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Crystallographic report

Diazido[bis(2-pyridyl)amine]zinc(II) hydrate, $[Zn(C_{10}H_9N_3)_2(N_3)_2]\cdot H_2O$

Miao Du* and Xiao-Jun Zhao

College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, P. R. China

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In mononuclear $[Zn(C_{10}H_9N_3)_2(N_3)_2]\cdot H_2O$, the zinc atom has an approximate octahedral geometry, coordinated with four pyridyl nitrogen atoms derived from two bis(2-pyridyl)amine molecules and two terminal nitrogen donors of the azide anions. Hydrogen-bonding interactions extend this structure to form a double-layer architecture. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; zinc(II); bis(2-pyridyl)amine; hydrogen bonds

COMMENT

The structure of neutral $[Zn(C_{10}H_9N_3)_2(N_3)_2]\cdot H_2O$, isolated with a lattice water molecule per complex, was determined in connection with a wider study of blue photoluminescent materials.[1,2] The zinc centre is six-coordinated by four nitrogen donors of the pyridine rings, and two terminal nitrogen atoms of the azide anions (Fig. 1). The six Zn–N bond distances are in the range of 2.120(4)–2.252(4) Å with a mean value of 2.181(4) Å. The zinc atom lies essentially in the least-squares plane defined by N1, N2, N4, and N7. The bidentate ligands coordinate to the Zn^{II} atom to form two six-membered chelate rings, each with a flattened boat configuration.

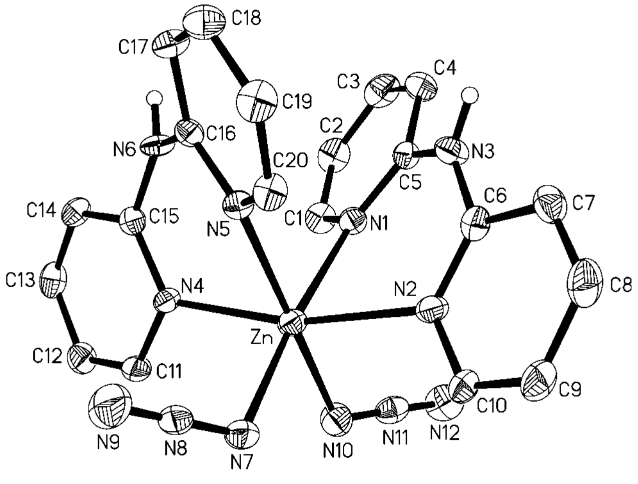

Figure 1. Molecular structure of $[Zn(C_{10}H_9N_3)_2(N_3)_2]\cdot H_2O$ (water moiety is omitted for clarity), with displacement ellipsoids drawn at the 30% probability level. Key geometric parameters: Zn–N1 2.252(4), Zn–N2 2.192(4), Zn–N4 2.154(4), Zn–N5 2.217(4), Zn–N7 2.120(4), Zn–N10 2.153(5), N7–N8 1.214(6), N8–N9 1.153(6), N10–N11 1.175(6), N11–N12 1.181(6) Å; N1–Zn–N2 80.43(15), N1–Zn–N4 89.86(14), N1–Zn–N5 88.59(14), N1–Zn–N7 174.59(15), N1–Zn–N10 88.36(16), N2–Zn–N4 166.19(13), N2–Zn–N5 88.56(14), N2–Zn–N7 94.77(16), N2–Zn–N10 93.89(16), N4–Zn–N5 81.35(14), N4–Zn–N7 95.29(16), N4–Zn–N10 95.65(16), N5–Zn–N7 93.82(16), N5–Zn–N10 175.72(14), N7–Zn–N10 89.47(18)°.

An analysis of the crystal packing shows the existence of intermolecular hydrogen bonds, which expand the structure to a double-layer supramolecular architecture. The $[Zn(C_{10}H_9N_3)_2(N_3)_2]$ moieties are connected through intermolecular $N6–H6A\cdots N7^{i}$ (i: $x+1, y, z$) bonds to form a one-dimensional chain along the [100] direction. Adjacent chains are further linked by the lattice water molecules through intermolecular $N3–H3B\cdots O1^{i}$ interactions between the N–H group of bis(2-pyridyl)amine and water, and $O1–H2\cdots N12^{ii}$ (ii: $x, y-1, z$) interactions between water and azide anions, forming a two-dimensional layer along the [110] plane. In addition, two neighbouring such layers facing each other are linked together through $O1–H1\cdots N12^{iii}$

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*Correspondence to: Miao Du, College of Chemistry and Life Science, Tianjin Normal University, Tianjin, 300074, People's Republic of China.
E-mail: dumiao@public.tpt.tj.cn
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(iii: $-x+1$, $-y+2$, $-z$) bonds between water and azide anions from another layer, resulting in a double-layer motif. Important hydrogen-bonding parameters: N6 $\cdots$ N7$^{\mathrm{i}}$ 3.11, N3 $\cdots$ O1$^{\mathrm{i}}$ 2.87, O1 $\cdots$ N12$^{\mathrm{ii}}$ 2.94, O1 $\cdots$ N12$^{\mathrm{iii}}$ 2.91 Å; N6–H6A $\cdots$ N7$^{\mathrm{i}}$ 150, N3–H3B $\cdots$ O1$^{\mathrm{ii}}$ 164, O1–H2 $\cdots$ N12$^{\mathrm{ii}}$ 173, O1–H1 $\cdots$ N12$^{\mathrm{iii}}$ 153°.

EXPERIMENTAL

Synthesis

A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (242 mg, 0.65 mmol) and bis(2-pyridyl)amine (239 mg, 1.40 mmol) was dissolved in methanol (30 ml), to which an excess of NaN_3 (143 mg, 2.20 mmol) was added slowly with stirring. Some white precipitate was formed after approximately 30 min, which was redissolved after the addition of excess water (20 ml). The resultant colourless solution was filtered and left to stand at room temperature. Well-defined block-shaped colourless single-crystals of $[Zn(C_{10}H_9N_3)_2(N_3)_2] \cdot H_2O$ were obtained by slow evaporation of the solvent within 1 week. Yield: 255 mg (77%). Anal. Found: C, 47.01; H, 4.22; N, 32.78. Calc.: C, 47.11; H, 3.95; N, 32.97%. The complex could also be isolated using the same synthetic procedure using $ZnCl_2$, $Zn(NO_3)_2$ or $Zn(OAc)_2$ as the source of zinc.

Crystallography

Intensity data for $[Zn(C_{10}H_9N_3)_2(N_3)_2] \cdot H_2O$ were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer on a colourless crystal with dimensions of 0.10 × 0.15 × 0.20 mm^3. $C_{20}H_{20}N_{12}OZn$, $M = 509.85$, triclinic, $P\bar{1}$, $a = 7.791(6)$, $b = 9.394(8)$, $c = 16.750(14)$ Å, $\alpha = 79.339(13)$, $\beta = 84.053(14)$, $\gamma = 69.598(13)°$, $V = 1128.2(16)$ Å^3, $Z = 2$, 3678 unique data ($\theta_{\max} = 25.0°$), 2768 data with $I \geq 2\sigma(I)$, $R_{\mathrm{obs}} = 0.046$, $\omega R = 0.103$ (all data), $\rho_{\max} = 0.45$ e$^-$ Å^{-3}. Programs used: SMART, SAINT, SHELXL97, and XP in SHELXTL. CCDC deposition number: 222666.

Acknowledgements

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