm^{-1} ; After storage for 4 months: $\tilde{\nu}$ = 2938 (w), 1619 (s), 1558 (w), 1508 (w), 1433 (s), 1230 (w), 1109 (vs), 1050 (vs), 968 (w), 930 (w), 812 (s), 620 (vs), 585 (s), 523 (s) and 493 (w); UV/Vis (EtOH): λ_{max} (ϵ) = 420–380 (2594), 362 (2939), 257 nm (6256 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$); UV/Vis (DMF): λ_{max} (ϵ) = 690 nm (117.6 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$); elemental analysis calcd (%) for $\text{C}_{67}\text{H}_{79}\text{Cl}_4\text{Cu}_4\text{N}_8\text{O}_{21}$: C 46.50, H 4.57, N 6.48; found: C 46.22, H 4.60, N 6.46.

Intensity data for 1 were collected at $T=100$ K using a Rigaku AFC11 CCD diffractometer (Mo $K\alpha$ radiation, $\lambda=0.71073$ Å) and the structure was easily solved by direct methods and completed and optimised by least-squares refinement against $|F|^2$ using SHELXL-2014.^[22] The O-bonded H atom was located in a difference map and refined as riding in its as-found relative position. The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding atoms. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$ was applied in all cases. The O atoms of one of the perchlorate anions are statistically disordered over two sets of sites.

1 $\text{C}_{76}\text{H}_{100}\text{Cl}_4\text{Cu}_4\text{N}_8\text{O}_{24}$, $M_r = 1905.59$, blue block, $0.16 \times 0.10 \times 0.08$ mm, tetragonal, space group $P4_2/c$ (No. 114), $Z=2$, $a = 14.69480$ (10) Å, $c = 19.0833$ (2) Å, $V = 4120.79$ (7) Å³. Number of measured and unique reflections = 38188 and 4679, respectively ($-17 \leq h \leq 19$, $-19 \leq k \leq 19$, $-24 \leq l \leq 25$; $2\theta_{\text{max}} = 54.9^\circ$; $R_{\text{int}} = 0.033$). Final $R(F) = 0.028$, $wR(F^2) = 0.064$ for 263 parameters and 4616 reflections with $I > 2\sigma(I)$ (corresponding R -values based on all 4679 reflections = 0.028 and 0.065, respectively). Flack absolute structure parameter = 0.000 (4), CCDC deposition number 1891223.

Synthesis of Copper Cube 1

The ligand 1,6-[di(pyridin-4-yl)hex-3-ene]^[20–21] was dissolved in a mixture of acetone and ethanol then layered onto a solution of $\text{Cu}(\text{ClO}_4)_2$ dissolved in water. After four days blue crystals were growing around the sides of the sample vial and some were on the base. The solution, which had a slight haze, was decanted carefully and the sample vial was washed with water. The decanted solution, in a beaker, was also decanted again leaving more blue crystals which were washed with water. The air dried crystals were combined and characterised by IR, UV/Vis, microanalysis, an X-ray single crystal structure determination, magnetic susceptibility measurements and epr spectroscopy.

2. Results and Discussion

The IR spectrum of the copper cube showed a weak carbonyl stretch at 1710 cm^{-1} owing to the presence of acetone (1715 cm^{-1}) in the lattice (Figure S1 and S2). The absorption for a carbonyl group would normally be strong but here it may be weak because by mass acetone is only 3% of the compound. However, after storage for a few months this peak vanished presumably because the lattice desolvated. The UV/Vis spectrum was weak owing to poor solubility of the copper cube in EtOH (Figure S3). It showed an absorption maximum at 362 nm with a broad shoulder at 380–420 nm but the spectrum was too weak to see the long wavelength blue absorption. However the blue crystals dissolved in DMF and showed a broad absorption maximum at 690 nm (Figure S4) with a crystal field stabilisation energy (CFSE) of 172.5 kJ/mol which is comparable with that for other Cu(II) ions.^[23] Over time they appeared to decompose as the solution turned hazy. The asymmetric unit of 1 consists of one Cu^{2+} ion, one (*E*)-1,6-di(pyridin-4-yl)hex-3-ene^[20–21] 2 ($\text{C}_{16}\text{H}_{18}\text{N}_2$) ligand, one $\mu^3\text{-OH}^-$ ion, two perchlorate ions (both with Cl site symmetry 2 and one featuring statistical disorder of its O atoms over two sets of sites) and one acetone solvent molecule of crystallisation. The $\bar{4}$ symmetry elements in the tetragonal crystal [at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for the asymmetric fragment] generate tetra-nuclear $[\text{Cu}_4(\text{OH})_4(\text{C}_{16}\text{H}_{18}\text{N}_2)_4]^{4+}$ ‘cubane’ clusters accompanied by one ClO_4^- counter ion and one $\text{C}_3\text{H}_6\text{O}$ molecule per copper ion, for an overall chemical formula of $[\text{Cu}_4(\text{OH})_4(\text{C}_{16}\text{H}_{18}\text{N}_2)_4](\text{ClO}_4)_4 \cdot 4(\text{C}_3\text{H}_6\text{O})$ (Figure 3). The dihedral angle between the N1 and N2 pyridine ring is 28.33 (14) $^\circ$ and both the $\text{C}_a\text{-C}_m\text{-C}_m\text{-CH}$ (= a = aromatic, m = methylene) fragments in the linking chain have *gauche* conformations [torsion angles = -60.2 (4) and 71.1 (3) $^\circ$] to result in an approximate overall U shape for this species. The ligand has a *trans* double bond which lowers the entropy and restricts conformational freedom. This is expected to favour coordination within a unique copper cube. A similar crystallisation of 1,6-di(pyridin-4-

