Asian Journal of Chemistry Vol. 22, No. 10 (2010), 8267-8269

NOTE

Synthesis and Structure of a Tetraazamacrocyclic Complex [NiL·Zn(SCN)$_4$]

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The complex [NiL·Zn(SCN)$_4$] (L = 5,5,7,12,12,14-hexa-methyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) was synthesized and characterized by IR spectra and elemental analysis and the structure was determined by single-crystal X-ray diffraction analysis. The result showed the crystal belongs to monoclinic, space group P2(1)/n with a = 11.842(3) Å, b = 14.835(3) Å, c = 16.463(4) Å, α = 90º, β = 92.087(4)º, γ = 90º, V = 2890.0(11)Å^3, Z = 4, Dc = 1.464 Mg/cm^3, F(000) = 1320, R = 0.0497, wR = 0.1326. In the crystal, Ni(II) ion was coordinated by four nitrogen atoms of the tetraazamacrocycle.

Key Words: Nickel complex, Tetraazamacrocycle, Synthesis, Crystal structure.

Because of its unique performance of coordination, azamacrocyclic ligands have attracted extensive attention. In the simulation of metal enzymes, the azamacrocyclic complexes are important in catalysis, structure, molecular recognition and mechanism of photosensitive materials[1-4]. Several complexes of this kind have already been reported[5-9]. In This paper, the synthesis and crystal structure of the complex [NiL·Zn(SCN)$_4$] (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) is reported.

IR spectrum was recorded on an Nexus-870 spectromer. Elemental analyses on an Elementar Vario EL-III elemental analyzer. [NiL]·(ClO$_4$)$_2$ was prepared according to the way of literature[10].

Synthesis: To a 20 mL solution (10 mL acetonitrile and 10 mL H_2O) of [NiL]·(ClO$_4$)$_2$ (2 mmol) was added to an aqueous solution (10 mL) of K_2[Zn(SCN)$_4$] (2 mmol) and mixed after 5 h a clear solution was obtained, which after standing at room temperature for 2 weeks crystals were obtained. The product was light reddish brown column-shaped crystals. IR spectrum (KBr, cm^{-1}): 3410, 2047, 1664, 1370. Elemental analysis (%) calcd. for $C_{20}H_{32}N_8NiS_4Zn$: C, 37.72; H, 5.06; N, 17.60. Found: (%) C, 37.79; H, 5.11; N, 17.52.

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Crystal structure determination: A light reddish brown crystal (0.66 mm × 0.33 mm × 0.15 mm) was selected for collection of crystallographic data at 293(2) K, and structure determinated with graphite monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 21446 reflections were collected in the range of $3.49^\circ \leq \theta \leq 27.49^\circ$, of which 6555 reflections were unique with Rint = 0.0310 and R = 0.0497, wR = 0.1326; where $w = 1/[\sigma^2(F_0^2) + (0.0768P)^2 + 1.2764P]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.327 and -1.026e/Å^3 (CCDC No.719389), respectively.

The atomic coordinates and thermal parameters are listed in Table-1 and the selected bond lengths and bond angles are presented in Table-2. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. From the Fig. 1, the Ni(II) ion is coordinated with four N atoms from the tetraazamacrocycle. So it is obviously that nickel(II) ion is in a slightly distorted square geometry. Fig. 2. shows the packing diagram in the unit cell, that the interactions between $[NiL]^{2+}$ and $[Zn(SCN)_4]^{2-}$ are electrostatic interactions.

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

Atom	x	y	z	U (eq)
Ni	2823(1)	1464(1)	7254(1)	38(1)
Zn	1701(1)	913(1)	1698(1)	63(1)
N(11)	3055(2)	1324(2)	8421(1)	40(1)
N(12)	4385(2)	1395(2)	7018(2)	49(1)
N(13)	2577(2)	1529(2)	6086(2)	52(1)
N(14)	1267(2)	1523(2)	7490(2)	45(1)
S(1)	-1999(1)	1473(1)	2540(1)	66(1)
S(2)	1557(3)	-1368(1)	-163(1)	209(2)
N(1)	210(3)	1123(3)	2150(2)	81(1)

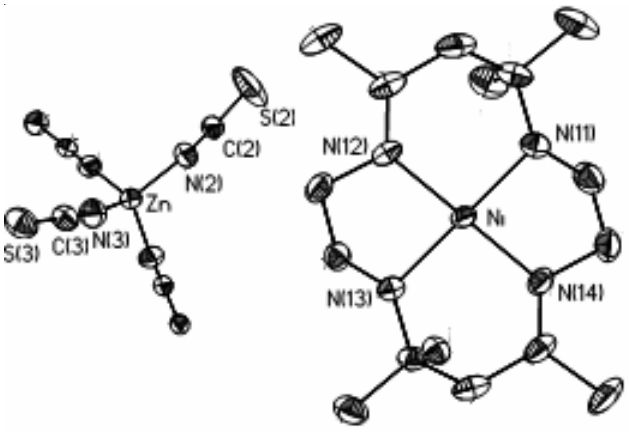

Fig. 1. Molecular structure of $[NiL{\cdot}Zn(SCN)_4]$

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

Bond	Length	Angle	(º)	Angle	(º)
Ni-N(11)	1.942(2)	N(14)-Ni-N(12)	179.55(11)	N(1)-Zn-N(4)	108.68(16)
Ni-N(14)	1.899(2)	N(14)-Ni-N(13)	95.11(11)	N(4)-Zn-N(3)	108.74(17)
Zn-N(1)	1.966(3)	N(12)-Ni-N(13)	84.96(11)	N(3)-Zn-N(2)	109.91(17)
Zn-N(3)	1.968(4)	N(14)-Ni-N(11)	84.57(10)	N(1)-Zn-N(2)	112.16(16)
S(1)-C(1)	1.627(4)	N(12)-Ni-N(11)	95.33(10)	N(4)-Zn-N(2)	107.20(15)
S(2)-C(2)	1.589(5)	N(13)-Ni-N(11)	176.66(11)	N(1)-C(1)-S(1)	179.50(4)

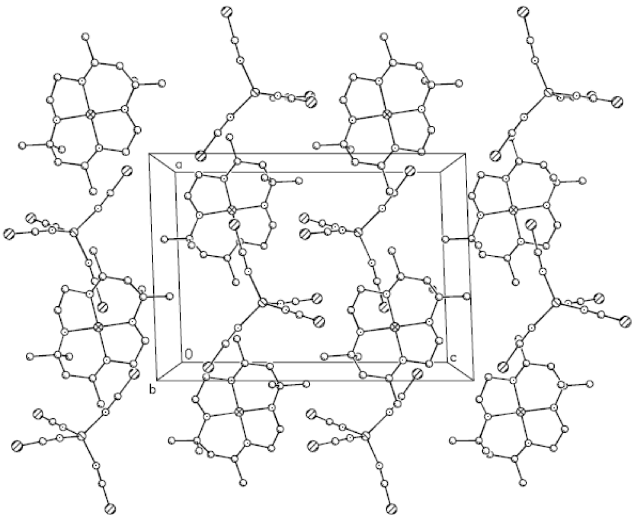

Fig. 2. Packing diagram of [NiL·Zn(SCN)$_4$]

ACKNOWLEDGEMENT

This work is financially supported by the National Natural Science Foundation of China (No. 20871039).

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(*Received*: 11 May 2010; *Accepted*: 7 August 2010) AJC-8970