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[(Pyridylcarbonyl)pyridyl]triazolopyridines, Useful Ligands for the Construction of Polynuclear Coordination Compounds – Synthesis, Crystal Structure and Magnetic Properties of a Novel Tetranuclear Copper(II) Cubane

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Dedicated to Professor Ramón Mestres on the occasion of his retirement

Keywords: Polydentate ligands / Triazolopyridine ligands / Copper(II) complexes / Tetranuclear complexes / Molecular magnetism

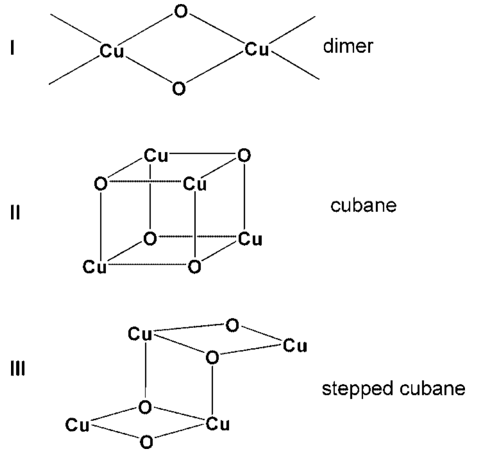
A new tetranuclear cubane Cu_4O_4 complex has been synthesised from assembly of Cu^{II} ions and the polydentate ligand (pyridin-2-yl){6-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridin-2-yl}methanone. Crystallographic analysis indicates that the Cu_4O_4 unit has an S_4 symmetry. The magnetic properties have been analysed using the $H = -2\sum_{i,j} J_{ij}S_iS_j$ spin Hamiltonian. Two distinct coupling constants, $2J_{1,3} = -37.4\ \text{cm}^{-1}$ and $2J_{1,2} = -2.6\ \text{cm}^{-1}$, obtained from the fitting of the experimental data have been rationalised on the basis of a density functional study of magnetostructural correlations in cubane complexes containing the Cu_4O_4 core.

Introduction

High-nuclearity transition-metal complexes are of importance as new magnetic materials,[1] single molecular magnets (SMM),[2–5] in the emerging science of nanomaterials,[6] and as models for the multimetal active sites of metal storage proteins.[7]

Despite the interest in the properties of such systems, synthetic methods have to reach the level of efficiency attained with mononuclear complexes, and the term "serendipity" is frequently used to explain why one polynuclear complex is obtained rather than another.

Copper(II) complexes are particularly popular since the ion is paramagnetic and polynuclear clusters are easily accessible. Copper(II) forms many dinuclear complexes in which it shows a basically square-planar coordination with two bridging ligands, very frequently hydroxide or alkoxide groups, linking the two metals (Scheme 1, **I**). Copper(II) readily accepts a fifth ligand above the plane, and this offers a means of association of two dimeric units to give either the so-called cubane unit (Scheme 1, **II**) or the stepped cubane (Scheme 1, **III**).[8]



Scheme 1. Di- and tetranuclear copper(II) species.

During our research on the chemistry of [1,2,3]triazolo[1,5-*a*]pyridines, we had synthesized (pyridin-2-yl)([1,2,3]triazolo[1,5-*a*]pyridin-7-yl)methanones of type **1**,[9,10] as starting materials to prepare poly(pyridylcarbonyl)pyridines of type **2**, polydentate ligands able to make high-nuclearity clusters (Scheme 2).[11] In this context we had found an interesting structural feature for the precursor **3A** (**1**, R =