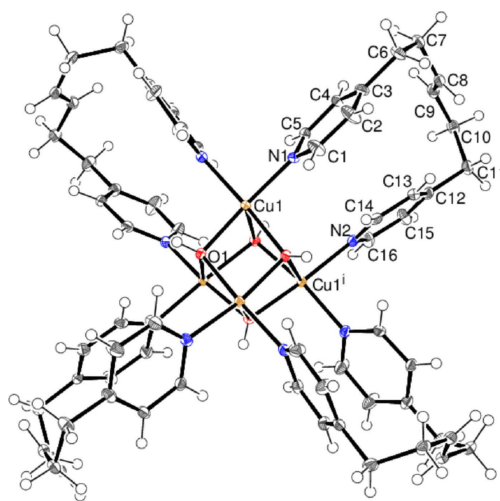


Figure 3. The molecular structure of the $[\text{Cu}_4(\text{OH})_4(\text{C}_{16}\text{H}_{18}\text{N}_2)_4]^{4+}$ cluster in 1 showing 50% displacement ellipsoids (perchlorate ions and acetone molecule omitted for clarity). Symmetry code: (i) $y, 1-x, 1-z$.

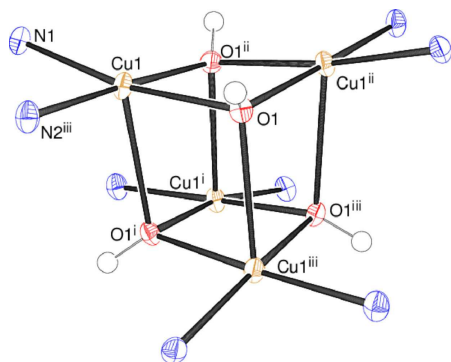


Figure 4. Detail of the central $\text{Cu}_4(\text{OH})_4$ cube and attached ligand N atoms in **1**. Symmetry codes: (i) $y, 1-x, 1-z$; (ii) $1-x, 1-y, z$; (iii) $1-y, x, 1-z$.

yl)hexane with $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ gave two infinite crystalline phases^[24] suggesting that the double bond is important in favouring the macrocycle formation with Cu(II) salts and in reducing the potential for disorder of the ligand in the lattice.^[21] The flexible hexyl spacer (C_6H_{12}) can exhibit disorder in the lattice of co-ordination networks.^[21]

The copper co-ordination geometry is well described as a CuN_2O_3 square-based pyramid with the two ligand N atoms [$\text{Cu}-\text{N} = 1.992$ (3) and 2.032 (2) Å; $\text{N}-\text{Cu}-\text{N} = 88.84$ (10)°] in a *cis* disposition in the basal plane. The geometry index or Addison tau parameter for Cu1 in the copper cube is 0.12 which indicates a slightly distorted square pyramidal geometry (tau = 0 for a regular square pyramid and tau = 1 for a regular trigonal bipyramid).^[25] The apical $\text{Cu1}-\text{O1}$ bond [2.336 (2) Å] is notably longer than the $\text{Cu1}-\text{O1}$ basal bonds [1.9493 (19) and 1.9803 (19) Å]. The $\text{Cu}-\text{O}$ bond-length distribution within the $\text{Cu}_4(\text{OH})_4$ cube (Figure 4) corresponds to the type I classification of Mergehenn and Haase^[5] and the short/long distribution of $\text{Cu}\cdots\text{Cu}$ separations in the cube as defined by Ruiz^[6] [two at 3.0028 (4) Å and four at 3.2599 (5) Å] is completely consistent with this. A much longer $\text{Cu1}-\text{O2}$ contact [2.877 (3) Å] to a

