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NOTE

Synthesis and Crystals Structures of Cu(II) and Ni(II) Tetrazamacrocyclic Complexes

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A tetrazamacrocycle ligand 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetrazamacrocyclotetradecane·$2ClO_4$ (L_1) and its copper(II) and nickel(II) complexes were synthesized and characterized by IR spectra, elemental analysis. The crystal structure of the L_1 was determined by single-crystal X-ray. The possessing parameters: P2(1)/c, a = 14.6346(8) Å, b = 1.7652(7) Å, c = 16.0691(9) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 2766.8(3) $Å^3$, Z = 4, Mr = 541.51, Dc = 1.300 g/cm^3, μ = 0.282 mm^{-1}, F(000) = 1168, T = 293(2) K, $R_1 = 0.0874$, $wR_2 = 0.2503$ for 3136 reflections with $I > 2\sigma(I)$.

Key Words: Tetraazamacrocycle, Crystal structure, Copper(II) and Nickel(II) complexes.

During recent years, there has been increasing interest of tetraazamacrocycle, the construction of functional system compound lies on the character of mutual effect in reagents. Further study of tetraazamacrocycle material may contribute to the development of modern chemistry[1-3]. Hence, the synthesis of a substance with novel structures is of great significance[4-7]. In this communication, the synthesis of the L_1 and its copper(II) and nickel(II) complexes and crystal structures are reported.

The ligand, 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene·$2ClO_4$ was prepared as reported earlier[1]. IR spectra were recorded on Nexus-870 spectrophotometer. Elemental analysis were performed on elemental Vario EL-(III) analyzer.

Synthesis: To a 20 mL methanol solution of ligand (10 mmol) were successively added KBH_4 (26 mmol) with stirring at temperature 343 K. The mixture was refluxed for 0.5 h to obtain a clear solution and after

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standing at room temperature for two weeks, colourless single crystals were obtained by slow evaporation. IR spectrum (KBr, ν_{max}, cm^{-1}): (N-H) 3280, 3230, (C-N) 1470, 1180, (ClO_4^-) 1090, 625. Elemental analysis confirmed the organic content (Found: (%) C, 44.42; H, 8.60; N, 10.28. Calcd. (%) for $C_{20}H_{46}N_4O_8$: C, 44.30; H, 8.51; N, 10.41).

In two 20 mL methanol solution of L_1 (10 mmol) were respectively added 20 mL methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (10 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mmol), then refluxed for 1 h and standing at room temperature for 0.5 h. The purple red and the yellow two powdery solids were obtained separately. Elemental analysis: Calcd. (%) for $CuL_1 \cdot (ClO_4)_2$: C, 29.82; H, 5.70; N, 6.99. Found: (%) C, 29.85; H, 5.72; N, 6.97; Calcd. (%) for $NiL_1 \cdot (ClO_4)_2$: C, 30.02; H, 5.74; N, 7.03. Found: (%) C, 30.04; H, 5.76; N, 7.01.

Crystal structure determination: A colourless crystal having approximate dimensions of 0.60 × 0.50 × 0.50 mm was selected for X-ray diffraction study. Diffraction experiments were performed on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoK_α radiation (λ = 0.71073 Å) at temperature 293(2) K, scan technique $2.89° \leq \theta \leq 27.48$. A total of 20049 reflections were collected, of which 3136 reflections were unique with R_{int} = 0.0194. 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 was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 181 variable parameters for 3136 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of $R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0| = 0.0874$ and $wR_2 = \{\Sigma[w(F_0^2-F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.2503$, where $w = 1/[\sigma^2(F_0^2) + (0.14904P)^2 + 1.7573P]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.825 and -0.473 e/A^3 (CCDC No. 646123), 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 showed the molecular structure of the ligand L_1 while the Fig. 2 showed the packing diagram of the L_1. From the Fig. 2, there is a positive negative charge interaction between ClO_4^- anion and tetraazamacrocycle ligand and the moleculars pack in a 2-D net layer structure.

TABLE-1

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

Atom	X	Y	Z	U(eq)
N(1)	3827(1)	186(2)	5649(1)	40(1)
C(6)	3248(3)	744(5)	3395(2)	79(1)
O(12)	3227(7)	1662(6)	6918(6)	89(3)

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

Bond	Length	Angle	(°)	Angle	(°)
N(1)-C(10)#1	1.459(3)	C(10)#1-N(1)-C(3)	113.6(2)	O(13')-Cl-O(12)	30.9(12)
C(1)-C(2)	1.461(6)	N(1)-C(3)-C(2)	114.1(2)	C(8)-C(7)-C(5)	117.5(3)
C(1)-C(3)	1.539(4)	N(2)-C(5)-C(7)	109.4(3)	O(13')-Cl-O(12')	126.1(14)
O(12)-C(13')	0.750(3)	O(13')-Cl-C(11)	116.7(7)	O(12')-Cl-O(14)	69.3(8)

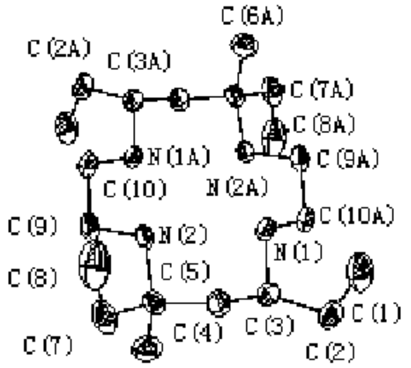

Fig. 1. Molecular structure of the L_1

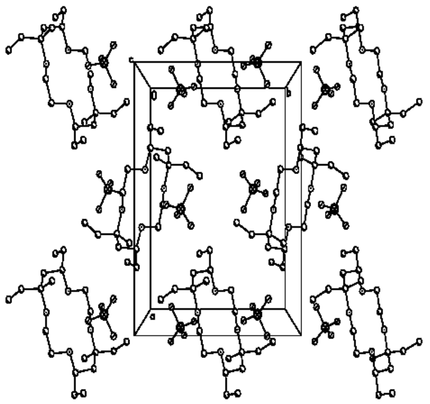

Fig. 2. Molecular packing arrangement

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