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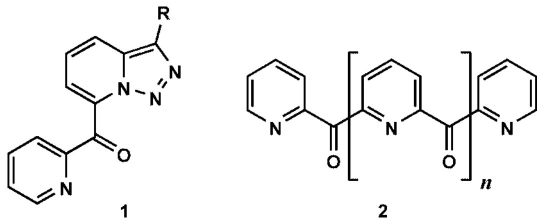
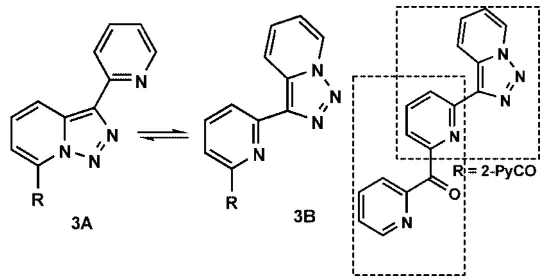
pyridin-2-yl) (Scheme 3). The ^{1}H NMR spectrum demonstrates that this compound exists almost entirely as its isomer **3B** (R = 2-PyCO).[10] To account for this structure we assumed that, in solution, the first formed compound **3A** (R = 2-PyCO) {3-(pyridin-2-yl)[1,2,3]triazolo[1,5-*a*]pyridin-7-yl derivative} is in equilibrium with the diazo form, an intermediate which may undergo a new ring-chain isomerisation,[12,13] giving **3B** {6-{[1,2,3]triazolo[1,5-*a*]pyridin-3-yl}pyridin-2-yl derivative} (see Scheme 3). By a ^{1}H NMR study and DFT/B3LYP/6-31G* calculations of a series of 7-substituted 3-(pyridin-2-yl)triazolopyridines, we had proved that the **A**/**B** ratio depends on the electronic properties of the substituent R. Electron-donating substituents [$SiMe_3$, $B(OR)_2$] favour the **A** form, electron-withdrawing substituents [COMe, Br, Cl, I, *p*-MeOPh] favour the **B** form, and only in the case R = Me, both forms are present (75% of **A**, 25% of **B**).[14]



Scheme 2.



Scheme 3.

The structure **3B** (R = 2-PyCO) has two interesting features as a potential ligand to form high-nuclearity transition-metal complexes (Scheme 3). On one hand, a part of the structure is analogue to that of the 3-(pyridin-2-yl)-triazolopyridines, which coordinates through the N2 and N11 atoms, i. e. to Cu^{II}, and Fe^{II} ions.[15,16] In particular, the Fe^{II} derivatives with NCS$^-$ and NCSe$^-$ coordinating anions undergo spin crossover behaviour. On the other hand, the 2,2′-dipyridyl ketone moiety is also present. This moiety can undergo metal-assisted nucleophilic attack by solvent molecules on its carbonyl function, thus yielding its *gem*-diol or hemiacetal form, depending on the solvent. Subsequent deprotonations of the hydroxyl groups can yield the mono- or dianion (in the case of the *gem*-diol form), which can adopt a large number of coordination modes, bridging up to five metal ions. The latter coordinating motive has been extensively studied by Perlepes et al.[17–20] and have important magnetic properties.

In this context, we have been investigating **3B** as a suitable candidate to have similar solvolysis, deprotonation, and coordination properties. Here we report the synthesis, crystal structure and magnetic behaviour of the tetranuclear cubane compound $[Cu(\mathbf{3B^*})]_4(NO_3)_4 \cdot 8H_2O$ where the ligand **3B*** is the hemiacetal of the (pyridin-2-yl){6-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridin-2-yl}methanone.

Results and Discussion

The molecular structure of a representative fragment of the cationic unit $[Cu(\mathbf{3B^*})]_4^{4+}$ is shown in Figure 1. The cubane shows an S_4 symmetry with the Cu^{II} ion in the middle of a strongly distorted $[CuO_3N_3]$ octahedron. Two nitrogen atoms belong to the [N(2) and N(11)] atoms of one ligand **3B*** while the remaining nitrogen atom belongs to the isolate pyridine group [N(21)^i] of a second **3B***. The three oxygen atoms correspond to the O(1) site, one belongs to the same ligand that the two nitrogen (N2 and N11) while the other two corresponds to two adjacent ligands. There are four short distances Cu–N(11) 2.0243(23), Cu–N(21) 1.9923(23), Cu–O(1) 1.9519(18), and Cu–O(1)^{ii} = 1.9984(18) Å and two elongated distances Cu–N(2)

