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Synthesis and Crystal Structure of Mononuclear *Bis*(2-aminopyridine)zinc Complex

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2-Aminopyridine reacts with $Zn(OAc)_2 \cdot 2H_2O$ in alcohol results in formation of the mononuclear *bis*(2-aminopyridine)-zinc complex and its structure was determined by X-ray diffraction analysis. The complex is also characterized by NMR, IR, MS, elemental analysis, The crystal is of prismatic, space group P2(1)/n ,with a = 9.1914(8) Å, b = 13.8595(12) Å, c = 13.2921(12) Å, α = 90.00 º, β = 92.474 º, γ = 90.00 º, λ = 0.7103 º, V = 1691.7(3), Z = 4, D_c = 1.459 g/cm^3, M_r = 371.69 and F(000) = 768, R_1 = 0.0416, wR_2 = 0.0793 for 3689 observed reflections with $I>2\sigma(I)$.

Key Words: Synthesis, Crystal structure, *Bis*(2-aminopyridine)zinc complex, $Zn(OAc)_2 \cdot 2H_2O$.

INTRODUCTION

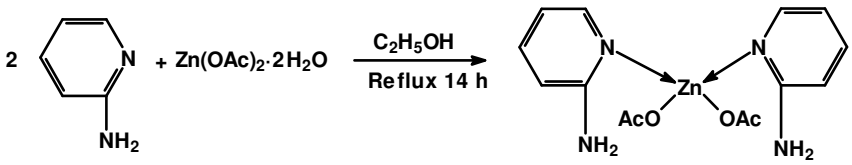
N-Zn Complexes have showed high activities in organic reactions and polymerizations[1-10]. In this paper, a simple one pot synthesis, characterization and crystal structure of novel N-Zn complex is described.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained using a Bruker AM-300 spectrometer. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer.

Preparation of *bis*(2-aminopyridine)zinc complex: 1.88 g (0.02 mmol) of 2-aminopyridine and 2.19 g (0.01 mmol) $Zn(OAc)_2 \cdot 2H_2O$ were added under free-water and free-oxygen condition in a dry 100 mL Schlenk flask. The mixture was dissolved in 30 mL of dry alcohol and refluxed for 14 h. The white crystals were obtained upon filteration (**Scheme-I**) yield 46 %). ^{1}H NMR (300 MHz, $CDCl_3$, 27 ºC), δ (ppm) = 8.12-8.19 (m, 1H), 7.84-7.91 (m, 1H), 7.69-7.72 (m, 1H), 7.59-7.62 (m,1H), 7.47-7.52 (t, 6.6 Hz, 1H), 7.20-7.30 (m, 4H), 4.56-4.60 (m, 1H), 4.33-4.39 (t, *J* = 0.9 Hz,

1H), 4.11-4.16 (t, J = 0.9 Hz, 1H), 3.72-3.81 (m, 1H), 1.72-1.81 (m, 1H), 0.83-0.91 (m, 6H). ^{13}C NMR, 23.52 (X2), 110.97 (X2), 113.93 (X2), 139.71 (X2), 148.75 (X2), 161.50 (X2), 206.76, 206.95. IR (KBr, ν_{max}, cm^{-1}): 3353, 3199, 1741, 1734, 1667, 1650, 1622, 1582, 1571, 1553, 1496, 1454, 1391, 1333, 1271, 1162, 1048, 1010, 931, 842, 790, 769, 744, 682, 650, 573, 556, 521, 479, 455, 422. Elemental analysis (%): Anal calcd. for $Zn[C_7H_9N_2O_2]_2$: C, 45.52; H, 4.88; N, 15.18; Found: C, 45.97; H, 4.84; N, 15.66.



Scheme-I: Synthetic route of N-Zn complex

Structure determination: A colourless block monoclinic crystal of the title compound with approximate of 0.488 mm × 0.475 mm × 0.256 mm was selected for the data collection on a Bruker Smart diffractometer with graphite monochromated MoK_α radiation (λ = 0.7103.) A total of 9915 reflections were collected in the range of $1.87 < \theta < 27.00^o$ by using 'phi and omega' scan techniques at 293(2)K, $C_{14}H_{18}N_4O_4Zn$, M = 371.69, monclinic, P2(1)/n, a = 9.1914(8) Å, $\alpha = 90^o$, b = 13.8595(12) Å, β = 92.474(2)º, c = 13.2921(12) Å, $\gamma = 90^o$, V = 1691 $Å^3$, Z = 4, D_{calc} = 1.459 Mg/m^3, the final R factor was R_1 = 0.0416, 3472 for reflections with $I_0 > 2\sigma(I_0)$, Rω = 0.0973 for all data, largest peak and hole were 0.649 and -0.380 e.$Å^{-3}$, respectively. The structure were elucidated by full-matrix least-squares on F^2 using the SHELXTL Program[11,12].

