metal-organic compounds

Tris(3,3′-diamino-2,2′-bipyridine)zinc(II) dinitrate

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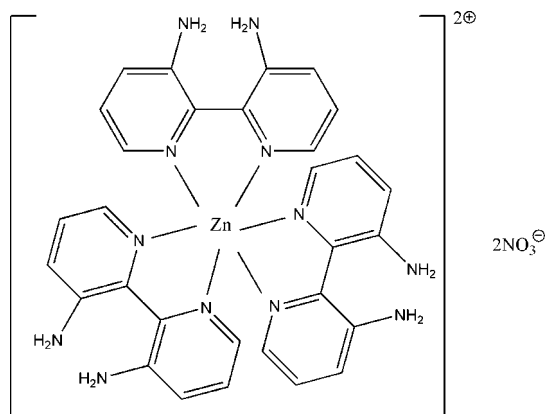Correspondence e-mail: shijingmin@beelink.com

In the title complex, $[Zn(C_{10}H_{10}N_4)_3](NO_3)_2$, the six-coordinate Zn^{II} atom lies at the intersection of three twofold axes in a slightly disorted octahedral coordination environment. The N atom of a nitrate anion is located on a threefold axis. In the crystal structure, intermolecular N—H···N and N—H···O hydrogen bonds between cations and anions form a two-dimensional network perpendicular to the c axis.

Related literature

For background information see: Kuang *et al.* (2006). For related structures, see: Shi *et al.* (2006*a*,*b*); Min *et al.* (2006); Zhang *et al.* (2007).

Experimental

Crystal data

$[Zn(C_{10}H_{10}N_4)_3](NO_3)_2$	$Z = 3$
$M_r = 748.05$	Mo $K\alpha$ radiation
Trigonal, $R32$	$\mu = 0.82$ mm^{-1}
$a = 14.6116 (19)$ Å	$T = 298 (2)$ K
$c = 13.199 (4)$ Å	$0.20 \times 0.14 \times 0.10$ mm
$V = 2440.4 (8)$ Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	4419 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1072 independent reflections
$T_{min} = 0.853$, $T_{max} = 0.922$	1005 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
$wR(F^2) = 0.081$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
$S = 1.05$	Absolute structure: Flack (1983), with 469 Friedel pairs
1072 reflections	Flack parameter: 0.03 (2)
78 parameters	
H-atom parameters constrained	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1^i	0.86	2.14	2.980 (4)	167
N3—H3B···N3^{ii}	0.86	2.40	2.851 (6)	113

Symmetry codes: (i) $-y + 1, x - y + 1, z$; (ii) $x - y + 1, -y + 2, -z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supplementary materials

Tris(3,3'-diamino-2,2'-bipyridine)zinc(II) dinitrate

C.-J. Wu, J.-N. Chen and J.-M. Shi

Comment

2,2'-Bipyridine and its derivatives play a pivotal role in the area of modern coordination chemistry. For example, some dye-sensitized solar cells deal with complexes of derivatives of 2,2'-bispyridine as a ligand (Kuang *et al.*, 2006). We have an interest in complexes containing 3,3'-diamino-2,2'-bipyridine and have synthesized the complexes containing Ni^{II}, Cd^{II}, Mn^{II} and Cu^{II} ions (Shi *et al.*, 2006*a*,*b*; Min *et al.*, 2006; Zhang *et al.*, 2007). Here we report the structure of the title complex (Fig. 1).

The Zn^{II} atom, located on the intersection of a threefold axis and a twofold axis, assumes a slightly distorted octahedral ZnN_6 coordination geometry. The nitrate anion lies on a threefold axis. In the 3,3'-diamino-2,2'-bipyridine ligand, each pyridine ring is essentially planar with a maximum deviation of −0.029 (4)Å for atom C1; the dihedral angle between the two pyridine rings is 34.77 (18), which is larger than that in the Ni(II) complex, but smaller than that in Cd(II) and Mn(II) complexes. Just as with the Ni(II), Mn(II) and Cd(II) complexes the deviation from planarity in the title compound is expected in terms of steric relief. The hydrogen bonds (Table 1) that arise from nitrate anions and amino group result in the connection of the cations and the nitrate anions and contribute to the formation of a supermolecular two-dimensional sheet parallel *ab* plane, as shown in Fig. 2.

Experimental

$Zn(NO_3)_2 \cdot 6H_2O$ (0.0354 g, 0.119 mmol) in H_2O (10 ml) was added to 6,6'-diamino-2,2'-bipyridine (0.0110 g, 0.059 mmol) in acetonitrile (5 ml), and the solution was stirred for a few minutes. Colorless crystals were obtained after allowing the solution to stand at room temperature for one week. The infrared stretching vibrations of pyridine ring and amino groups appeared at 1638 cm^{-1}, 1465 cm^{-1} and 1384 cm^{-1}.