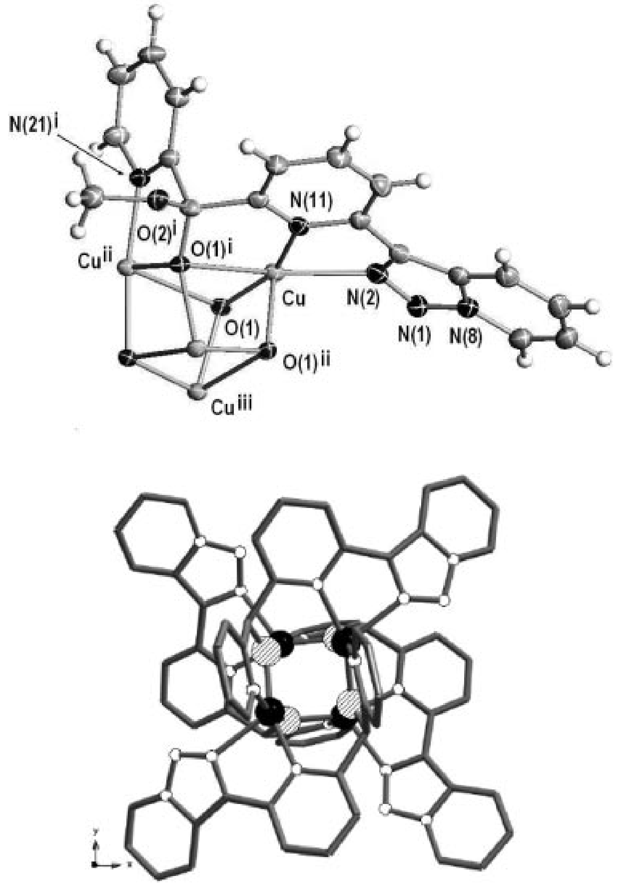


Figure 1. Ellipsoid plot of a representative fragment of the $[Cu(\mathbf{3B^*})]_4^{4+}$ cation with the representative atom numbering (left). Thermal ellipsoids are represented at 50% probability level. View of a complete $[Cu(\mathbf{3B^*})]_4^{4+}$ cation seen along 001 direction [copper (black spheres), oxygen (striped spheres), nitrogen (white spheres)].

2.250(2), and Cu–O(1)^{i} = 2.5775(19) Å [i: $-x + 2$, $-y + 1/2$, $+z$; ii: $-y + 5/4$, $+x - 3/4$, $-z + 5/4$].

The O(1) atom connects three Cu^{II} ions which in addition are coordinated to three O(1) atoms in an approximately orthogonal fashion defining a distorted cube in which the oxygen and copper atoms are arranged in an alternate way. The angles defined by these atoms in the distorted cube are Cu–O(1)–Cu^{i} 89.20(7), Cu^{i}–O(1)–Cu^{iii} 89.15(7), Cu–O(1)–Cu^{iii} 110.10(9)° and O(1)–Cu–O(1)^{i} 87.83(7), O(1)–Cu–O(1)^{ii} 88.16(7) and O(1)^{i}–Cu–O(1)^{ii} 72.58(7)°. The N(11)-pyridine ring forms dihedral angles of 22.00(7)° and 87.02(10)° with the triazolopyridine and the N(21)-pyridine rings, respectively. The NO_3^- anions and the H_2O molecules interact via hydrogen bonding defining a 3D supramolecular framework with large dodecagon-like section channels where the cationic cubane [Cu(**3B***)]$_4^{4+}$ complexes are intalled (see Figures 2 and 3).

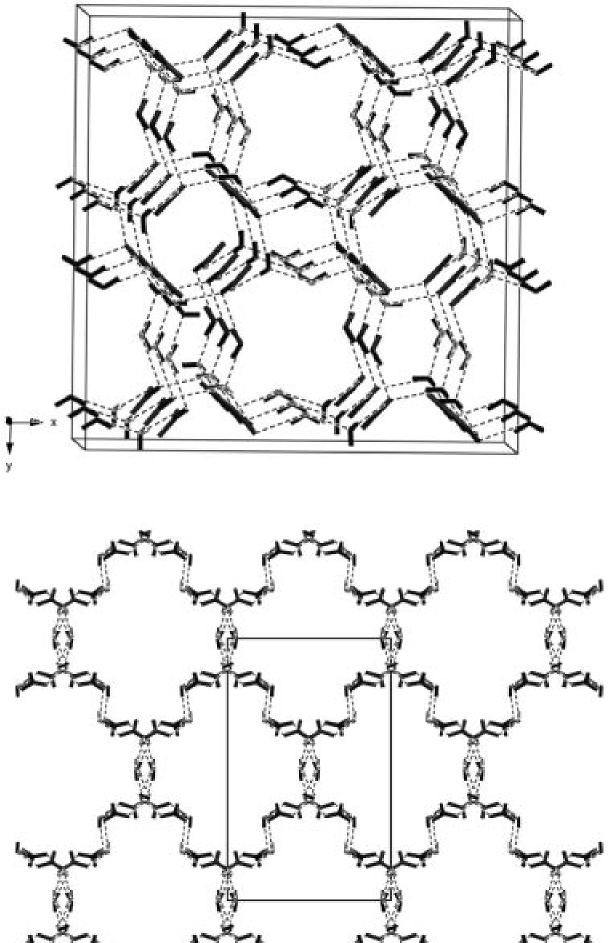


Figure 2. Supramolecular 3D framework defined by hydrogen bond interactions between NO_3^- and H_2O. View of the unit cell along *z* direction (left) and perspective view along *y* direction (right). The tetranuclear cations, which fill the dodecagonal motives, have been eliminated for simplicity. Doted lines represent the hydrogen bonds.

