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Synthesis and characterisation of a hexanuclear copper (I) cluster coordination compound

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A novel hexanuclear copper (I) cluster coordination compound has been synthesised by the reaction of *N*-ethoxycarbonyl-*N'*-*o*-chlorophenylthiourea with cupric chloride in ethanol solution.

Keywords: cluster, hexagonal ring, crystal structure

Various multinuclear copper cluster coordination compounds have been reported in the last decade with a great number of simple and sophistical ligands.[1-3] However, to date little is known about metal clusters involving more than four metal centres. Acylthiourea ligands have been of great interest in recent years because of the existence of acyl and thiocarbonyl groups in the molecules, which enhance their coordination ability. Our research efforts have been focused on the coordination behaviour and molecular structure of thiourea coordination compound with transition metals.[4,5] Usually, the coordination compounds of copper (II/I) with thiourea derivatives have tetrahedral and triangular coordination geometries.[5,6] In earlier literature,[4] we reported the reaction of *N*-benzoyl-*N'*-(2-hydroxyethyl)thiourea with cupric chloride. In this reaction, desulfurisation and cyclisation occur and an oxazoline ring is formed in the resulting complex. As far as we are aware, this novel synthetic method to an oxazoline copper complex was not reported in the previous publications on hydroxyethyl thiourea. Here we report the coordination reaction of *N*-ethoxycarbonyl-*N'*-*o*-chlorophenylthiourea with cupric chloride. In this reaction, an unexpected Cu_6 hexanuclear cluster compound (**1**) is obtained, which is completely different from the other products of the reactions of thiourea with transition metals.

The *N*-ethoxycarbonyl-*N'*-*o*-chlorophenylthiourea was prepared according to our previous work.[7] To ethanol (20 ml) containing *N*-ethoxycarbonyl-*N'*-o-chlorophenylthiourea (2 mmol) was added an ethanol solution of cupric chloride (1mmol). After stirring the solution at room temperature for 2 h, the mixture was filtered to obtain solid product, which was then dried in air. The solid was dissolved in chloroform and single crystals of the hexameric coordination compound **1** were obtained, after two weeks, by slow evaporation of the chloroform solution. Yield 40%. m. p. 148–150°C. *Anal.* Cala. For $C_{60}H_{60}Cl_6Cu_6N_{12}O_{12}S_6$: C, 37.35; H, 3.11; N, 8.71. Found: C, 38.23; H, 3.67; N, 8.95. IR (KBr disc): 3115vs, 1675vs, 1507vs, 1337s, 1230vs, 1045m, 939m, 720w. ^{1}H NMR ($CDCl_3$): δ1.28 (1H, CH_3), δ4.25 (2H, CH_2), δ7.25–8.40 (4H, C_6H_4), δ11.50 (1H, NH).

In many cases of the synthesis of copper complexes, irreversible Cu(II)/Cu(I) systems have been observed.[8,9] In our process for the synthesis of **1**, the cuprous coordination compound was obtained from the reaction of cupric ions with thiourea. The reducing agent in this reaction is thiourea ligand as reported in previous publications.[10,11]

Compound **1** was subjected to single crystal X-ray crystallography.[12] The structure was solved directly using the SHELXS-97 program[13] and refined with the SHELXL-97 program.[14] In the molecular crystal structure, a central Cu_6 unit is formed, Copper (I) ions bond to each other with Cu–Cu bonds, and form a hexagonal ring structure. The hexagonal ring presents chair conformation as in cyclohexane, and forms an octahedral structure. This structure accords with the copper cluster structural stability and energetic calculation results in the previous literature.[15] Cu-Cu bond distances are 2.713Å, 2.899Å and 2.980Å. Cu1–Cu2A, Cu1–Cu3A, Cu1A–Cu2, Cu1A–Cu3, Cu2–Cu3 and Cu2A–Cu3A are connected together respectively through sulfur bridge atoms of thiourea ligands. The Cu–S bond distance range is 2.226Å to 2.266 Å. On the other hand, the nitrogen atom, which is between thiocarbonyl and carbonyl groups, loses one proton to form a nitrogen anion, and coordinates with the Cu(I) ion. Cu–N bond distances are 2.017Å, 2.026Å and 2.007Å.