RESULTS AND DISCUSSION

Several interesting observations could be made about the structure (Figs. 1-3). The complex was composed of two 2-amino pyridine, $Zn(Ac)_2$ core, the bond lengths of C(1)~C(5) and N(1) atoms, C(6)~C(10) and N(3) atoms are each coplanar (Tables 1 and 2). The bond lengths are in range of 1.349~1.490 Å and the C-C-C angles are nearly 120°, the complexed bond lengths of N(1)~Zn, N(3)~Zn are 2.064(19), 2.068(19) Å, respectively (Table-3). The C(11)~ O(2), C(13)~O(4) bond distances are all nearly equal to 1.22 Å, indicating some double-bond character. The bond lengths of O(4)~Zn 1.961(17) Å are longer than that of O(2)~Zn 1.987(17) Å. The bond angles of O(2)-Zn-N(1) 104.3 ° are not equal to O(4)-Zn-N(3) 99.98(7)°. It deserves to mention that there exists hydrogen-bonds in this

complex. Four 2-amino pyridine molecules, two $Zn(OAc)_2$ cores are connected together to construct a hydrogen-bonded dinuclear structure (Fig. 3). The hydrogen-bond distance of N(4)-H(4B)---O(3) , N(4)-H(2B)---O(1), N(4)-H(2A)---O(3) and N(4)-H(4A)---O(1) are 3.043(3), 2.922(3), 3.038(3), 2.918 and 3.043(3) Å, respectively (Table-4).

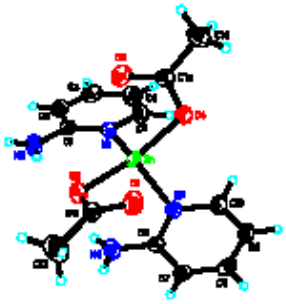


Fig. 1. Crystal structure of complex

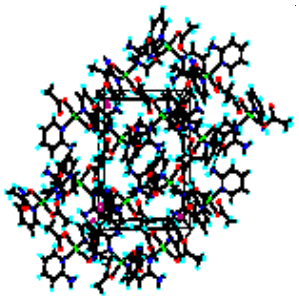


Fig. 2. Packing structure of complex

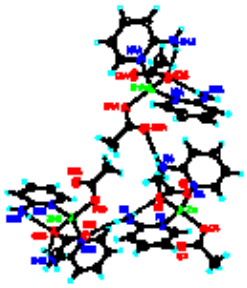


Fig. 3. Structure of two $(Apy)_2{\cdot}Zn(OAc)_2$

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

	x	y	z	U (eq)
Zn	7815(1)	3306(1)	8228(1)	36(1)
O(1)	5558(2)	3902(1)	7164(2)	58(1)
O(2)	6253(2)	2462(1)	7637(1)	46(1)
O(3)	9280(2)	3490(2)	6534(2)	58(1)
O(4)	8961(2)	4427(1)	7832(1)	47(1)
N(1)	9367(2)	2356(1)	8803(2)	37(1)
N(2)	8364(3)	948(2)	8147(2)	52(1)
N(3)	6986(2)	3826(1)	9546(1)	36(1)
N(4)	5837(3)	2388(2)	9895(2)	55(1)
C(1)	9430(3)	1387(2)	8685(2)	37(1)
C(2)	10584(3)	858(2)	9139(2)	47(1)
C(3)	11621(3)	1316(2)	9712(2)	55(1)
C(4)	11556(3)	2306(2)	9840(2)	58(1)
C(5)	10428(3)	2785(2)	9377(2)	51(1)
C(6)	6191(3)	3299(2)	10165(2)	37(1)
C(7)	5752(3)	3660(2)	11081(2)	46(1)
C(8)	6122(3)	4585(2)	11343(2)	54(1)
C(9)	6924(3)	5143(2)	10700(2)	55(1)
C(10)	7330(3)	4739(2)	9825(2)	49(1)
C(11)	5324(3)	3037(2)	7219(2)	43(1)
C(12)	3922(3)	2603(3)	6840(3)	80(1)
C(13)	9535(3)	4239(2)	6997(2)	41(1)
C(14)	10525(4)	4994(2)	6602(3)	74(1)

