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Supplementary materials

Tetranuclear Cu(II) Complex Supported by a Central μ_4 -1,1,3,3 Azide Bridge

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Materials and Physical Measurements. The chemicals used were obtained from the following sources: Triethylenetetramine, Cupric chloride dihydrate and sodium azide from S.D. Fine Chem (India). 2-hydroxy acetophenone from Spectrochem (India). All other chemicals and solvents were reagent grade materials and were used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin-Elmer model 240 C elemental analyzer. Infrared spectra was recorded as KBr pellet on a Nicolet Nexus-870 FTIR spectrophotometer. The solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about $10^{-3} M$ and a Shimadzu UV 3100 UV-vis-NIR spectrophotometer respectively. The room temperature magnetic susceptibilities in the solid state were measured using a home built Gouy balance fitted with a polytronic d.c. power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (ca. 30 mg) using a Quantum Design MPMS XL-5 SQUID susceptometer operating at a constant magnetic field of 1 T between 2 and 300 K. The experimental magnetic moment was corrected for the diamagnetic response from the sample, which was evaluated from Pascal's constants

Crystallographic data of 1. $C_{60}H_{98}N_{11}O_{22}CICu_4$: $M_r = 1614.52$, monoclinic, space group *C 2/m* (No.12), a = 14.769(4) Å, b = 18.012(8) Å, c = 13.517(9) Å, $\beta = 103.60(2)^\circ$, V = 3495.0(3) Å³, $\rho_{calcd} = 1.504$ g/cm³ and Z = 2. With the use of 3079 unique reflections collected at 293 K with Mo K α radiation ($\lambda = 0.71073$ Å) out to θ range = 2.16 to 24.97° on a Bruker-Nonius Mach3 CAD4 single-crystal X-ray diffractometer, the structure was solved by using the SHELX-97 programme and refined by full-matrix least squares methods. The refinement converged to final R1 = 0.0810, wR2 = 0.1915; and GOF = 0.997 with the largest difference peak and hole as 0.899 and -0.980 e Å⁻³ respectively. CCDC number 292303.

Table for selected bond length and bond angles of 1

Bond lengths

Cu(1)-O(2)	1.880(5)	Cu(1)-N(2)	2.072(6)
Cu(1)-N(1)	1.945(6)	Cu(1)-N(3)	2.406(8)
Cu(1)-O(1)	1.987(4)	N(4)-N(3)	1.136(11)

Bond angles

O(2)-Cu(1)-N(1)	93.3(2)	O(2)-Cu(1)-O(1)	90.0(2)
N(1)-Cu(1)-O(1)	154.0(3)	O(2)-Cu(1)-N(2)	179.8(2)
N(1)-Cu(1)-N(2)	86.5(2)	N(2)-Cu(1)-O(1)	90.2(2)
O(2)-Cu(1)-N(3)	89.8(3)	N(1)-Cu(1)-N(3)	122.2(3)

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O(1)-Cu(1)-N(3)	83.5(2)	N(2)- Cu(1)-N(3)	90.3(3)
Cu(1)-O(1)-Cu(1)#	105.2(3)	Cu(1)-N(3)-Cu(1)#	82.0(3)

Experimental procedure for synthesis of complex $[Cu^{II}_4(\mu-L)(\mu-N_3)]$ ·Cl·16H₂O (1). To the dichloromethane solution (15 ml) of the ligand (0.50g, 1.00 mmol) methanolic solution of CuCl₂.2H₂O (0.34 g, 2.00 mmol) was added dropwise followed by dilute methanolic solution of NEt₃ (0.14 ml, 1.00 mmol) with stirring at ambient temperature in air. The reaction mixture was then stirred for 1hour more. The complex [Cu₂L(H₂O)]Cl·2H₂O (2) was precipitated as a green solid (~85 % yield) which was isolated, washed with water, and dried under vacuum over P₄O₁₀. In the second step the complex 2 (0.50 g, 0.72 mmol) was dissolved in MeCN (15 ml) and methanolic solution of NaN₃ (0.03g, 0.45 mmol) was added dropwise with stirring. The resulting solution was stirred for 30 mins more. The green colored solid of complex 1 was precipitated (~70 % yield), was filtered washed with water, and dried under vacuum over P₄O₁₀. Complex 1 can also be prepared by the direct reaction of H₃L, CuCl₂, NaN₃ and NEt₃ in the 1:2:1:2 molar ratio. The single crystals suitable for X-ray analysis was obtained from 1:1 MeOH-MeCN during 5 days. Anal. Calcd for C₆₀H₉₈N₁₁O₂₂ClCu₄: Mwt = 1614.52. C, 44.63; H, 6.11; N, 9.54; Cu, 15.75. Found: C, 44.64; H, 6.27; N, 9.88; Cu, 16.28 % . Molar conductance, A_M: (DMF solution) 78 ohm⁻¹ cm² mol⁻¹. UV-visible spectrum [λ_{max} , nm (ε , Imol⁻¹cm⁻¹]: (DMF solution) 585 (860), 407 (2760), 364 (20735), 273 (26845). Infrared spectrum (cm⁻¹, KBr disk):v = 3411(b), 2948(m), 2042(vs), 1600(s), 1533(s), 1441(s), 1346(s), 1233(s), 755(s).

Caution!! Azide derivatives are potentially explosive, only a small amount of materials should be prepared, and they should be handled with proper care.

Figures with captions



Figure S1. The Packing Diagram of $[Cu^{II}_4(\mu-L)_2(\mu-N_3)]^+$ cation viewed down c (001) axis, Cl⁻ ions and water molecules are deleted for clarity.

References

(1) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttinegen, Germany, 1997.