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Synthesis and Crystal Structure of the One-dimensional Supramolecular Tetraazamacrocyclic Copper(II) Compound

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The copper(II) complex $[CuL](ClO_4)_2$ (L = 7,14-dimethyl-5,12-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been synthesized and crystal structure was determined by X-ray diffraction. Crystal data: $C_{24}H_{32}Cl_2CuN_4O_8$, orthorhombic, space group Fdd2, $a = 28.725(3)$ Å, $b = 41.074(5)$ Å, $c = 9.2397(11)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 10902(2)$ Å^3, Mr = 638.98, Z = 16, Dc = 1.557 g/cm^3, F(1000) = 5296, I = 1.052 mm^{-1}. The final R = 0.0827 and wR = 0.2319 for 5667 observed reflections ($I > 2\sigma(I)$). The centre copper(II) ion is coordinated by five atoms in a prolonged square pyramidal geometry. The compound is in one-dimensional supramolecular state.

Key Words: Crystal structure, Copper(II) complex, Tetraazamacrocycle, Supramolecular.

INTRODUCTION

Recently the chemistry of transition metal complexes containing macrocyclic ligands has become increasingly important[1–5]. There are several reasons for this interest in the complexes, *e.g.*, the azamacrocyclic ligands 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, dissolution in a polar solvent of metal and organic salts, preparation of ion-selective electrodes, isotope separations and in the understanding of some natural processes through mimicry of metalloenzymes[6–10].

However, the structurally characterized transition metal complexes containing macrocyclic ligand 7,14-dimethyl-5,12-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene(L), are still very rare. Herein, we report the synthesis of $[CuL](ClO_4)_2$ and its crystal structure.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. The

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7,14-dimethyl-5,12-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene was synthesized according to literature[11]. $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared by our laboratory. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analyses were performed on an Elementar Vario EL-III elemental analyzer.

Synthesis

Safety Note: Although we have experienced no problems with the compound reported in this work, perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with great caution.

$[CuL](ClO_4)_2$: To a mixed solution of acetonitrile (15 mL) and L (0.3 mmol) was added to 20 mL water solution of NaN_3 (2.7 mmol) with stirring. The resulting solution was continuously stirred for 30 min and then filtered. Well shaped deep purple cubic crystals were obtained from the mother liquor by slow evaporation at room temperature for two weeks. They were collected by filtration, washed with a small amount of water and dried in air. IR (KBr, cm^{-1}): 1660 ν(C=N); 769 and 708 ν(Ar-H); 3314 ν(N—H); 1100 and 623 $\nu(ClO_4^-)$). Elemental Analysis (%) Found: C, 45.23; H, 4.95; N, 8.74; Calcd. for $C_{24}H_{32}Cl_2CuN_4O_8$: C, 45.11; H, 5.05; N, 8.77.

Crystal structure determination

The crystal with dimensions of 0.60 mm × 0.50 mm × 0.40 mm was selected and mounted on a glass fibre in a random orientation for X-ray diffraction study at 293(2) K. Using a Siemens SMART CCD area-detector diffractometer with graphite monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) at temperature 293 ± 2 K. A total of 19130 reflections were collected in the range of 3.00–27.48° of which 5667 reflections were unique with R(int) = 0.0324. Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system[12] was used in the solution and refinements of the structure. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added according to the theoretical model. The final full-matrix least-squares refinement including 353 parameters for 5667 reflections with $I > 2\sigma(I)$ gave $R = 0.0827$, $wR_2 = 0.2319$, $i^0w = 1/[s^2(F_0^2) + (0.1557P)^2 + 14.1735P]i\pm$, where $P = (F_0^2 + 2F_C^2)\}$, s = 1.070. The maximum peak and the minimum peak were corresponding to 1.0720 and $-0.993e/Å^{-3}$ respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond lengths and bond angles are given in Table-2. The molecular structure of $[CuL](ClO_4)_2$ is shown in Fig. 1, which contains $[CuL]^{2+}$ cation, and two perchlorate anions.

