metal-organic compounds

[6-Phenyl-2,4-bis(2-pyridylamino)-1,3,5-triazine]sulfatonickel(II) dihydrate

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The title complex, $[Ni(SO_4)(C_{19}H_{17}N_7)]\cdot 2H_2O$ or $[Ni(SO_4)$-(dpdapt)]·$2H_2O$ [dpdapt is 6-phenyl-2,4-bis(2-pyridylamino)-1,3,5-triazine], has a distorted trigonal–bipyramidal coordination where the equatorial plane contains the N atoms of the pyridine rings and one of the O atoms of the sulfate group, while the axial positions are occupied by the other O atom and the N atom of the triazine ring of the dpdapt ligand. The complex lies across a mirror plane. The H atoms of the NH group of the dpdapt ligand and of the solvent water molecule are involved in hydrogen bonds, which form an infinite two-dimensional corrugated sheet parallel to the *ac* plane. The water molecule is disordered over two positions; the site occupancy factors are 0.58 and 0.42.

Related literature

For related literature, see: Chang *et al.* (1999); Cotton *et al.* (1998); Jing *et al.* (2000); Nathan & Traina (2003); Peng *et al.* (2000); Sheu *et al.* (1996); Shieh *et al.* (1997); Wang *et al.* (1999, 2006); Xu *et al.* (2004); Yang *et al.* (1997).
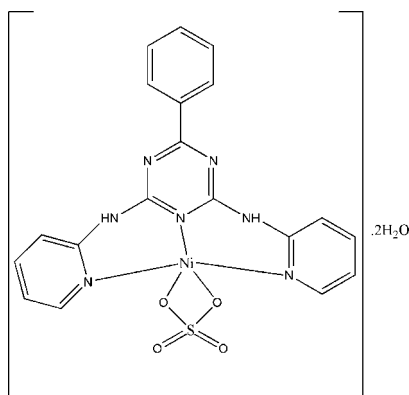
Experimental

Crystal data

$[Ni(SO_4)(C_{19}H_{17}N_7)]\cdot 2H_2O$	V = 2224.5 (5) Å^3
M_r = 532.18	Z = 4
Orthorhombic, $Pnnm$	Mo $K\alpha$ radiation
a = 15.912 (2) Å	μ = 1.02 mm^{-1}
b = 11.4246 (15) Å	T = 298 (2) K
c = 12.2370 (16) Å	0.28 × 0.23 × 0.15 mm

Data collection

Bruker APEXII area-detector diffractometer	11003 measured reflections
	2104 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	1719 reflections with $I > 2\sigma(I)$
T_{min} = 0.764, T_{max} = 0.862	R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	175 parameters
$wR(F^2)$ = 0.092	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
2104 reflections	$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2···O4	0.86	2.04	2.833 (6)	153
N2—H2···O41	0.86	1.93	2.782 (7)	170
O4—H41···O2^i	0.86	1.97	2.757 (6)	153
O41—H42···O41^{ii}	0.85	2.01	2.774 (14)	149

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

[6-Phenyl-2,4-bis(2-pyridylamino)-1,3,5-triazine]sulfatonickel(II) dihydrate

F.-M. Wang

Comment

Transition metal complexes with polypyridylamine ligands, possessing diverse structures and special optical and electro-magnetic properties (Xu *et al.*, 2004), have aroused great interest among researchers, tri-pyridyldiamine ligand usually ex-hibits donor as well as acceptor properties and can be used as a popular chelating ligand (Jing *et al.*, 2000; Nathan, *et al.*, 2003; Wang *et al.*,2006). In recent years great efforts have been taken to synthesize and characterize metal chain complexes which can be used to study the metal-metal interactions (Yang *et al.*, 1997; Cotton *et al.*, 1998). Also, metal string complexes with their potential application as new nano-materials such as molecular metal wires have attracted much attention and been investigated in great hard (Peng *et al.*, 2000; Wang *et al.*,1999). By now a series of polynuclear metal chain complexes have been successfully synthesized and characterized (Sheu *et al.*,1996; Shieh *et al.*, 1997; Chang *et al.*, 1999). Herein we report the synthesis and crystal structure of the title complex.

The Ni1 atom in the title complex has a distorted trigonal bipyramidal coordination where the equatorial plane contains the N atoms of the peripheral pyridine rings and one of the O atom of the sulfate whereas the axial positions are occupied by the other O atom and the N atom of the central pyridine ring of the dpdapt ligand (Fig. 1). The complex lies around a mirror plane. The dihedral angle between the two pyridyl ring planes of the dpdapt ligand is 39.2°. The H atoms of one NH group of the dpdapt ligand and the solvent water molecule are involved in hydrogen bonds which form an infinite two-dimensional corrugated sheet parallel to the *ac*-plane (Table 1).

