Crystal structure of (4′-(2-pyridyl)-2 ,2′:6′,2″-terpyridine)zink(II) diazide, $Zn(C_{20}H_{14}N_4)(N_3)_2$

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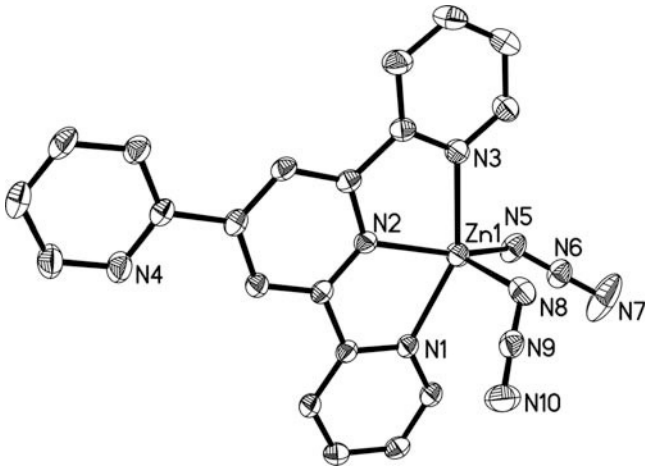

Abstract

$C_{20}H_{14}N_{10}Zn$, triclinic, $P\bar{1}$ (no. 2), a = 8.810(1) Å, b = 8.913(1) Å, c = 13.112(2) Å, α = 79.281(2)°, β = 73.733(2)°, γ = 81.731(2)°, V = 966.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.096, T = 296 K.

Source of material

4′-(2-pyridyl)-2 ,2′:6′,2″-terpyridine (2-pytpy) was synthesized according to literature [1], all the other reagents and solvents were commercially available and used as purchased. A mixture of 2-pytpy (31.0 mg, 0.1 mmol), $ZnCl_2$ (13.6 mg, 0.1 mmol) and NaN_3 (13.0 mg, 0.2 mmol) in CH_3OH (15 mL) was placed in a Teflon-lined stainless vessel and heated to 433 K for 48 h. After cooling to room temperature, the pale yellow crystals were obtained (yield, 51 %). Elemental analysis —found: C, 52.28 %; H, 3.09 %; N, 30.48 %; calculated for $C_{20}H_{14}N_{10}Zn$: C, 52.24 %; H, 3.07 %; N, 30.46 %.

Experimental details

The large anisotropy in one direction for N7 is because the N7 is the terminal atom in the azide ligand and does not participate in coordination.

Discussion

The pseudohalide ions, especially the azido ions, have been demonstrated to be extremely versatile ligands which can exhibite various coordination modes such as μ-1,1 (end-on, EO), μ-1,3 (end-to-end, EE), μ-1,1,3, and others [1-3]. A variety of molecular architectures for azido compounds of different dimensionality have been synthesized using pyridine, 2,2-bipyridine and other polydentate N-donor organic species as auxillary ligands [4-6]. We have reported the structures based on the self-assembly of Cd^{2+}, pseudohalide and pyridyl substituted terpyridine ligands [7].

In the crystal structure of the title compound, the Zn^{II} centre is five-coordinated with the expected pattern of longer Zn—N bonds to the terminal rings of 2-pytpy (2.191(2), 2.168(2) Å) than to the central ring (2.089(2) Å). The coordination of the metal is best described as a square pyramid in which the axial site is occupied by N8 and the square-base by N1, N2, N3 and N5. The bond distances of Zn—N and the angles around the distorted pyramidal zinc atom are all similar to the reported values in $[Zn(tpy)Cl_2]$ complex [8]. The azido ions as terminal ligands are nearly linear and bond to Zn^{II} with bent angles of Zn1–N5–N6 127.2(2)° and Zn1–N8–N9 121.9(2)°. The 2-pytpy functions as a tridentate chelating ligand with the substituted pyridyl ring uncoordinated. Three pyridyl rings from tridentate domain are nearly coplanar with interannular torsion angles of 3.66° and 4.02°, respectively. The pyridyl substituent is also coplanar with the terpyridine domain with the torsion angle of 5.78° between the substituted and central pyridin rings.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.11 × 0.14 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.03 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4959, 3386
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2873
$N(param)_{refined}$:	281
Programs:	SHELXS-97 [9], SHELXL-97 [10], SHELXTL [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	1.0938	1.2994	0.1030	0.055
H(2)	2*i*	1.3154	1.3688	0.1347	0.059
H(3)	2*i*	1.4621	1.1896	0.2310	0.063
H(4)	2*i*	1.3773	0.9468	0.2957	0.055
H(7)	2*i*	1.2839	0.7167	0.3495	0.048
H(9)	2*i*	0.9562	0.4615	0.3279	0.050
H(12)	2*i*	0.7398	0.4691	0.2691	0.069
H(13)	2*i*	0.5317	0.4903	0.1897	0.077
H(14)	2*i*	0.4726	0.7181	0.0853	0.069
H(15)	2*i*	0.6181	0.9199	0.0662	0.061
H(17)	2*i*	1.0461	0.2796	0.4305	0.058
H(18)	2*i*	1.1747	0.0790	0.5236	0.069
H(19)	2*i*	1.4081	0.1144	0.5592	0.074
H(20)	2*i*	1.5052	0.3502	0.5029	0.077