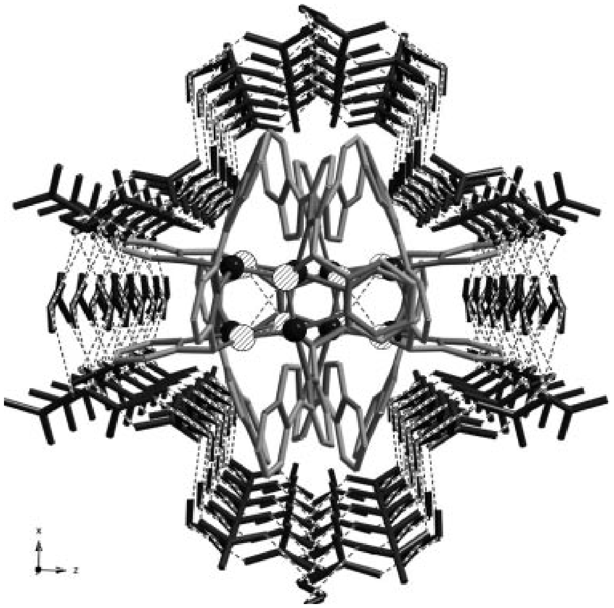


Figure 3. View of a dodecagonal channel loaded with two adjacent [Cu(**3B***)]$_4^{4+}$ cations. Dotted lines represent the hydrogen bonds. Hatched and black spheres correspond to the oxygen atoms of the cubane and the copper ions, respectively.

The hydrogen bond lengths [Å] and angles [°] are: $H_2O(21)\cdots O(11)NO_2$: H(1A)···O(11) 2.10(3), O(21)···O(11) 2.950(4), O(21)–H(1A)···O(11) 159(5); $H_2O(21)$–H(1B)···O(22)^{iv}: H(1B)···O(22)^{iv} 1.85(2), O(21)···O(22)^{iv} 2.740(5), O(21)–H(1B)···O(22)^{iv} 166(6); $H_2O(22)\cdots O(13)^{v}NO_2$: H(2A)···O(13)^{v} 2.12(3), O(22)···O(13)^{v} 2.893(4), O(22)–H(2A)···O(13)^{v} 152(4); $H_2O(22)\cdots O(11)NO_2$: H(2B)···O(11) 2.03(2), O(22)···O(11) 2.853(4), O(22)–H(2B)···O(11) 165(4); $H_2O(22)\cdots O(12)^{v}NO_2$: H(2A)···O(12) 2.58(3), O(22)···O(12) 3.351(4), O(22)–H(2A)···O(12) 152(4) and $H_2O(22)\cdots O(12)^{v}NO_2$: H(1A)···O(12)^{v} 2.59(5), O(22)···O(12)^{v} 3.262(5), O(22)–H(1A)···O(12)^{v} 132(5) [iv: $-x + 3/2$, $-y + 3/2$, $-z + 3/2$ and v: $-y + 5/4$, $x - 1/4$, $z - 1/4$].

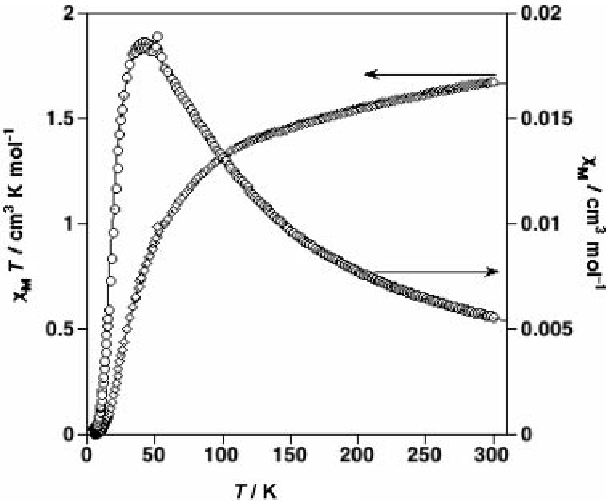


Figure 4. χ_M and $\chi_M T$ product vs. *T* plots of [Cu(**3B***)]$_4$(NO$_3$)$_4$·8H$_2$O.