Refinement

The H atoms were placed in calculated positions and refined as riding, with C—H = 0.93 Å, $U_{iso}(H) = 1.2_{eq}(C)$; N—H = 0.86 Å, $U_{iso}(H) = 1.2_{eq}(N)$ for amino group.

Figures

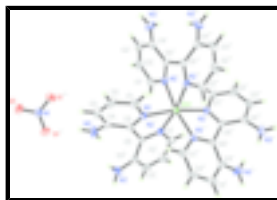Fig. 1. The molecular structure showing the atom numbering scheme with thermal ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $x − y + 1$, $−y + 2$, $−z$; (ii) $−y + 1$, $x − y + 2$, z; (iii) $−x + y − 1$, $−x + 1$, z; (iv) $y − 1$, $x + 1$, $−z$; (v) $−x$, $−x + y$, $−z$; (vi) $−y + 1$, $x − y + 1$, z; (vii) $−x + y$, $−x + 1$, z]. Only one of the two nitrate anions in the formula unit is showm.
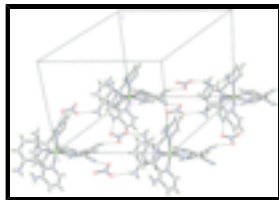
Fig. 2. Part of the crystal structure with hydrogen bonds shown as dashed lines.

Tris(3,3'-diamino-2,2'-bipyridine)zinc(II) bis(nitrate)

Crystal data

$[Zn(C_{10}H_{10}N_4)_3](NO_3)_2$	$Z = 3$
$M_r = 748.05$	$F_{000} = 1158$
Trigonal, $R32$	$D_x = 1.527$ Mg m^{-3}
Hall symbol: R 3 2"	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 14.6116 (19)$ Å	Cell parameters from 918 reflections
$b = 14.6116 (19)$ Å	$\theta = 2.2–19.0º$
$c = 13.199 (4)$ Å	$\mu = 0.82$ mm^{-1}
$\alpha = 90º$	$T = 298 (2)$ K
$\beta = 90º$	Prism, colourless
$\gamma = 120º$	$0.20 \times 0.14 \times 0.10$ mm
$V = 2440.4 (8)$ Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	1072 independent reflections
Radiation source: fine-focus sealed tube	1005 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.051$
$T = 298(2)$ K	$\theta_{max} = 26.0º$
φ and ω scans	$\theta_{min} = 2.2º$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -18 \rightarrow 10$
$T_{min} = 0.853$, $T_{max} = 0.922$	$k = -15 \rightarrow 18$
4419 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
1072 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}

78 parameters	Extinction correction: none	
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 469 Friedel pairs	
Secondary atom site location: difference Fourier map	Flack parameter: 0.03 (2)	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.0000	1.0000	0.0000	0.0332 (2)
N2	0.0862 (2)	0.9399 (2)	0.08301 (16)	0.0354 (6)
C5	0.1754 (2)	0.9566 (2)	0.0369 (2)	0.0363 (7)
C3	0.1693 (4)	0.8141 (4)	0.1330 (2)	0.0585 (9)
H3	0.1969	0.7711	0.1505	0.070*
C1	0.0411 (3)	0.8668 (3)	0.1543 (3)	0.0487 (8)
H1	−0.0206	0.8564	0.1851	0.058*
C2	0.0846 (3)	0.8054 (3)	0.1838 (3)	0.0593 (10)
H2	0.0559	0.7588	0.2380	0.071*
C4	0.2154 (3)	0.8876 (2)	0.0541 (3)	0.0478 (8)
N1	0.3333	0.6667	0.0452 (2)	0.0415 (8)
O1	0.3647 (2)	0.6020 (2)	0.04535 (17)	0.0631 (7)
N3	0.2931 (3)	0.8874 (3)	−0.0037 (3)	0.0721 (10)
H3A	0.3133	0.8425	0.0085	0.087*
H3B	0.3217	0.9323	−0.0522	0.087*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0295 (3)	0.0295 (3)	0.0407 (4)	0.01473 (14)	0.000	0.000
N2	0.0331 (16)	0.0286 (15)	0.0419 (12)	0.0135 (13)	0.0018 (12)	0.0051 (12)
C5	0.0318 (15)	0.0314 (16)	0.0463 (18)	0.0163 (13)	−0.0014 (13)	−0.0018 (13)
C3	0.065 (3)	0.044 (2)	0.077 (2)	0.0356 (19)	−0.006 (3)	0.011 (2)
C1	0.051 (2)	0.047 (2)	0.0494 (19)	0.0249 (16)	0.0071 (15)	0.0095 (15)
C2	0.073 (3)	0.048 (2)	0.059 (2)	0.031 (2)	−0.0009 (19)	0.0202 (17)
C4	0.0407 (19)	0.0358 (17)	0.069 (2)	0.0204 (15)	−0.0072 (16)	−0.0034 (16)
N1	0.0402 (13)	0.0402 (13)	0.044 (2)	0.0201 (7)	0.000	0.000
O1	0.0538 (17)	0.0466 (17)	0.0985 (16)	0.0322 (15)	0.0023 (13)	0.0010 (13)
N3	0.062 (2)	0.059 (2)	0.116 (3)	0.0456 (18)	0.022 (2)	0.0168 (19)