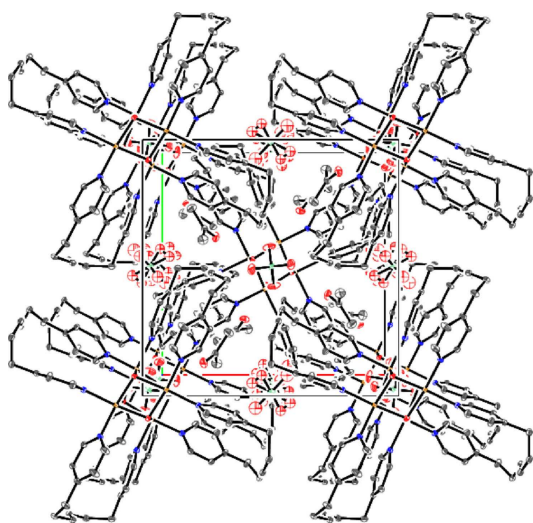


Figure 5. The windmill packing in **1** viewed down [001]

perchlorate O atom would complete an extremely distorted CuN_2O_4 octahedron for the metal-ion but given that its bond valence is only 0.05, we do not regard it as a significant bond.^[26]

In the crystal of **1** the $[\text{Cu}_4(\text{OH})_4(\text{C}_{16}\text{H}_{18}\text{N}_2)_4]^{4+}$ cations form a 'windmill' arrangement when viewed down [001] (Figure 5). An $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond from the cubane hydroxyl group to the O atom of the acetone solvent molecule ($\text{H}\cdots\text{O} = 2.04$ Å, $\text{O}-\text{H}\cdots\text{O} = 166^\circ$) is a notable feature of the packing, which is consolidated by weak $\text{C}-\text{H}\cdots\text{O}$ interactions.

Magnetic susceptibility measurements were performed on polycrystalline sample of **1** in the range 300–2 K with an applied field of 0.1 T (Figure 6 Top). The $\chi_{\text{M}}T$ product remains almost constant down to 50 K with a value of around $1.5 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$. This value corresponds for paramagnetic spin-only behaviour of four Cu(II) ($S = 1/2$) isolated centres. Below this temperature the $\chi_{\text{M}}T$ product gradually starts to increase and takes a value of 1.56 at 3 K. This behaviour could be caused by the presence of weak ferromagnetic exchange interactions within the cluster. The inset of Figure 6 shows the isothermal magnetisation (M) measured up to 5 T at temperatures of 2 and 5 K. The experimental data can be modeled using an isotropic spin-spin