The magnetic properties of the title compound are displayed in Figure 4 in the form of χ_M and $\chi_M T$ vs. T, where χ_M represents the magnetic susceptibility per mol of compound and T the temperature. The $\chi_M T$ product is equal to $1.67\,cm^3\,K\,mol^{-1}$, which corresponds quite well to the expected value for four weakly or uncoupled S = ½ centres. This value decreases continuously up to reach a value close to cero below 10 K. In contrast the χ_M value increases continuously from $5.50 \times 10^{-3}\,cm^3\,mol^{-1}$ at 300 K until $1.86 \times 10^{-2}\,cm^3\,mol^{-1}$ at ca 43 K where the χ_M vs. T curve passes through a maximum and then decreases to reach values close to cero below 10 K. This behaviour corresponds to intramolecular antiferromagnetic coupling. This magnetic behaviour can be explained in terms of the isotropic Heisenberg–Dirac–van Vleck Hamiltonian (1).

$$H = -2\sum_{i,j} J_{ij} S_i S_j \tag{1}$$

which in the case of a tetranuclear Cu_4O_4 core with S_4 symmetry becomes Equation (2) (see also Figure 5, a).

$$H = -2J_{1,2}(S_1S_2 + S_3S_4) - -2J_{1,3}(S_1S_3 + S_2S_3 + S_2S_4 + S_1S_4) \tag{2}$$

The analytical of χ_M vs. T curve deduced from Equation (2) can be expressed as follows in Equation (3).

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \cdot \frac{A}{B} + N\alpha \tag{3}$$

where

$A = 2\exp(2J_{1,2}/kT) + \exp[(4J_{1,2} - 2J_{1,3})7kT] + 5\exp[(4J_{1,2} + 2J_{1,3})/kT]$

$B = 1 + 6\exp[(2J_{1,2})7kT] + \exp[(4J_{1,2} - 4J_{1,3})7kT] + 3\exp[(4J_{1,2} - 2J_{1,3})7kT] + 5\exp[(4J_{1,2} + 2J_{1,3})/kT]$

The relevant parameters have been obtained by least-squares fitting of Equation (3) to the experimental data. The parameter $N\alpha$ has been fixed at $240 \times 10^{-6}\,cm^3\,mol^{-1}$. The best fit for calculated and experimental χ_M values has been found for $2J_{13} = -37.4\,cm^{-1}$, $2J_{12} = -2.6\,cm^{-1}$, $g = 2.16$ and $R = 1 \times 10^{-4}$. R is the agreement factor defined as $\Sigma_i\{(\chi_M)_i^{exp} - [(\chi_M)_i^{calc}]^2/[(\chi_M)_i^{exp}]^2\}$. The solid line in Figure 4 corresponds to the calculated curve showing that an excellent agreement between the experimental and theoretical χ_M data is achieved. The magnitude and sign of J_{12} and J_{13} is determined by the angle Cu–O–Cu, Cu–O distances (d_1, d_2) and the orientation of the orbitals bearing the unpaired electrons (ie $d_{x^2-y^2}$) (see Figure 5, b–d). The exchange pathway determining the $J_{1,2}$ value involves two short and two long Cu–O distances (Figure 5, d), consequently direct overlap between the $d_{x^2-y^2} - d_{z^2}$ orbitals instead of the $d_{x^2-y^2} - d_{x^2-y^2}$ orbitals is observed. Hence, $J_{1,2}$ is expected to be very small and in general positive (ferromagnetic) due to the small participation of the d_{z^2} orbital in the ground state of the Cu^{II} [α(Cu–O–Cu) = 89.15°, d_2 = 2.578 Å]. Although the exchange pathway $J_{1,3}$ is not appropriate for strong magnetic coupling it is expected to be significantly stronger than $J_{1,2}$ and antiferromagnetic in nature, given that the occurrence of a short Cu–O distance (d_1 = 1.998 Å) and a β(Cu–O–Cu) angle equal to 110.10° facilitates partial overlap between the $d_{x^2-y^2}$ orbitals.

