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Hydrothermal Synthesis and Crystal Structure of A New 3D-Supramolecular Complex: $phen_2Zn\text{-}2N_3$

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The complex $phen_2Zn\text{-}2N_3$, where phen is 1,10-phenanthroline, has been synthesized and its crystal structure was determined by X-ray diffraction. Crystal data: orthorhombic, space group Fdd2, a = 8.2 05(2) Å, b = 11.052(3) Å, c = 12.508(3) Å, α = 82.852(6) deg, β = 81.899 (6) deg, γ = 73.086(7) deg, V = 1070.2(5) $Å^3$, Mr = 509.84, F(000) = 618, Z = 2, Dc = 1.582Mg/m^3, μ = 1.185 mm^{-1}. The final R1 = 0.0406 and wR2 = 0.0828 for 8261 observed reflections ($I > 2\sigma(I)$). Zinc(II) ion is coordinated by six atoms in a prolonged octahedron geometry. The compound is in 3-dimensional supramolecular state.

Key Words: Zinc complex, Supramolecule, Crystal structure, 1,10-Phenanthroline.

INTRODUCTION

The transition metal complexes with nitrogen as donors ligands received much attention because of their wide use in nonlinear optical materials[1,2]. 1,10-Phenanthroline (phen) has extended planar π systems and can be used in model compounds to mimic the noncovalent interactions in biological processes[3]. Being a bidentate ligand, phen is good candidate for the investigation of the stereochemical activity[4-8].

The coordination chemistry of zinc(II) with N donor ligands has been studied extensively in recent years. They play a number of diverse and important roles in biological systems and have received considerable attention from inorganic chemists[9]. A few phenanthroline zinc complexes have been described recently. However, the structurally characterized transition metal complexes containing $phen_2\text{-}Zn\text{-}2N_3$ are novel. In this communication, we report here the preparation and crystal structure of the six-coordinated zinc complex.

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EXPERIMENTAL

All reagents were of AR grade and used without further purification. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analysis were performed on an Elementar Vario EL-III analyzer.

Synthesis

A mixture of $ZnSO_4$ (0.064 g, 0.4 mmol), 1,10-phenanthroline (0158 g, 0.8 mmol), NaN_3 (0.052 g, 0.8 mmol) and H_2O (25 mL) were carried out in a autoclave. The autoclave was heated at the temperature of 150 ºC for 48 h to carry out the reaction sufficiently. After cooling, the mixture was filtered and the filtrate was sealed in a 25 mL cone bottle under normal atmospheric temperature and normal pressure for 10 d. The product was light yellow pillar-shaped crystal. IR (KBr, ν_{max}, cm^{-1}): (N-H) 3340, (N=N=N) 2050, (C=N) 1510, (N-H) 725. Elemental analysis (%): Calcd. (%) for $C_{24}H_{16}N_{10}Zn$: C, 56.54; H, 3.16; N, 27.47; Found (%): C, 56.40; H, 3.30; N, 27.25.

Crystal structure determination: A light yellow crystal of the title compound with approximate dimensions of 0.30 × 0.30 × 0.20 mm was selected and mounted on a glass fiber in a random orientation for X-ray diffraction study. The diffraction data were collected on a Siemens Smart CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 293(2) K, using ω scan technique in the rang of $2.78° \le \theta \le 27.48°$. A total of 8261 reflections were collected with 4815 unique ones (R(int) = 0.0172) in the ranges of $-7 \le h \le 10$, $-14 \le k \le 14$, $-16 \le l \le 16$. 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. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to the theoretical model. The final full-matrix least-squares refinements including 316 parameters for 4815 reflections with I > 2, gave R1 = 0.0342, wR2 = 0.0790,

$\{w = 1/[s^2(F_0^2) + (0.0355P)^2 + 0.5067P]$, where $p = (F_0^2 + 2F_C^2)/3\}$,

The maximum peak and the minimum peak was corresponding to 0.418 and -0.341e/$Å^3$, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond lengths and bond angles are in Table-2. Anisotropic displacement parameters in Table-3. Hydrogen coordinates in Table-4. The cation has the configuration with approximate two-fold symmetry. Fig. 1 shows a perspective view of $phen_2Zn\text{-}2N_3$ with atomic numbering scheme and Fig. 2 shows a perspective view of the crystal packing in the unit cell.

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

Auto	X	Y	Z	U(eq)
Zn	5010(1)	2879(1)	2341(1)	31(1)
N(1)	7114(3)	1267(2)	2600(2)	49(1)
N(11)	4596(2)	2542(2)	753(1)	33(1)
N(12)	3319(2)	1560(2)	2656(1)	33(1)
N(22)	2678(2)	4560(2)	2358(1)	33(1)

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

Bond	Length	Angle	(º)
Zn-N(4)	2.0710(2)	N(11)-C(11)	1.324(3)
Zn-N(11)	2.1554(17)	N(11)-C(22)	1.352(3)
Zn-N(21)	2.1722(16)	C(13)-C(14)	1.406(3)
N(1)-N(2)	1.1720(3)	N(4)-Zn-N(1)	94.060(8)
N(5)-N(6)	1.1470(3)	N(11)-C(22)-C(14)	122.330(19)