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	2*i*	0.90137(4)	1.00407(3)	0.14564(2)	0.0496(2)	0.0354(2)	0.0533(2)	–0.0088(1)	–0.0233(2)	0.0071(1)
N(1)	2*i*	1.1051(2)	1.0865(2)	0.1757(2)	0.043(1)	0.030(1)	0.049(1)	–0.0049(9)	–0.015(1)	0.0018(9)
N(2)	2*i*	1.0001(2)	0.8164(2)	0.2355(2)	0.041(1)	0.031(1)	0.039(1)	–0.0068(9)	–0.0111(9)	–0.0017(8)
N(3)	2*i*	0.7636(3)	0.8179(3)	0.1523(2)	0.044(1)	0.041(1)	0.044(1)	–0.0065(9)	–0.014(1)	–0.0021(9)
N(4)	2*i*	1.3410(3)	0.4526(3)	0.4334(2)	0.054(1)	0.044(1)	0.067(2)	–0.005(1)	–0.020(1)	0.009(1)
N(5)	2*i*	0.8792(3)	1.1291(3)	0.0069(2)	0.082(2)	0.038(1)	0.048(1)	0.002(1)	–0.020(1)	0.004(1)
N(6)	2*i*	0.8258(3)	1.2553(3)	–0.0067(2)	0.073(2)	0.048(2)	0.047(1)	0.005(1)	–0.024(1)	–0.000(1)
N(7)	2*i*	0.7768(6)	1.3789(4)	–0.0256(3)	0.227(5)	0.069(2)	0.085(2)	0.063(3)	–0.053(3)	–0.010(2)
N(8)	2*i*	0.7359(3)	1.1167(3)	0.2591(2)	0.047(1)	0.064(2)	0.065(2)	–0.003(1)	–0.023(1)	–0.013(1)
N(9)	2*i*	0.7718(3)	1.1639(3)	0.3267(2)	0.045(1)	0.032(1)	0.063(2)	–0.006(1)	–0.015(1)	0.006(1)
N(10)	2*i*	0.8034(4)	1.2127(3)	0.3936(2)	0.089(2)	0.056(2)	0.080(2)	–0.016(1)	–0.036(2)	–0.014(2)
C(1)	2*i*	1.1528(3)	1.2273(3)	0.1414(2)	0.051(2)	0.031(1)	0.054(2)	–0.004(1)	–0.019(1)	0.002(1)
C(2)	2*i*	1.2850(3)	1.2701(3)	0.1603(2)	0.058(2)	0.031(1)	0.060(2)	–0.012(1)	–0.017(1)	–0.003(1)
C(3)	2*i*	1.3714(3)	1.1642(3)	0.2178(2)	0.052(2)	0.042(2)	0.070(2)	–0.012(1)	–0.023(1)	–0.007(1)
C(4)	2*i*	1.3214(3)	1.0195(3)	0.2556(2)	0.047(2)	0.032(1)	0.061(2)	–0.003(1)	–0.023(1)	–0.001(1)
C(5)	2*i*	1.1887(3)	0.9836(3)	0.2336(2)	0.040(1)	0.030(1)	0.041(1)	–0.003(1)	–0.010(1)	–0.004(1)
C(6)	2*i*	1.1273(3)	0.8292(3)	0.2680(2)	0.041(1)	0.030(1)	0.038(1)	–0.004(1)	–0.009(1)	–0.001(1)
C(7)	2*i*	1.1961(3)	0.7057(3)	0.3263(2)	0.041(1)	0.036(1)	0.044(1)	–0.005(1)	–0.013(1)	–0.001(1)
C(8)	2*i*	1.1329(3)	0.5647(3)	0.3500(2)	0.044(1)	0.033(1)	0.036(1)	–0.002(1)	–0.006(1)	–0.001(1)
C(9)	2*i*	1.0011(3)	0.5539(3)	0.3136(2)	0.051(2)	0.030(1)	0.043(1)	–0.009(1)	–0.011(1)	–0.001(1)
C(10)	2*i*	0.9377(3)	0.6818(3)	0.2560(2)	0.045(1)	0.032(1)	0.038(1)	–0.008(1)	–0.008(1)	–0.003(1)
C(11)	2*i*	0.8000(3)	0.6843(3)	0.2111(2)	0.044(1)	0.040(2)	0.039(1)	–0.009(1)	–0.009(1)	–0.005(1)
C(12)	2*i*	0.7144(4)	0.5603(3)	0.2270(2)	0.064(2)	0.046(2)	0.066(2)	–0.019(1)	–0.024(2)	0.001(1)
C(13)	2*i*	0.5904(4)	0.5730(4)	0.1798(3)	0.061(2)	0.064(2)	0.073(2)	–0.029(2)	–0.019(2)	–0.009(2)
C(14)	2*i*	0.5547(3)	0.7077(4)	0.1186(2)	0.048(2)	0.074(2)	0.057(2)	–0.018(2)	–0.017(1)	–0.010(2)
C(15)	2*i*	0.6431(3)	0.8275(4)	0.1072(2)	0.048(2)	0.055(2)	0.052(2)	–0.009(1)	–0.017(1)	–0.003(1)
C(16)	2*i*	1.2059(3)	0.4309(3)	0.4119(2)	0.049(2)	0.034(1)	0.037(1)	–0.000(1)	–0.008(1)	–0.003(1)
C(17)	2*i*	1.1403(4)	0.2921(3)	0.4453(2)	0.061(2)	0.038(2)	0.047(2)	–0.006(1)	–0.017(1)	0.000(1)
C(18)	2*i*	1.2168(4)	0.1732(3)	0.5008(2)	0.084(2)	0.031(2)	0.054(2)	–0.005(1)	–0.018(2)	0.006(1)
C(19)	2*i*	1.3544(4)	0.1938(4)	0.5222(2)	0.072(2)	0.044(2)	0.059(2)	0.009(2)	–0.019(2)	0.006(1)
C(20)	2*i*	1.4119(4)	0.3356(4)	0.4876(3)	0.062(2)	0.055(2)	0.074(2)	–0.002(2)	–0.030(2)	0.011(2)

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