Asian Journal of Chemistry; Vol. 24, No. 2 (2012), 939-940

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

NOTE

Synthesis and Crystal Structure of $[CuL]\cdot(SCN)_2$

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(*Received*: 25 May 2011; *Accepted*: 24 October 2011) AJC-10566

A new metal-organic complex $[CuL]\cdot(SCN)_2$ (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane·$2ClO_4$) has been synthesized by the reaction of CuL with potassium thiocyanate and investigated by infrared spectrometry, elemental analysis and X-ray diffraction. The crystal belongs to monoclinic crystal system and has space group P2(1)/c with a = 7.6549(6) Å, b = 9.4174(8) Å, c = 16.3539 (16)Å. α = 90 °, β = 101.508(4)°, γ = 90°, v = 1155.24(17)Å^3, z = 2, Dc = 1.334Mg/m^3, M_r = 464.19, F(000) = 494 and μ = 1.141 mm^{-1}. The final R = 0.0861, wR = 0.2352 for 8186 observed reflections with I > 2σ(I). In terms of the crystal structure, copper(II) ion is four-coordinated with four nitrogen atoms in the skeleton of tetraazamacrocyclotetradecane, showing a slightly distorted square geometry.

Key Words: Tetaraazamacrocycle, Synthesis, Copper(II) complex, Crystal structure.

The structure of the azamacrocyclic metal complexes is similar to the basic structural units of the metalloenzymes which exist widely in the nature[1,2]. In recent years, it has been discovered that the azamacrocyclic complexes are important in biosimulation, biomimic catalysis, molecular recognition, photosensing material and magnetic materials[3-5]. Many this kind of such complexes have been reported also[6-8].

In this paper, the synthesis and crystal structure of the complex $[CuL]\cdot(SCN)_2$ (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazamacrocyclotetra decane·$2ClO_4$) are reported.

All reagents were of AR grade and used without further purification. The CuL was synthesized according to the literature[9]. IR spectra was record on a Nexus-870 spectrophotometer. Elemental analyses for C, H and N were performed on a Elementar Vario EL-III analyzer. The crystal structure was determined by Siemens SMART CCD area-detector diffractometer.

Synthesis: 25 mL CH_3CN solution of CuL (10 mmol) was respectively added to 25 mL H_2O solution of KSCN (30 mmol), then refluxed for 1 h. After filtered, the bluish violet colour rhomboid crystals were isolated from the solution at room temperature over two weeks. IR (KBr, ν_{max}, cm^{-1}): 3420, 3150, 2970, 2040,1620, 1460, 1190, 1090. Anal. calcd.: C, 46.58; H, 7.82; N, 18.10 %. Found: C, 46.52; H, 7.87; N, 18.14 %.

Structure determination: A single crystal (0.40 mm × 0.35 mm × 0.30 mm) was selected for crystallographic data collection at 293(±2) K and structure determinated with graphite-monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 8186 reflections were collected in the range of 3.47° ≤ θ ≤ 27.48°, of which 2621 reflections were unique with Rint = 0.0151 and R = 0.0861, wR = 0.2352, where $w = 1/[\sigma^2(F_0^2) + (0.1293P)^2 + 2.5277P]$ and $P = (F_0^2 + 2FC^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.568 and -1.189e/Å^3 (CCDC No.667028), respectively.

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond lengths and bond angels are in Table-2. The molecular structure of $[CuL]\cdot(SCN)_2$ is shown in Fig. 1, in which the center copper(II) ion is coordinated to four nitrogen atoms from the skeleton of tetrazamacrocyclotetradecane, showing a slightly distorted square geometry. As shown in the packing diagram (Fig. 2), there are positive

TABLE-1
ATOMIC COORDINATES (×10^4) AND THERMAL PARAMETERS (×103 Å2)

Atom	X	Y	Z	U(eq)
Cu	5000	5000	5000	54(1)
S	8236(5)	1442(3)	4301(2)	132(1)
N(1)	4918(4)	7036(3)	4542(2)	36(1)
N(2)	2833(4)	4365(3)	4155(2)	36(1)
N(3)	7810(30)	4192(11)	4253(8)	315(13)
C(1)	5698(7)	6926(7)	3141(3)	67(2)
C(2)	3912(9)	8964(6)	3527(4)	74(2)
C(3)	4288(6)	7361(4)	3632(2)	42(1)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