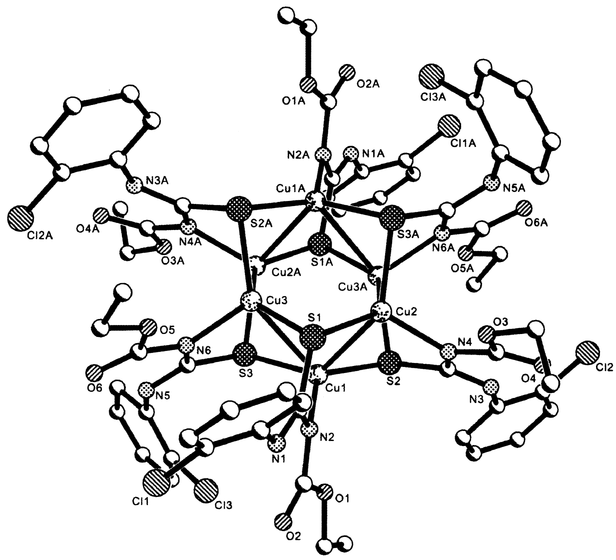

Fig. 1 View of the crystal structure of compound **I** showing the atomic numbering. Selected bond distances (Å) and angles (°): Cu1–Cu2 2.7132(15), Cu1–Cu3 2.8994(16), Cu1–N2 2.017(6), Cu1–S2 2.234(2), Cu1–S3 2.266(2), Cu2–Cu3A 2.9799, Cu2–N4 2.026(6), Cu2–S1 2.233(2), Cu2–S3A 2.2837, Cu3–N6 2.007(7), Cu3–S1 2.226(2), N2–Cu1–S2 126.2(2), N2–Cu1–S3 118.0(2), S2–Cu1–S3 109.63(9), N2–Cu1–Cu2 87.60(19), S2–Cu1–Cu2 79.06(7), S3–Cu1–Cu2 130.86(8), N2–Cu1–Cu3 85.32(19), S2–Cu1–Cu3 133.10(8), S3–Cu1–Cu3 73.40(6), Cu2–Cu1–Cu3 67.49(4).

The six Cu(I) ions have similar coordination environments. Each Cu(I) ion possesses a distorted tetragonal pyramidal geometry. Nitrogen atoms are located in axial positions. Cu2, Cu3, S2 and S3 around Cu1 in one least-squares plane with mean deviation 0.0258Å occupy equatorial positions. Cu1,

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Table 1 Crystal data and structure refinement for complex **I**

Crystal dimension (mm)	0.18×0.14×0.10
Formula	$C_{60}H_{60}Cl_6Cu_6N_{12}O_{12}S_6$
M_r	1927.62
Crystal system	Triclinic
Space group	P-1
a /Å	11.811 (4)
b /Å	12.287 (5)
c /Å	14.396 (5)
β /°	67.373(6)
U / Å^3	1878.3(12)
Z	2
Dc/ g cm^{-3}	1.704
μ (mm^{-1})	2.113
F (000)	972.0
Radiation	MoKα
Graphite monochromator	λ=0.71073Å
Diffractometer	Bruker Smart-1000 CCD area detector
Temperature (K)	293 (2)
Scan method	φ and ω scans
h; k; l range	−14→13; −14→13; −17→13
θ_{max} /°	25.00
No. of observed reflexions	3497
No. of parameters	473
Unique reflexions, R_{int}	6570, 0.057
R^a_1, wR^b_2	0.065; 0.1652
Max, minimum residue/eÅ^{-3}	0.604, −0.738

Cu2A, S1 and S2A around the Cu3 atom are similarly located in one least-squares plane with mean deviation 0.0003Å.

The Cu_6 cluster structure obtained in this reaction is definitely different from the oxazoline copper (I) coordination compound reported by Zhang *et al.*[4] Comparing with the hydroxyethyl thiourea used in ref. 4, the ligand used in this reaction has no hydroxy group, and the reactive character of *o*-chlorophenyl group is constant. The different results of the coordination reaction of cupric chloride with related ligands appears to arise from the electron attractive effect of the substituted group on the benzene ring in the ligand, but how the electron attractive effect influences the coordination character of the ligand still remains to be established by more research.

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