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NOTE

Synthesis and Crystal Structure of a Tetraazamacrocyclic Copper(II) Complex

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The copper(II) complex $[CuL]\cdot(ClO_4)_2$ (L= 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazamacrocyclotetradecane·$2ClO_4$) has been synthesized and determined by X-ray diffraction. The crystal is monoclinic, space group P2(1)/n with unit cell parameters: a = 8.463(3)Å, b = 9.178(3)Å, c = 15.567(5)Å. α = 90º, β = 98.120(4)º, γ = 90º, v = 1197.0(6)Å^3, z = 2, Dc = 1.518 Mg/m^3, Mr = 546.93, F(000) = 574 and μ = 1.183 mm^{-1}. The final R and wR are 0.0379 and 0.1034, respectively for 2705 observed reflections with $I>2\sigma(I)$. The center copper(II) ion is four-coordinated in a slightly distorted square geometry.

Key Words: Tetaraazamacrocycle, Copper(II) complex, Structure.

The azamacrocyclic transition metal complexes have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid-liquid or solid-liquid phase-transfer reactions, preparation of ion-selective electrodes, isotope separations, understanding of some natural processes through mimicry of metalloenzymes, and so on[1-6].

In this communication, the synthesis and the structure of the complex $[CuL]\cdot(ClO_4)_2$ (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazamacrocyclotetradecane·$2ClO_4$) were reported.

All reagents were of AR grade and used without further purification. 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: 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetrazamacrocyclotetradecane·$2ClO_4$ (L) was synthesized according to the literature[7]. A mixture

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of 25 mL methanol solution of L (10 mmol) were respectively added 25 mL methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (10 mmol), then refluxed for 1 h. After filtered, the solution was kept at room condition for 6 d and then the blue colour rectangle crystals resulted from it. IR (KBr, ν_{max}, cm^{-1}): 1470, 1430 [m, ν(C=C)], 1090, 627 [s, $\nu(ClO_4^-)$]. Anal. calcd. (%) for $C_{16}H_{36}Cl_2CuN_4O_8$: C, 35.19; H, 6.63; N, 10.24. Found: C, 35.24; H, 6.37; N, 10.06.

Structure determination: A single crystal (0.40 mm × 0.30 mm × 0.30 mm) was selected for crystallographic data collection at 293(2)K and structure determinated with graphite-monochromatic MoKα radiation (λ = 0.71073Å). A total of 8580 reflections were collected in the range of $3.45 \leq \theta \leq 27.48°$, of which 2705 reflections were unique with $R_{int} = 0.0157$. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system[8] was used in the solution and refinements of the structure. The final full-matrix least-squares refinement including 142 variable parameters for 5997 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of R = 0.0734 and wR = 0.2139, where $w = 1/[\sigma^2(F_0^2)+(0.0631P)_2 + 0.6705P]$ and $P = (F_0^2 + 2FC^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.471 and -0.351e/Å^3 (CCDC No.646137), 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 $[CuL]\cdot(ClO_4)_2$ is shown in Fig. 1, in which the center copper(II) ion is four-coordinated in a slightly distorted square geometry. Fig. 2 shows the packing diagram in the unit cell, in which there are positive negative charge interactions between $[CuL]^{2+}$ cation and two perchlorate anions.

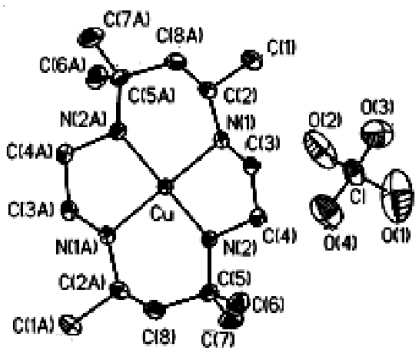

Fig. 1. Structure of the title compound

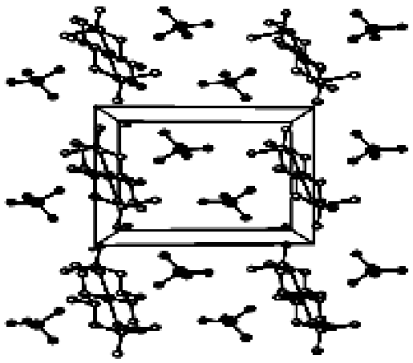

Fig. 2. Molecular packing arrangement

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

Atom	X	Y	Z	U(eq)
Cu	0	5000	5000	27(1)
N(1)	1104(2)	4389(2)	3984(1)	31(1)
N(2)	502(2)	2940(2)	5464(1)	32(1)
C(1)	1422(4)	4458(4)	2410(2)	67(1)
C(2)	453(3)	4979(2)	3108(1)	38(1)
Cl	6278(1)	2808(1)	4567(1)	57(1)
O(1)	7124(6)	1494(4)	4681(4)	192(2)

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

Bond	Dist.	Bond	Dist.	Angles	(º)	Angles	(º)
Cu-N(1)	2.0263(16)	N(1)-C(2)	1.498(3)	N(1)-Cu-N(1)#1	180.0	N(2)-Cu-N(2)#1	180.00(9)
Cu-N(2)	2.0470(17)	N(2)-C(4)	1.482(3)	N(1)-Cu-N(2)	85.63(7)	C(3)-N(1)-C(2)	112.86(16)
Cu-N(1)#1	2.0263(16)	C(1)-C(2)	1.527(3)	N(1)#1-Cu-N(2)	94.37(7)	C(3)-N(1)-Cu	106.31(12)
Cu-N(2)#1	2.0470(17)	Cl-O(1)	1.401(4)	N(1)-Cu-N(2)#1	94.37(7)	C(3)-N(1)-Cu	106.31(12)

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REFERENCES

1. P. Caravan, T.J. Ellison, T.J. McMurry and R.B. Laufer, *Chem. Res.*, **99**, 2293 (1999).
2. K.L. Zhang, Z. Wang, C.M. Jin and X.Z. You, *Transition Met. Chem.*, **27**, 95 (2002).
3. N.F. Curtis, *Inorg. Chim. Acta*, **317**, 27 (2001).
4. J.H. Bi, J.M. Song, Z.X. Huang, Y.H. Wang, L.T. Kong and N.L. Hu, *Asian J. Chem.*, **18**, 2365 (2006).
5. D.F. Cook, N.F. Curtis, O.P. Gladkikh and D.C. Weatherburn, *Inorg. Chim. Acta*, **355**, 15 (2003).
6. J.H. Bi, F.X. Xie, X.D. Zhao, Q. Chen, J.D. Xu and S.S. Ni, *Asian J. Chem.*, **16**, 137 (2004).
7. N.F. Curtis, *J. Chem. Soc.*, 4409 (1960).
8. G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Gottingen, Germany (1997).

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