Experimental

Dpdapt (0.022 g, 0.0098 mmol), NiSO4 (0.015 g, 0.0085 mmol). were added in a mixed solvent of acetonitrile, the mixture was heated for eight hours under reflux. During the process stirring and influx were required. The resultant was then filtered to give a pure solution which was infiltrated by diethyl ether freely in a closed vessel, two weeks later some single crystals of the size suitable for X-Ray diffraction analysis.

Refinement

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.97Å (methylene) and N—H = 0.86Å with U_{iso}(H) = 1.2Ueq (C or N).

The water molecule is disordered over two positions with occupancy factor ratio of 0.58/0.42. H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O—H= 0.85 (1) Å and H···H= 1.39 (2) Å) with U_{iso}(H) = 1.5Ueq(O). In the last stage of refinement, they were treated as riding on the water O atom.
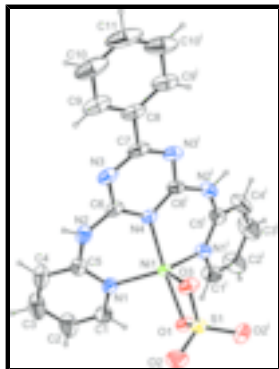
supplementary materials

Figures

Fig. 1. Molecular view of I with the atom-labelling-scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small sphers of arbitrary radii. Disordered water molecule has been omitted for clarity [symmetry code (i): x, y, $1 - z$]

[6-Phenyl-2,4-bis(2-pyridylamino)-1,3,5-triazine]sulfatonickel(II) dihydrate

Crystal data

[Ni(SO$_4$)(C$_{19}$H$_{17}$N$_7$)]·2H$_2$O	$F_{000} = 1096$
$M_r = 532.18$	$D_x = 1.589$ Mg m^{-3}
Orthorhombic, *Pnnm*	Mo *K*α radiation
	$\lambda = 0.71073$ Å
Hall symbol: -P 2 2n	Cell parameters from 2104 reflections
$a = 15.912$ (2) Å	$\theta = 2.1–25.2°$
$b = 11.4246$ (15) Å	$\mu = 1.02$ mm^{-1}
$c = 12.2370$ (16) Å	$T = 298$ (2) K
$V = 2224.5$ (5) Å^3	Block, green
$Z = 4$	$0.28 \times 0.23 \times 0.15$ mm

Data collection

Bruker APEXII area-detector diffractometer	2104 independent reflections
Radiation source: fine-focus sealed tube	1719 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.038$
$T = 298(2)$ K	$\theta_{max} = 25.2°$
φ and ω scan	$\theta_{min} = 2.1°$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$h = -18 \rightarrow 19$
$T_{min} = 0.764$, $T_{max} = 0.862$	$k = -10 \rightarrow 13$
11003 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained

$wR(F^2) = 0.092$

$w = 1/[\sigma^2(F_o{}^2) + (0.P)^2 + 1.0521P]$

where $P = (F_o{}^2 + 2F_c{}^2)/3$

$S = 1.07$

$(\Delta/\sigma)_{max} < 0.001$

2104 reflections

$\Delta\rho_{max} = 0.30$ e Å^{-3}

175 parameters

$\Delta\rho_{min} = -0.37$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$	Occ. (<1)
Ni1	0.18503 (2)	0.06288 (4)	0.5000	0.03885 (16)	
S1	0.08564 (5)	0.24842 (8)	0.5000	0.0454 (2)	
O2	0.05011 (14)	0.2996 (2)	0.40209 (18)	0.0782 (7)	
O3	0.17834 (15)	0.2561 (2)	0.5000	0.0575 (7)	
O1	0.06843 (14)	0.1189 (2)	0.5000	0.0506 (6)	
N1	0.17888 (12)	−0.0097 (2)	0.35331 (18)	0.0490 (5)	
N2	0.31683 (13)	0.04742 (19)	0.30851 (19)	0.0544 (6)	
H2	0.3449	0.0721	0.2531	0.065*	
N3	0.43009 (13)	0.1129 (2)	0.4028 (2)	0.0560 (6)	
N4	0.30740 (17)	0.0560 (2)	0.5000	0.0426 (7)	
C1	0.10833 (18)	−0.0686 (3)	0.3268 (3)	0.0676 (8)	
H1	0.0637	−0.0684	0.3758	0.081*	
C2	0.0999 (2)	−0.1282 (4)	0.2316 (3)	0.0919 (12)	
H2A	0.0505	−0.1681	0.2154	0.110*	
C3	0.1663 (3)	−0.1282 (4)	0.1595 (3)	0.0961 (13)	
H3	0.1622	−0.1684	0.0937	0.115*	
C4	0.2380 (2)	−0.0693 (3)	0.1846 (3)	0.0768 (10)	
H4	0.2830	−0.0683	0.1361	0.092*	
C5	0.24299 (17)	−0.0110 (2)	0.2830 (2)	0.0506 (6)	
C6	0.35177 (15)	0.0718 (2)	0.4067 (2)	0.0455 (6)	
C7	0.4653 (2)	0.1345 (3)	0.5000	0.0562 (10)	
C8	0.5512 (2)	0.1856 (3)	0.5000	0.0656 (12)	
C9	0.59136 (18)	0.2092 (3)	0.4015 (4)	0.0821 (11)	
H9	0.5649	0.1922	0.3356	0.098*	
C10	0.6715 (2)	0.2585 (3)	0.4022 (5)	0.1124 (18)	

H10	0.6985	0.2755	0.3367	0.135*	
C11	0.7105 (4)	0.2819 (5)	0.5000	0.127 (3)	
H11	0.7642	0.3141	0.5000	0.152*	
O4	0.4158 (3)	0.0491 (4)	0.1161 (5)	0.0835 (15)	0.58
H41	0.4458	0.1115	0.1204	0.125*	0.58
H43	0.4464	−0.0088	0.1369	0.125*	0.58
O41	0.3923 (4)	0.1150 (6)	0.1133 (6)	0.0748 (17)	0.42
H42	0.3790	0.0943	0.0489	0.112*	0.42
H44	0.3635	0.1736	0.1335	0.112*	0.42

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0269 (2)	0.0473 (3)	0.0424 (3)	0.00399 (17)	0.000	0.000
S1	0.0370 (5)	0.0476 (5)	0.0517 (5)	0.0082 (4)	0.000	0.000
O2	0.0715 (14)	0.0913 (16)	0.0720 (14)	0.0225 (12)	−0.0080 (11)	0.0278 (12)
O3	0.0383 (14)	0.0467 (15)	0.087 (2)	−0.0007 (11)	0.000	0.000
O1	0.0344 (13)	0.0467 (14)	0.0706 (17)	0.0008 (11)	0.000	0.000
N1	0.0419 (12)	0.0513 (13)	0.0538 (13)	−0.0002 (10)	0.0028 (10)	−0.0051 (10)
N2	0.0518 (14)	0.0571 (15)	0.0541 (14)	−0.0098 (10)	0.0143 (11)	0.0008 (10)
N3	0.0359 (12)	0.0479 (13)	0.0843 (17)	0.0003 (10)	0.0097 (11)	0.0012 (12)
N4	0.0348 (15)	0.0403 (16)	0.0528 (18)	0.0031 (12)	0.000	0.000
C1	0.0502 (17)	0.082 (2)	0.070 (2)	−0.0170 (15)	0.0045 (15)	−0.0190 (16)
C2	0.086 (3)	0.114 (3)	0.076 (2)	−0.043 (2)	0.006 (2)	−0.036 (2)
C3	0.124 (3)	0.100 (3)	0.064 (2)	−0.049 (3)	0.015 (2)	−0.032 (2)
C4	0.097 (3)	0.077 (2)	0.0568 (19)	−0.0252 (19)	0.0279 (18)	−0.0147 (16)
C5	0.0556 (16)	0.0442 (14)	0.0522 (16)	−0.0044 (12)	0.0063 (13)	−0.0014 (12)
C6	0.0356 (13)	0.0386 (13)	0.0625 (17)	0.0032 (10)	0.0071 (12)	0.0031 (11)
C7	0.0316 (19)	0.035 (2)	0.102 (3)	0.0035 (15)	0.000	0.000
C8	0.032 (2)	0.040 (2)	0.125 (4)	0.0030 (16)	0.000	0.000
C9	0.0443 (17)	0.0491 (18)	0.153 (4)	0.0024 (13)	0.014 (2)	0.009 (2)
C10	0.050 (2)	0.063 (2)	0.224 (6)	−0.0063 (17)	0.030 (3)	0.017 (3)
C11	0.037 (3)	0.069 (4)	0.274 (11)	−0.007 (3)	0.000	0.000
O4	0.082 (4)	0.071 (3)	0.097 (3)	−0.006 (2)	0.033 (3)	0.000 (3)
O41	0.058 (4)	0.097 (5)	0.070 (4)	−0.004 (4)	0.014 (3)	−0.001 (4)