TABLE-2
SELECTED BOND LENGTHS [°] FOR N-Zn COMPLEX

Bond	Dist.	Bond	Dist.
Zn-O(4)	1.9614(17)	N(3)-C(10)	1.353(3)
Zn-O(2)	1.9865(17)	N(4)-C(6)	1.348(3)
Zn-N(1)	2.0643(19)	C(1)-C(2)	1.404(4)
Zn-N(3)	2.0697(19)	C(2)-C(3)	1.352(4)
O(1)-C(11)	1.220(3)	C(3)-C(4)	1.385(4)
O(2)-C(11)	1.277(3)	C(4)-C(5)	1.356(4)
O(3)-C(13)	1.225(3)	C(6)-C(7)	1.393(3)
O(4)-C(13)	1.276(3)	C(7)-C(8)	1.368(4)
N(1)-C(5)	1.349(3)	C(8)-C(9)	1.387(4)
N(1)-C(1)	1.353(3)	C(9)-C(10)	1.357(4)
N(2)-C(1)	1.335(3)	C(11)-C(12)	1.490(4)
N(3)-C(6)	1.340(3)	C(13)-C(14)	1.496(4)

TABLE-3
SELECTED BOND ANGLES [°] FOR N-Zn COMPLEX

Angle	(°)	Angle	(°)
O(4)-Zn-O(2)	138.36(8)	C(3)-C(2)-C(1)	119.9(3)
O(4)-Zn-N(1)	103.53(8)	C(2)-C(3)-C(4)	120.0(3)
O(2)-Zn-N(1)	104.30(8)	C(5)-C(4)-C(3)	117.7(3)
O(4)-Zn-N(3)	99.98(7)	N(1)-C(5)-C(4)	124.1(3)
O(2)-Zn-N(3)	104.67(8)	N(3)-C(6)-N(4)	118.6(2)
N(1)-Zn-N(3)	100.49(8)	N(3)-C(6)-C(7)	121.8(2)
C(11)-O(2)-Zn	105.25(16)	N(4)-C(6)-C(7)	119.6(2)
C(13)-O(4)-Zn	108.61(16)	C(8)-C(7)-C(6)	118.8(3)
C(5)-N(1)-C(1)	118.0(2)	C(7)-C(8)-C(9)	119.9(3)
C(5)-N(1)-Zn	113.53(17)	C(10)-C(9)-C(8)	118.1(2)
C(1)-N(1)-Zn	128.49(16)	N(3)-C(10)-C(9)	123.5(3)
C(6)-N(3)-C(10)	117.9(2)	O(1)-C(11)-O(2)	121.5(2)
C(6)-N(3)-Zn	124.10(16)	O(1)-C(11)-C(12)	121.8(3)
C(10)-N(3)-Zn	117.90(17)	O(2)-C(11)-C(12)	116.6(3)
N(2)-C(1)-N(1)	118.7(2)	O(3)-C(13)-O(4)	122.2(2)
N(2)-C(1)-C(2)	121.0(2)	O(3)-C(13)-C(14)	121.5(3)
N(1)-C(1)-C(2)	120.3(2)	O(4)-C(13)-C(14)	116.3(2)

TABLE-4
HYDROGEN BONDS FOR N-Zn COMPLEX [Å] AND [°]

D–H···A	d (D–H)	d (H···A)	d (D···A)	< (DHA)
N(4)-H(4B)···O(3)	0.841(17)	2.088(18)	2.922(3)	171(3)
N(2)-H(2B)···O(1)	0.834(17)	2.237(19)	3.038(3)	161(3)
N(2)-H(2A)···O(2)	0.821(16)	2.170(2)	2.918(3)	152(2)
N(4)-H(4A)···O(2)	0.845(17)	2.270(2)	3.043(3)	153(3)

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