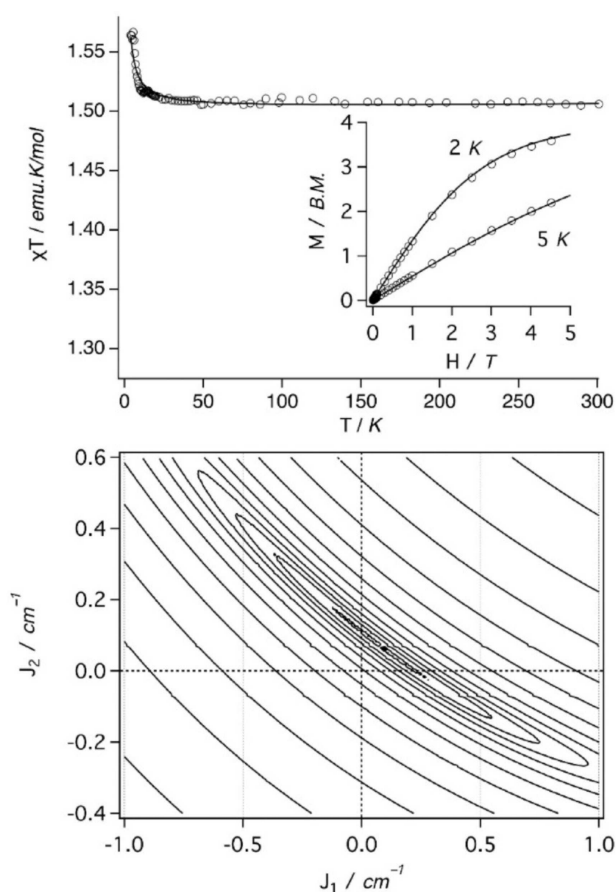


Figure 6. Top: temperature dependence of the product of the magnetic susceptibility times the temperature at 0.1 T; Inset: isothermal magnetisations measured at $T = 2$ and 5 K; Empty circles: experimental data; Full lines: simulated curves using best simultaneous fit; Bottom: surface error plot of $\chi_{\text{M}}T$ vs T as a function of J_1 and J_2 revealing a banana minimum; Full lines: isoerror lines from the innermost with $R = 4.0 \times 10^{-6}$ to the most external ($R = 8.192 \times 10^{-3}$) and the value of each line is double the next more internal.

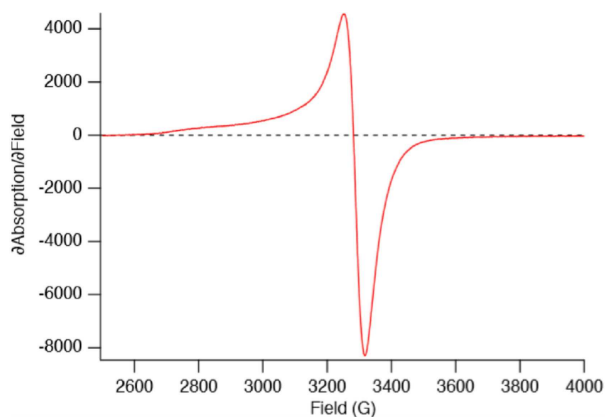


Figure 7. EPR spectroscopy measurements on compound 1 at 100 K.

interaction by the following Heisenberg-Dirac-van Vleck Hamiltonian:

$$H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_1+S_2)(S_3 + S_4)$$

where J_1 and J_2 are the isotropic exchange parameter among the nearest and most distant copper, respectively, and $S_1=S_2=S_3=S_4=1/2$. Simultaneous fit of both the susceptibility and magnetisation data, performed with the Magpack program,^[27–28] yields $J_1=0.096$, $J_2=0.062$ cm⁻¹ and $g=2.00$ ($R=3.4\times 10^{-6}$) values for the Cu(II) tetramer. Solutions of similar quality are obtained for other parameters and this fit is not very sensible to the J_1/J_2 ratio. The dependence of the fit with respect to them is shown in a two-dimensional plot of the error factor R on the values J_1 and J_2 (Figure 6 Bottom). The minimum error region ($R=4.0\times 10^{-6}$) has a banana shape where both J 's can be interconverted and with limits at $(J_1, J_2)=(-0.12, 0.17)$ and $(0.28, -0.025)$ cm⁻¹.

EPR measurements were performed on a polycrystalline sample of **1** at 100 K (Figure 7). From crossing zero and small shoulder at low field: $g_{\text{per}}=2.06$ and $g_{\text{par}}=2.35$ approx. (g average=2.16). The exchange parameters are not affected by the EPR result and this scale is comparable with the result from the susceptibility measurements.

3. Conclusions

These parameters are in the same range found for other families of polynuclear complexes containing a Cu₄O₄ core and show similar magnetostructural correlation studies.^[12] In these studies, the J_1 interaction can be both ferromagnetic and antiferromagnetic, whereas the J_2 interaction must be weakly ferromagnetic for cubane type 2+4 similar to complex **1**. In our case, both interactions have Cu–O–Cu angle very close to 98.5°. This angle makes the border between the ferromagnetic (angles smaller than 98.5°) and antiferromagnetic (angles larger than 98.5°) interactions, and this may justify the very low absolute values of the interactions obtained from the fit of complex **1**. The square based pyramid coordination geometry of each copper atom

shows an elongated apical Cu–O bond which is an example of Jahn-Teller distortion.^[29] Of particular interest is the partially unsaturated dipyriddy ligand, containing a *trans* double bond, which will favour the formation of a unique complex and reduce the potential for disorder in the lattice. Ligands of this type may play an important role in advancing the science of transition metal-ion supramolecular cluster synthesis by stabilising clusters and catalysing their formation.

Supplementary

Figure S1–S4: IR and UV/Vis spectra of compound **1**

Acknowledgements

We are grateful to the National Mass Spectrometry Service Center for mass spectra and to the UK National Crystallography Service for data sets.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: copper(II) perchlorate · magnetic properties · Jahn-Teller distortion · clusters

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Manuscript received: August 8, 2019