Geometric parameters (Å, °)

Zn1—N2[i]	2.159 (2)	C3—C4	1.404 (5)
Zn1—N2[ii]	2.159 (2)	C3—H3	0.9300
Zn1—N2[iii]	2.159 (2)	C1—C2	1.390 (5)
Zn1—N2[iv]	2.159 (2)	C1—H1	0.9300
Zn1—N2	2.159 (2)	C2—H2	0.9300
Zn1—N2[v]	2.159 (2)	C4—N3	1.368 (4)
N2—C1	1.325 (4)	N1—O1[vi]	1.239 (2)
N2—C5	1.345 (4)	N1—O1[vii]	1.239 (2)
C5—C4	1.414 (4)	N1—O1	1.239 (2)
C5—C5[iii]	1.467 (6)	N3—H3A	0.8600
C3—C2	1.357 (5)	N3—H3B	0.8600
N2[i]—Zn1—N2[ii]	169.86 (16)	C4—C5—C5[iii]	124.6 (2)
N2[i]—Zn1—N2[iii]	96.53 (8)	C2—C3—C4	120.3 (3)
N2[ii]—Zn1—N2[iii]	91.45 (14)	C2—C3—H3	119.8
N2[i]—Zn1—N2[iv]	96.53 (8)	C4—C3—H3	119.8
N2[ii]—Zn1—N2[iv]	76.28 (14)	N2—C1—C2	121.1 (3)
N2[iii]—Zn1—N2[iv]	96.53 (8)	N2—C1—H1	119.5
N2[i]—Zn1—N2	91.45 (14)	C2—C1—H1	119.5
N2[ii]—Zn1—N2	96.53 (8)	C3—C2—C1	119.4 (3)
N2[iii]—Zn1—N2	76.28 (14)	C3—C2—H2	120.3
N2[iv]—Zn1—N2	169.86 (16)	C1—C2—H2	120.3
N2[i]—Zn1—N2[v]	76.28 (14)	N3—C4—C3	119.5 (3)
N2[ii]—Zn1—N2[v]	96.53 (8)	N3—C4—C5	123.5 (3)
N2[iii]—Zn1—N2[v]	169.86 (16)	C3—C4—C5	117.0 (3)
N2[iv]—Zn1—N2[v]	91.45 (14)	O1[vi]—N1—O1[vii]	120.000 (2)
N2—Zn1—N2[v]	96.53 (8)	O1[vi]—N1—O1	120.000 (2)
C1—N2—C5	120.9 (3)	O1[vii]—N1—O1	120.000 (3)
C1—N2—Zn1	122.1 (2)	C4—N3—H3A	120.0
C5—N2—Zn1	113.92 (18)	C4—N3—H3B	120.0
N2—C5—C4	120.4 (3)	H3A—N3—H3B	120.0
N2—C5—C5[iii]	114.69 (17)		
N2[ii]—Zn1—N2—C1	101.6 (2)	C5—N2—C1—C2	0.2 (5)
N2[iii]—Zn1—N2—C1	−168.5 (3)	Zn1—N2—C1—C2	159.3 (3)
N2[v]—Zn1—N2—C1	4.2 (3)	C4—C3—C2—C1	2.7 (6)
N2[ii]—Zn1—N2—C5	−98.0 (3)	N2—C1—C2—C3	−5.7 (6)
N2[iii]—Zn1—N2—C5	−8.12 (15)	C2—C3—C4—N3	−172.8 (4)
N2[v]—Zn1—N2—C5	164.6 (2)	C2—C3—C4—C5	5.2 (6)
C1—N2—C5—C4	8.2 (4)	N2—C5—C4—N3	167.3 (3)
Zn1—N2—C5—C4	−152.5 (2)	C5[iii]—C5—C4—N3	−6.8 (5)

| C1—N2—C5—C5$^{\text{iii}}$ | −177.2 (3) | N2—C5—C4—C3 | −10.7 (5) |
| Zn1—N2—C5—C5$^{\text{iii}}$ | 22.1 (4) | C5$^{\text{iii}}$—C5—C4—C3 | 175.2 (4) |

Symmetry codes: (i) −x, −x+y, −z; (ii) −y+1, x−y+2, z; (iii) x−y+1, −y+2, −z; (iv) y−1, x+1, −z; (v) −x+y−1, −x+1, z; (vi) −x+y, −x+1, z; (vii) −y+1, x−y+1, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1$^{\text{vii}}$	0.86	2.14	2.980 (4)	167
N3—H3B···N3$^{\text{iii}}$	0.86	2.40	2.851 (6)	113

Symmetry codes: (vii) −y+1, x−y+1, z; (iii) x−y+1, −y+2, −z.

Fig. 1

Fig. 2