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NOTE

Synthesis and Crystal Structure of One-Dimensional Linear Supramolecular Tetraazamacrocyclic Nickel(II) Complex

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The nickel(II) complex $[NiL]\cdot(ClO_4)_2$ (L = 5,5,7,12,12, 14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been synthesized and its crystal structure was determined by X-ray diffraction. The crystal is monoclinic, space group P2(1)/c, a = 10.2600(8) Å, b = 10.7600(5) Å, c = 10.9000(7) Å, $\alpha = 90^o$, $\beta = 111.410(2)^o$, $\gamma = 90^o$, V = 1120.29(12) $Å^3$, Mr = 538.07, Z = 2, Dc = 1.595 g/cm^3, F(1000) = 564, I = 1.155 mm^{-1}. The final R = 0.0336 and wR = 0.0880 for 2517 observed reflections ($I > 2\sigma(I)$). The center nickel(II) ion is coordinated by four N atoms in a little distortion plane square geometry. The compound is in one-dimensional linear supramolecular state.

Key Words: Crystal structure, Tetaraazamacrocycle, Nickel(II) complex, Supramolecular.

Recently, the chemistry of transition metal complexes containing macrocyclic ligand has become increasingly important[1-7]. However, the structurally characterized transition metal complexes containing macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (L), are still very rare. Herein, the synthesis of one-dimensional linear supramolecular tetraazamacrocyclic nickel(II) complex and its crystal structure are reported.

The ligand, 5,5,7,12,12, 14-hexamethyl-1,4,8,11-tetraazacyclotetradeca -4,11-diene (L) was synthesized according to the literature[8,9]. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analyses were performed on a Elemental Vario EL-III elemental analyzer. The crystal structure was determined by Siemens SMART CCD area-detector diffractometer.

Synthesis of $[NiL]\cdot(ClO_4)_2$: The mixture of ligand (3 mmol) and $Ni(ClO_4)_2\cdot 6H_2O$ (3 mmol) in 100 mL methanol solution was refluxed for 1 h

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at 70 ºC. The precipitate is filtered to obtain a clear brownish yellow solution and after standing at 25 ºC for three weeks, well-shaped light yellow cube crystals were obtained by slow evaporation. IR(KBr, ν_{max}, cm^{-1}): 3170 (N-H); 1660 (C=N); 1100 and 623 (ClO_4^-). Elemental Anal. of $C_{16}H_{32}Cl_2NiN_4O_8$ Found (%): C, 35.63; H, 5.95; N, 10.64; Calcd. (%) C, 35.71; H, 5.99; N, 10.41.

Crystal structure determination: The crystal with dimensions of 0.60 mm × 0.60 mm × 0.50 mm was selected for X-ray diffraction study at 293(2) K, with graphite.monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 7757 reflections were collected in the range of 4.02 to 27.48º of which 2517 reflections were unique with R(int) = 0.0104. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system[10]. The final full-matrix least-squares refinements including 142 parameters for 2517 reflections with $I > 2\sigma(I)$ gave R = 0.0336, wR_2 = 0.0880, $\{w = 1/[s^2(F_0^2) + (0.0478P)^2 + 0.7450P]$, where $p = (F_0^2 + 2F_C^2)\}$, s = 1.066. The maximum peak and the minimum peak was corresponding to 0.381 and -0.337e/$Å^{-3}$ (CCDC: 646130), respectively.

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond lengths and bond angles are in Table-2. The molecular structure of the $[NiL]\cdot(ClO_4)_2$ is shown in Fig. 1, in which the center nickel(II) ion is coordinated by four N atoms of the macrocycle in a little distortion plane square geometry. The molecular packing arrangement in

TABLE-1
ATOMIC COORDINATES ($\times10^4$) AND THERMAL PARAMETERS ($Å^2 \times10^3$)

Atom	X	Y	Z	U(eq)
NI	0	5000	5000	21(1)
N(1)	1343(1)	4536(1)	4209(1)	25(1)
N(2)	-1365(2)	4931(1)	3247(1)	27(1)
C(1)	3401(2)	4714(2)	6189(2)	36(1)
C(2)	3590(2)	3596(2)	4283(2)	46(1)
C(3)	2245(3)	2631(2)	5541(2)	44(1)
C(4)	2632(2)	3850(2)	5056(2)	28(1)

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

Bond	Distance	Angle	(º)	Angle	(º)
NI-N(2)	1.9145(15)	N(2)#1-NI-N(2)	180.00	N(1)-C(4)-C(1)	106.23(14)
NI-N(1)	1.9392(13)	N(2)-Ni-N(1)	85.74(6)	N(1)-C(4)-C(3)	110.78(15)
N(1)-C(5)	1.4800(2)	N(2)#1-NI-N(1)	94.26(6)	C(1)-C(4)-C(3)	111.70(16)
N(2)-C(7)	1.2780(2)	C(5)-N(1)-C(4)	114.11(14)	N(1)-C(4)-C(2)	110.30(14)
C(1)-C(4)	1.5170(3)	C(5)-N(1)-NI	107.88(11)	N(1)-C(5)-C(6)	106.79(16)
C(5)-C(6)	1.4970(3)	C(4)-N(1)-NI	117.53(10)	N(2)-C(6)-C(5)	107.13(16)
CL-O(1)	1.4260(2)	C(7)-N(2)-C(6)	118.89(16)	O(2)-CL-O(3)	107.77(19)

the unit cell is shown in Fig. 2. The adjacent macrocyclic molecules linked to each other by a positive negative charge interaction between perchlorate anion and $[NiL]^{2+}$ cation, so that the compound is in one-dimensional linear supramolecular state.

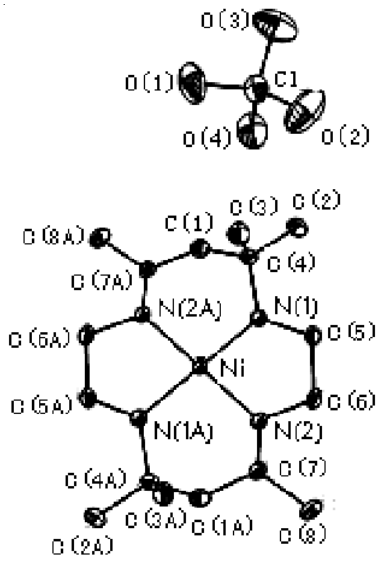

Fig. 1. Structure of $[NiL]\cdot(ClO_4)_2$ (omitted hydrogen atoms)

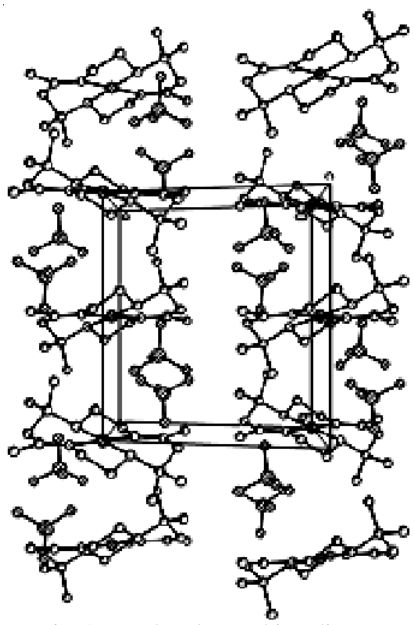

Fig. 2. Molecular packing diagram of $[NiL]\cdot(ClO_4)_2$ in the unit cell

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