Bond	Distance	Angles	(º)
Cu-N(1)	2.055(3)	N(2)-Cu-N(2)#1	180.000(1)
Cu-N(2)	2.026(3)	N(2)-Cu-N(1)	93.74(13)
S-C(9)	1.485(9)	N(2)#1-Cu-N(1)	86.26(13)
N(1)-C(3)	1.502(5)	C(8)#1-N(1)-C(3)	115.2(3)
N(2)-C(7)	1.476(5)	C(8)#1-N(1)-Cu	105.2(2)
N(2)-C(5)	1.492(5)	C(3)-N(1)-Cu	122.2(2)
N(3)-C(9)	1.125(11)	C(7)-N(2)-C(5)	113.1(3)
C(1)-C(3)	1.524(7)	C(7)-N(2)-Cu	105.8(2)
C(2)-C(3)	1.540(6)	C(5)-N(2)-Cu	118.5(2)
C(3)-C(4)	1.529(6)	N(1)-C(3)-C(1)	110.3(4)

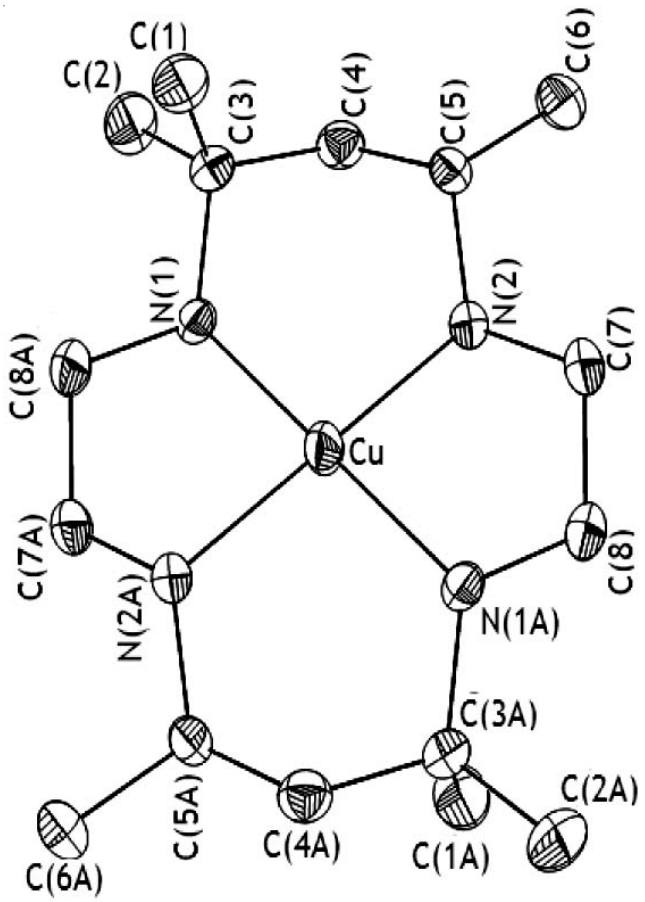

Fig. 1. Structure of the $[CuL]^{2+}$ cation

negative charge interactions between $[CuL]^{2+}$ cation and two thiocyanate anions.

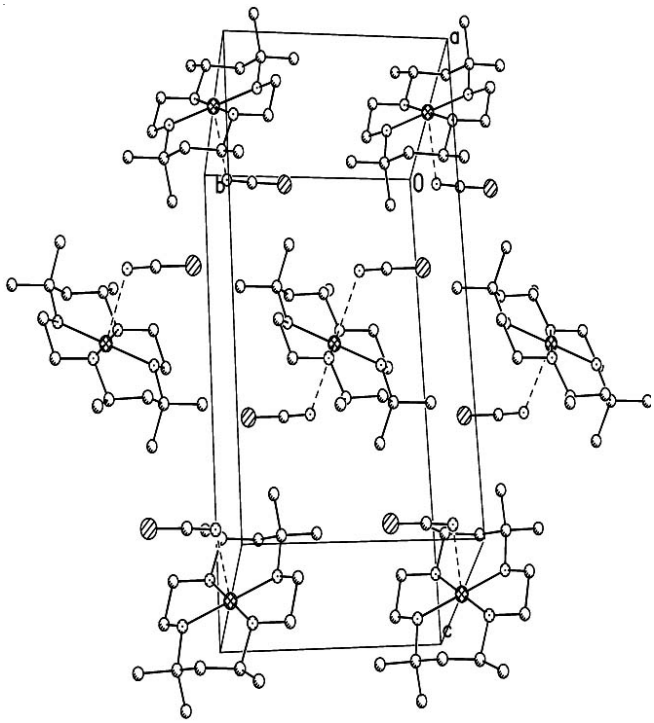

Fig. 2. Molecular packing arrangement

ACKNOWLEDGEMENTS

This work is financially supported by Natural Science Foundation of China (20871039). Follow-up support from the Nature Science Foundation of Anhui Universities (KJ2011Z299) and Key Disciplines Foundation of Hefei Normal University.

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