Álvarez and co-workers have recently performed magnetostructural correlations in polynuclear complexes containing Cu_4O_4 cubane structure employing theoretical calculations based on DFT.[21] For S_4, also referred 4+2, cubanes their theoretical calculations predict that $J_{1,2}$ is small in magnitude, ferromagnetic and little dependent on the geometrical parameters. On the contrary, $J_{1,3}$ displays larger influence of the geometry and changes from ferro- to antiferromagnetic in nature for β angles larger than 104°. These predictions clearly justify the results obtained for the title compound. The negative sign of J_{12} may be a consequence of its very small magnitude together with some correlation in the evaluation of the J_{13} parameter.

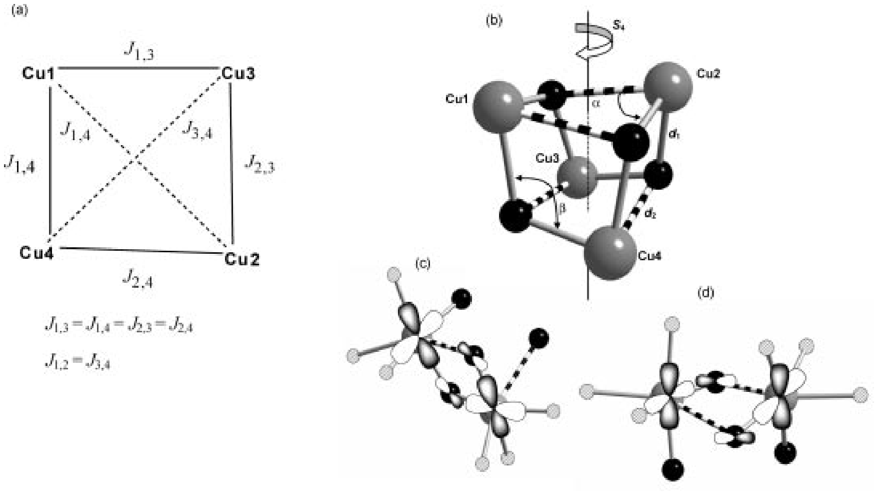


Figure 5. Scheme of the spin-coupling model used for the analysis of the magnetic data (a). Arrangement of the copper atoms in the cubane (b). Magnetic exchange pathways (c) and (d), see text.

Conclusions

In summary we have demonstrated the capability of the polydentate ligand (pyridin-2-yl){6-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridin-2-yl}methanone to afford tetranuclear Cu^{II} complexes. A next step in this research will require the synthesis of novel tetranuclear complexes with other divalent and trivalent first row transition metal ions.

Experimental Section

Synthesis: To a solution of (pyridin-2-yl){6-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridin-2-yl}methanone (**3B**) (48 mg, 0.15 mmol) in ethanol (30 mL), a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (40 mg, 0.16 mmol) in water (10 mL) was added. A green solution was formed. It was leaved covered at room temperature till the formation of green crystals, which were filtered and recrystallized from methanol (31.48 mg, 40% yield). $C_{72}H_{72}Cu_4N_{24}O_{28}$ (1975.7): calcd. C 43.76, H 3.65, N 17.02; found C 43.41, H 3.72, N 16.75.

Magnetic Susceptibility Measurements: The variable-temperature magnetic susceptibility measurements were performed on small single crystals by using a Quantum Design MPMS2 SQUID susceptometer equipped with a 5.5 T magnet and operating at 1 T and 1.8–375 K. Experimental data were corrected for diamagnetism using Pascal's constants.

Crystal Data: Green needle, 0.42 × 0.12 × 0.10 mm size, tetragonal, $I4_1/a$, $a = 23.089(3)$, $c = 14.463(3)$ Å, $V = 7710(2)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.702\ g\,cm^{-3}$, $\theta_{max} = 28.29$, Mo-K_α, $\lambda = 0.71073$ Å, ω-scan, diffractometer Nonius Kappa CCD, $T = 120(2)$ K, 27774 reflections collected of which 4765 were independent ($R_{int} = 0.077$), direct primary solution and refinement on F^2 (SHELXS-97 and SHELXL-97, G. M. Sheldrick, University of Göttingen, 1997), 304 refined parameters, OH_2 hydrogen atoms were located in a difference Fourier synthesis, other hydrogen atoms were included using a riding model or as rigid methyl groups, $R_1[I > 2\sigma(I)] = 0.0441$, wR_2(all data) = 0.1132.

CCDC-641246 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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