The cation has the configuration with approximate two-fold symmetry, with bond lengths Cu-N_{amine} 2.009(5) and 2.031(5) Å, Cu-N_{imine} 1.990(6) and 1.992 (5) Å, and trans-N-Ni-N angles 172.1(3) and 167.9(2)°. The cation has the macrocycle in square-planar coordination to singlet ground state copper(II), with slight tetrahedral twisting of the N_4 plane, with the copper 0.187(5)Å from this plane, displaced towards an axially sited perchlorate O-atom with Cu—O 2.355(6) Å. Both N—H groups are oriented to the other side of the plane. The bond length about N12-C9 1.258(9) and N14-C21 1.248(8) Å (Table-1) confirms the presence and location of the two imine functions. Both 5-membered chelate rings are in asymmetric gauche conformations and 6-membered chelate rings are in asymmetric twist conformations. The substituents are all equatorially oriented. The centre copper(II) ion is coordinated by five atoms in a prolonged asymmetric square-pyramidal geometry. The five-coordinated structure found in this complex represents an unusual example where the constructing environment of the macrocyclic ligand forces the metal out of the plane of the four nitrogen atoms and allows only one perchlorate anion to occupy an axial site.

The molecular packing arrangement in the unit cell is shown in Fig. 2. The adjacent macrocyclic molecules linked to each other by the π-π acting between adjacent phenyls of the macrocyclic skeleton, so that the compound is in one-dimensional linear supramolecular state. There is a molecular channel between the chains of supramolecule that suggest the potential application foreground of this compound in the fields of molecular sieve, selective sorbent and selective catalyzer etc.

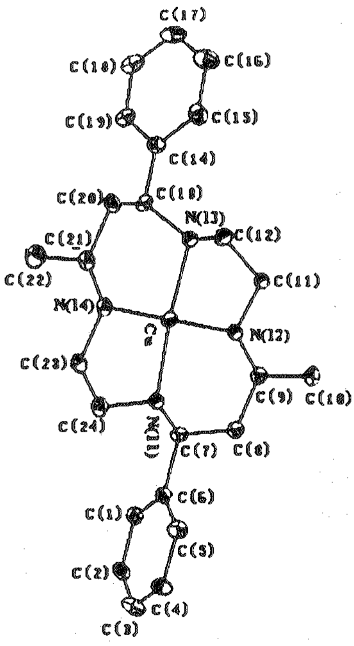

Fig. 1. The structure of $[CuL](ClO_4)_2$ (omitted hydrogen atoms and the anion ClO_4^-)

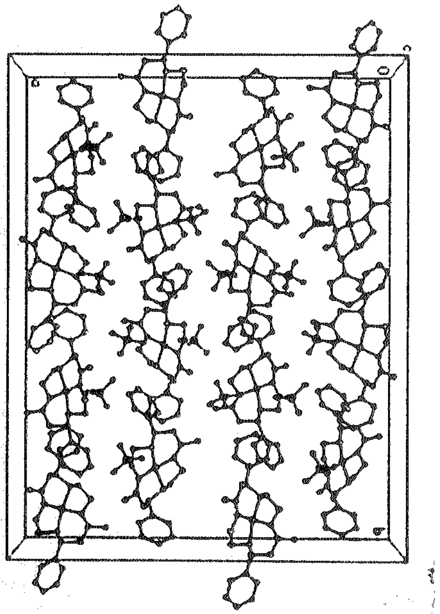

Fig. 2. Molecular packing diagram of $[CuL](ClO_4)_2$ in the unit cell

TABLE-1
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \times 10^3$)

ATOM	X	Y	Z	UEQ
Cu	1159(1)	778(1)	4054(1)	37(1)
N(11)	1066(2)	337(1)	4950(6)	27(1)
N(12)	1627(2)	621(1)	2629(7)	36(1)
N(13)	1364(2)	1231(1)	3448(6)	31(1)
N(14)	762(2)	937(1)	5675(6)	29(1)
C(1)	614(2)	–433(2)	4054(8)	34(1)
C(2)	498(3)	–740(2)	4667(9)	39(2)
C(3)	747(3)	–857(2)	5814(9)	47(2)
C(4)	1115(3)	–678(2)	6368(9)	39(2)
C(5)	1245(3)	–381(2)	5741(8)	35(2)
C(6)	990(2)	–265(2)	4557(8)	32(1)
C(7)	1125(2)	67(1)	3889(8)	29(1)
C(8)	1618(2)	54(2)	3304(8)	32(1)
C(9)	1818(2)	346(2)	2563(8)	32(1)
C(10)	2257(2)	289(2)	1731(9)	38(2)
C(23)	590(2)	656(1)	6552(8)	31(1)
C(24)	609(2)	352(2)	5644(8)	36(1)
Cl(1)	375(1)	709(1)	1154(3)	77(1)
Cl(2)	2068(1)	661(1)	–2745(3)	51(1)
O(1)	501(2)	752(2)	2534(8)	65(2)
O(2)	181(5)	408(4)	1060(20)	176(7)
O(3)	734(8)	701(6)	163(12)	225(10)
O(4)	17(4)	968(4)	865(19)	207(10)
O(5)	1638(3)	715(3)	–2034(15)	114(4)
O(6)	2246(5)	940(3)	–3240(30)	201(10)
O(7)	2019(3)	425(3)	–3822(17)	142(6)
O(8)	2425(3)	519(3)	–1800(10)	105(3)