Geometric parameters (Å, °)

Ni1—N4	1.949 (3)	C2—H2A	0.9300
Ni1—O1	1.963 (2)	C3—C4	1.359 (5)
Ni1—N1	1.980 (2)	C3—H3	0.9300
Ni1—O3	2.210 (3)	C4—C5	1.378 (4)
Ni1—S1	2.6447 (10)	C4—H4	0.9300
S1—O2	1.448 (2)	C7—C8	1.486 (5)
S1—O3	1.478 (2)	C8—C9	1.390 (4)
S1—O1	1.505 (3)	C9—C10	1.395 (4)
N1—C5	1.335 (3)	C9—H9	0.9300
N1—C1	1.349 (3)	C10—C11	1.374 (6)
N2—C6	1.353 (3)	C10—H10	0.9300

N2—C5	1.387 (3)	C11—H11	0.9300
N2—H2	0.8600	O4—H41	0.8594
N3—C6	1.333 (3)	O4—H43	0.8603
N3—C7	1.338 (3)	O4—H42	1.1338
N4—C6	1.354 (3)	O41—H41	0.8568
C1—C2	1.356 (4)	O41—H42	0.8499
C1—H1	0.9300	O41—H44	0.8478
C2—C3	1.377 (5)		
N4—Ni1—O1	163.28 (11)	C1—C2—H2A	120.9
N4—Ni1—N1	91.87 (7)	C3—C2—H2A	120.9
O1—Ni1—N1	95.15 (7)	C4—C3—C2	120.0 (3)
N1—Ni1—N1^i	130.12 (14)	C4—C3—H3	120.0
N4—Ni1—O3	95.06 (10)	C2—C3—H3	120.0
O1—Ni1—O3	68.22 (10)	C3—C4—C5	119.0 (3)
N1—Ni1—O3	114.57 (7)	C3—C4—H4	120.5
N4—Ni1—S1	129.03 (8)	C5—C4—H4	120.5
O1—Ni1—S1	34.25 (7)	N1—C5—C4	121.7 (3)
N1—Ni1—S1	107.82 (6)	N1—C5—N2	119.8 (2)
O3—Ni1—S1	33.96 (6)	C4—C5—N2	118.6 (3)
O2^i—S1—O2	111.65 (19)	N3—C6—N2	115.1 (2)
O2—S1—O3	111.45 (11)	N3—C6—N4	124.4 (3)
O2—S1—O1	109.03 (12)	N2—C6—N4	120.5 (2)
O3—S1—O1	103.90 (14)	N3—C7—N3^i	125.5 (3)
O2—S1—Ni1	123.86 (10)	N3—C7—C8	117.25 (17)
O3—S1—Ni1	56.69 (10)	C9^i—C8—C9	120.2 (4)
O1—S1—Ni1	47.21 (9)	C9—C8—C7	119.9 (2)
S1—O3—Ni1	89.35 (12)	C8—C9—C10	119.6 (5)
S1—O1—Ni1	98.53 (12)	C8—C9—H9	120.2
C5—N1—C1	118.4 (2)	C10—C9—H9	120.2
C5—N1—Ni1	123.48 (17)	C11—C10—C9	119.8 (6)
C1—N1—Ni1	117.93 (19)	C11—C10—H10	120.1
C6—N2—C5	130.3 (2)	C9—C10—H10	120.1
C6—N2—H2	114.8	C10^i—C11—C10	121.1 (6)
C5—N2—H2	114.8	C10—C11—H11	119.5
C6—N3—C7	115.1 (3)	H41—O4—H43	107.8
C6^i—N4—C6	114.9 (3)	H41—O4—H42	87.4
C6—N4—Ni1	121.04 (15)	H43—O4—H42	149.1
N1—C1—C2	122.7 (3)	H41—O41—H42	109.1
N1—C1—H1	118.7	H41—O41—H44	123.0
C2—C1—H1	118.7	H42—O41—H44	110.8
C1—C2—C3	118.3 (3)		

Symmetry codes: (i) *x*, *y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O4	0.86	2.04	2.833 (6)	153
N2—H2···O41	0.86	1.93	2.782 (7)	170

O4—H41···O2^{ii}	0.86	1.97	2.757 (6)	153
O41—H42···O41^{iii}	0.85	2.01	2.774 (14)	149

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

Fig. 1