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NOTE

Hydrothermal Synthesis and Structure of Tetraazamacrocyclic Copper Complex

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A new tetraazamacrocycle copper(II) complex with the m.f. $C_{24}H_{40}N_8S_4Cu_2$ was synthesized by hydrothermal reaction and characterized by IR spectra and single-crystal X-ray diffraction. The crystal is in a triclinic system, space group P-1 with unit cell parameters: a = 8.861(3)Å, b = 18.832(7)Å, c = 20.826(6)Å, α = 74.194(12)º, β = 80.025(13)º, γ = 79.714(9)º, V = 3261.5(19)Å^3, Z = 4, Mr = 695.96, Dc = 1.417 Mg/cm^3, μ = 1.588 mm^{-1}, F(000) = 1448, T = 298(2) K, R = 0.0695, wR = 0.1584 for 11405 reflections with I > 2σ(I). The crystal structure analysis shows that the Cu(II) ion was coordinated by four nitrogen atoms of the tetraazamacrocycle.

Keywords: Copper complex, Tetraazamacrocycle, Hydrothermal synthesis, Crystal structure.

In recent years, there has been increasing interest of azamacrocyclic transition metal complexes in the design of molecular construction due to their stability and ease of chemical modification[1-4]. In our laboratory, a series of azamacrocyclic transition metal complexes were synthesized and reported[5-9].

In this paper, a tetraaza macrocyclic copper complex $CuL{\cdot}Cu(NCS)_4$ (L = 5,7,2,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) is reported.

All reagents were of AR grade and used without further purification. $L{\cdot}(ClO_4)_2$ was prepared by our laboratory. IR spectra were recorded on a Nicolet 380 spectrophotometer. The crystal structure was determined by Siemens SMART CCD area-detector diffractometer.

Synthesis: An acetonitrile solution (10 mL) of $L{\cdot}(ClO_4)_2$ (10 mmol) and aqueous solution (15 mL) of a mixed $Cu(ClO_4)_2$ (5 mmol) and $K_2[Cu(SCN)_4]$ (5 mmol) were carried out in a autoclave and heated to 90 ºC for 48 h. After cooling, the black blue columnar single crystals were obtained. Yield 36 %. IR spectrum (KBr, ν_{max}, cm^{-1}): 3410, 3190,2080, 1650, 1480, 1380, 1060, 989.

Crystal structure determination: A single crystal (0.42 mm × 0.35 mm × 0.15 mm) was selected for crystallographic data collection at 298(2) K and structure determinated with graphite monochromatic MoK$_\alpha$ radiation (λ = 0.71073Å). A total of 20898 reflections were collected in the range of 1.71º ≤ θ ≤ 25.03º, of which 11405 reflections were unique with Rint = 0.0303 and R = 0.0695 and wR = 0.1584, where w = 1/[$s^2(F_0^2)$ + (0.0710P)^2 + 4.1425P], P = (F_0^2 + 2F_0^2)/3. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.763 and -0.548 e/Å^3 (CCDC No. 646136), respectively.

The atomic coordinates and thermal parameters are listed in Table-1 and the selected bond lengths and bond angles in Table-2. Fig. 1 shows the molecular structure of the present copper(II) compound. Fig. 2 shows the packing diagram of the title compound. From the Fig. 1, it is easy to see that the copper(II) ion is four-coordinated with four nitrogen atoms of the tetraazamacrocycle.

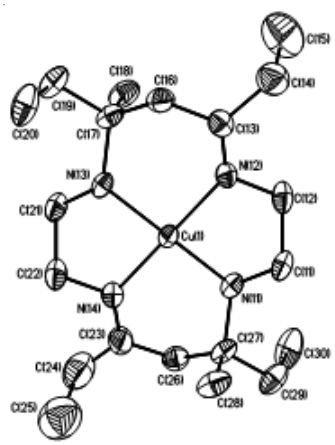

Fig. 1. Molecular structure of the $[CuL]{\cdot}Cu(NCS)_4$

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^3 Å^2)

Atom	X	Y	Z	U(eq)
Cu(1)	583(1)	4944(1)	7529(1)	44(1)
Cu(4)	-5716(1)	-2333(1)	2361(1)	75(1)
N(11)	1536(5)	5867(2)	7075(2)	47(1)
N(12)	-372(5)	5471(2)	8233(2)	48(1)
N(1)	-7005(7)	-2835(3)	3137(3)	83(2)
N(3)	-6933(6)	-1599(3)	1725(3)	74(2)
S(1)	-8555(3)	-3673(1)	4282(1)	103(1)
S(3)	-8495(2)	-603(1)	730(1)	84(1)

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Length	Angle	(°)	Angle	(°)
Cu(1)-N(11)	1.995(4)	N(14)-Cu(1)-N(12)	179.81(18)	C(11)-N(11)-C(27)	116.6(4)
Cu(1)-N(12)	1.978(4)	N(14)-Cu(1)-N(11)	94.36(18	C(11)-N(11)-Cu(1)	105.7(3)
Cu(4)-N(1)	1.930(7)	N(12)-Cu(1)-N(11)	85.60(18)	C(27)-N(11)-Cu(1)	117.8(3)
Cu(4)-N(3)	1.948(6)	N(4)-Cu(4)-N(1)	111.9(3)	C(11)-N(11)-C(27)	116.6(4)
S(1)-C(1)	1.622(8)	N(4)-Cu(4)-N(3)	111.5(2)	C(1)-N(1)-Cu(4)	173.2(6)
S(3)-C(3)	1.619(7)	N(3)-Cu(4)-N(2)	107.6(2)	C(2)-N(2)-Cu(4)	178.0(6)

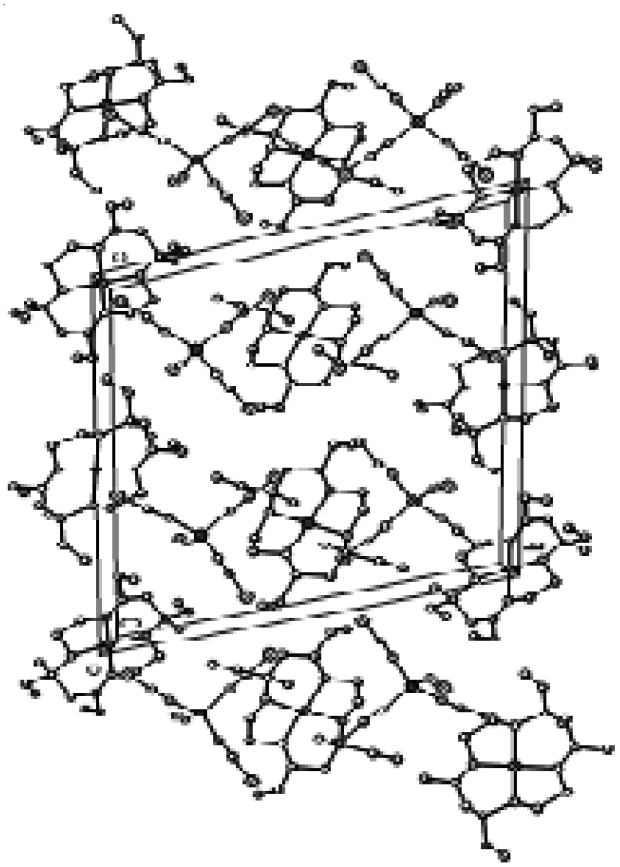

Fig. 2. Molecular packing arrangement in the unit cell

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