TABLE-2
BOND DISTANCES (Å) AND ANGLES (°)

Bond	Distance	Angle	(°)	Angle	(°)
Cu-N(12)	1.990(6)	N(12)-Cu-N(14)	172.1(3)	C(4)-C(5)-C(6)	118.8(7)
Cu-N(14)	1.992(5)	N(12)-Cu-N(11)	94.0(2)	C(1)-C(6)-C(5)	120.5(6)
Cu-N(11)	2.009(5)	N(12)-Cu-N(13)	85.3(2)	C(9)-C(8)-C(7)	119.7(5)
Cu-N(13)	2.031(5)	N(14)-Cu-N(11)	84.8(2)	C(10)-C(9)-C(8)	115.8(6)
Cu-O(1)	2.355(6)	N(14)-Cu-N(13)	94.3(2)	N(14)-C(23)-C(24)	109.0(5)
N(11)-C(24)	1.461(8)	N(11)-Cu-N(13)	167.9(2)	O(6)-Cl(2)-O(5)	110.9(8)
N(11)-C(7)	1.492(8)	N(11)-Cu-O(1)	95.7(3)	O(7)-Cl(2)-O(5)	110.6(7)
N(12)-C(9)	1.258(9)	N(12)-Cu-O(1)	97.6(3)	O(6)-Cl(2)-O(8)	106.0(9)
N(12)-C(11)	1.512(8)	N(13)-Cu-O(1)	96.3(3)	O(7)-Cl(2)-O(8)	102.8(7)
N(13)-C(13)	1.491(8)	N(14)-Cu-O(1)	90.3(2)	O(5)-Cl(2)-O(8)	113.4(7)
N(13)-C(12)	1.501(9)	C(24)-N(11)-C(7)	114.9(5)	Cl(1)-O(1)-Cu	142.4(4)
N(14)-C(21)	1.248(8)	C(24)-N(11)-Cu	105.2(4)	N(11)-C(24)-C(23)	108.2(5)
N(14)-C(23)	1.494(8)	C(7)-N(11)-Cu	112.7(4)	O(1)-Cl(1)-O(2)	106.9(10)
C(6)-C(7)	1.543(9)	C(23)-N(14)-Cu	110.1(4)	O(1)-Cl(1)-O(3)	115.7(8)
C(9)-C(10)	1.494(9)	C(6)-C(1)-C(2)	120.0(7)	O(2)-Cl(1)-O(3)	104.1(13)
C(13)-C(14)	1.512(9)	C(3)-C(2)-C(1)	119.8(7)	O(1)-Cl(1)-O(4)	105.2(9)
C(21)-C(22)	1.523(10)	C(2)-C(3)-C(4)	120.0(7)	O(2)-Cl(1)-O(4)	110.6(9)
Cl(1)-O(1)	1.337(8)	C(3)-C(4)-C(5)	120.8(7)	O(3)-Cl(1)-O(4)	114.2(10)

Conclusion

In the present study, we have synthesized a new one-dimensional supramolecular tetraazamacrocyclic copper(II) compound $[CuL](ClO_4)_2$ (L = 7,14-dimethyl-5,12diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), which was confirmed structurally by IR spectra, elemental analysis and single-crystal X-ray diffraction analysis. In future, we would like to extend these studies to molecular sieve and selective sorbent. The study of the selective catalyzer about this compound is in progress.

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Supplementary Material: Structure data have been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 236174 for $[CuL](ClO_4)_2$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44)(1223)-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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