TABLE-3
ANISOTROPIC DISPLACEMENT PARAMETERS (× 10^3 Å^2)

Auto	U11	U22	U33	Y23	U13	U12
Zn	38(1)	27(1)	27(1)	-5(1)	-3(1)	-7(1)
N(1)	41(1)	39(1)	60(1)	4(1)	-4(1)	-2(1)
N(4)	51(1)	34(1)	54(1)	-7(1)	0(1)	-16(1)
N(5)	47(1)	48(1)	54(1)	-3(1)	-4(1)	-19(1)

TABLE-4
HYDROGEN COORDINATES (× 10^4) AND ISOTROPIC DISPLACEMENT PARAMETERS (× 10^3 Å)

Auto	X	Y	Z	U(eq)
H(11A)	5848	3621	-146	48
H(12A)	5421	3148	-1817	56
H(13A)	3923	1703	-1898	55
H(15A)	2235	219	-884	59
H(16A)	1142	-597	707	61

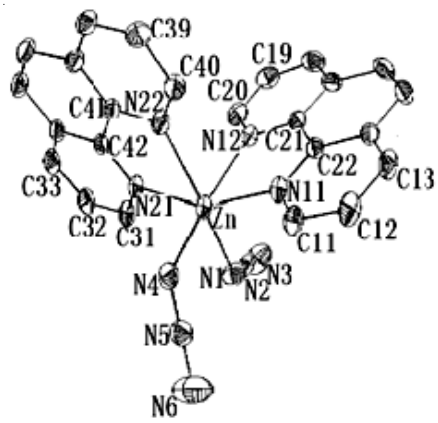

Fig. 1. Structure of $[phen_2Zn\text{-}2N_3]$

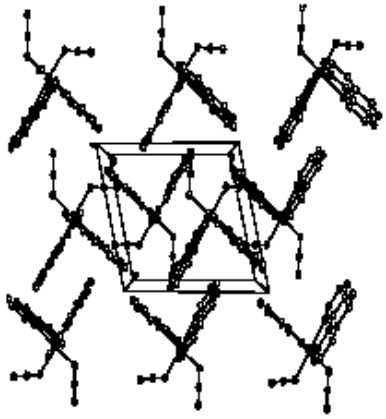

Fig. 2. Packing arrangement in unit cell

In present studies, a zinc complex that contained both the phenanthroline and the N_3^- ligand has been prepared. The zinc atom has a six-coordinate geometry with two phen molecules acting as a chelating ligand *via* four N atoms. Two N_3^- molecules coordinate to Zn in order to complete its coordination sphere (Fig. 1). The Zn atom is in a slightly distorted octahedral geometry which defined by N21-N22-N12-N11, with Zn-N21 2.1722(16), Zn-N22 2.2455(17), Zn-N11 2.1554(17), Zn-N12 2.2541(18), Zn-N4 2.071(2), Zn-N1 2.1176(19), N11-Zn-N22 89.84(6), N21-Zn-N22 75.32(6), N4-Zn-N12 170.68(7).

The bond lengths and angles for phenanthroline-zinc (Table-2) are in good agreement with those reported for the free ligand as well as the related zinc complexes. Zn-N distances in $phen_2Zn\text{-}2N_3$ are from 2.071(2) to 2.2541(18). As shown in Fig. 3, it can be seen that the layers of phenanthroline are parallel with the layer separation of about 3.415 Å, implying the existence of some π-π stacking interactions between the phenanthroline rings[10]. Through the π-π stacking interactions, many of these layers pack in a 3-D net structure supramolecular complex, 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 for the hydroxylation of phenol *etc.*

Conclusion

Crystal structure of novel complex has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. The studies of the absorption and catalysis characteristics about this complex are in progress.

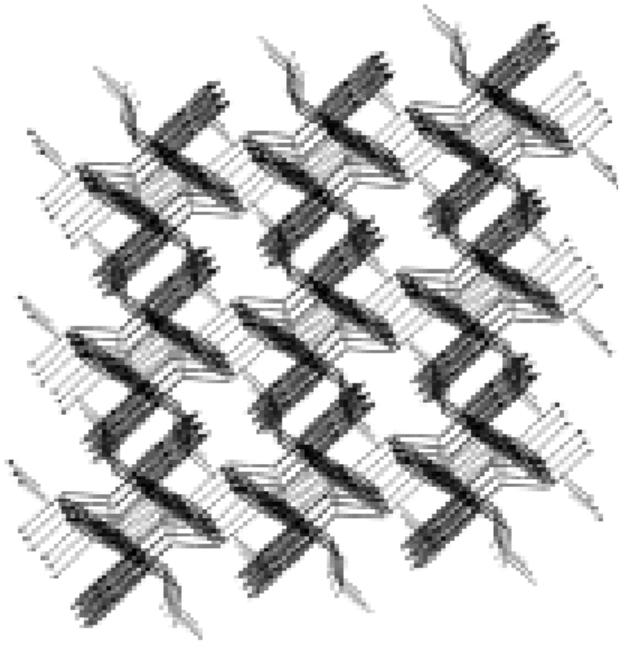

Fig 3. View of the layered structure

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