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[*N*-(3-Aminopropyl)-1,3-propanediamine]diaquasulfatonickel(II) Monohydrate, $[Ni(SO_4)(dpt)(H_2O)_2].H_2O$ [dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$]

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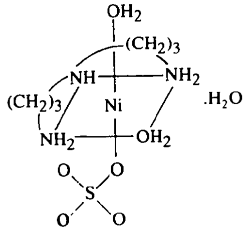
Abstract

The coordination polyhedron about the Ni^{II} atom in $[Ni(SO_4)(dpt)(H_2O)_2].H_2O$, [dpt = *N*-(3-aminopropyl)-1,3-propanediamine] is a distorted octahedron consisting of three N atoms of the dpt ligand coordinating meridionally, one O atom from the monodentate sulfate group and two aqua O atoms. The two six-membered chelate rings are in chair forms. Molecular packing is stabilized by an extensive network of hydrogen bonds involving the triamine N atoms, sulfate O atoms and water molecules.

Comment

Thermally induced solid-state phase transitions in nickel(II)–triamine complexes are documented in the literature (Mukherjee *et al.*, 1994; Koner, Pariya & Ray Chaudhuri, 1993). There has been extensive study (Pariya, Ghosh, Ghosh, Mukherjee, Mukherjee & Ray Chaudhuri, 1995; Ihara, Fukuda & Sone, 1987; Halfpenny, Levason, McAuliffe, Hill & McCullough, 1979) directed towards understanding the role of anions in the metal coordination and conformational changes of the chelate rings of the resulting metal–amine complexes. Pariya, Ghosh & Ray Chaudhuri (1995) have recently reported the synthesis of $Ni(dpt)SO_4.3H_2O$ [dpt = *N*-(3-aminopropyl)-1,3-propanediamine] with a proposed structure of $[Ni(dpt)(H_2O)_3].SO_4$ based on spectral data. An X-ray structure analysis of this complex, (I), was motivated by our continued interest in establishing the coordination geometry around the metal centre and conformation of the chelate rings. An *ORTEP*II (Johnson, 1976) view of the complex with atom-labelling and ring-numbering scheme is shown in Fig. 1.



(I)

The coordination polyhedron around the metal atom is best described as a distorted octahedron with an N_3O_3 chromophore. The three ligand N atoms and one aqua O atom (O6) define the basal plane [Ni distance 0.031 (1) Å] and the remaining two O atoms (one from the sulfate group and the other belonging to the water molecule) are in axial positions. The in-plane distortion is due to the asymmetric nature of the ligand atoms and is reflected by the deviations of the angles formed by the basal plane atoms at the metal centre [83.9 (1)–96.2 (1)°] from 90°. The Ni—N distances, in the range 2.084 (2)–2.099 (3) Å, are consistent with the corresponding values for Ni^{II}–triamine systems with octahedral metal coordination (Table 4). The observed lengthening of Ni—O1 [2.171 (2) Å] compared with Ni—O5 [2.104 (2) Å] and Ni—O6 [2.127 (2) Å] is due to steric constraints introduced by the coordinating bulky SO_4 ligand. An almost ideal chair conformation is displayed by ring *A* with C5 0.716 (4) Å above and Ni 0.655 (1) Å below the least-squares plane through the remaining endocyclic atoms, while ring *B* adopts a significantly distorted chair form with Ni 0.373 (1) Å above and C2 0.753 (4) Å below the plane defined by the other four ring atoms. The dihedral angle between the planar parts of the two chelate rings is 151.9 (2)°. The Cremer & Pople (1975) ring puckering parameters are: $q_2 = 0.196\,(4)$, $q_3 = -0.513\,(3)$, $Q = 0.549\,(4)$ Å, $\theta = 159.2\,(3)°$, $\varphi = -20.0\,(10)°$ for ring *A*; $q_2 = 0.376\,(3)$, $q_3 = -0.407\,(3)$, $Q = 0.554\,(4)$ Å, $\theta = 137.3\,(3)°$, $\varphi = 21.9\,(6)°$ for ring *B*. There are several intramolecular hydrogen bonds (Table 3) which control the overall

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chelate ring conformations. The crystal packing is stabilized by an extensive network of hydrogen bonds involving amine N atoms, sulfate O atoms and water molecules. Table 3 lists ten such D—H···A distances and the symmetry relations between the donors and acceptors.

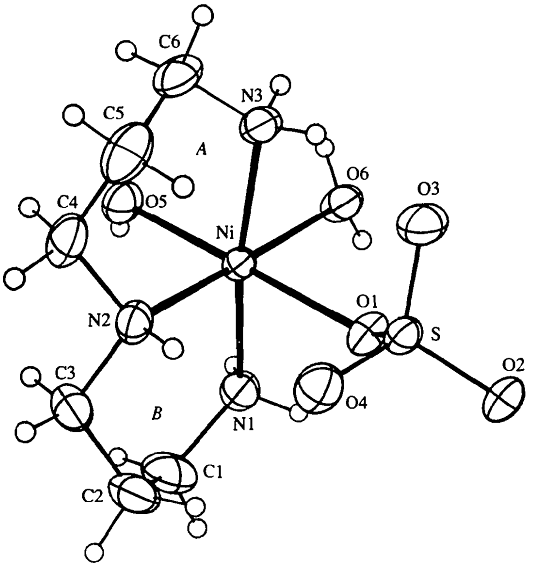

Fig. 1. *ORTEP*II (Johnson, 1976) view of the molecule showing the atom-labelling and ring-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title complex was synthesized by adding the dpt ligand (1 mmol) dropwise with constant stirring to an aqueous solution (10 ml) of $NiSO_4.6H_2O$ (1 mmol). Single crystals suitable for X-ray diffraction were obtained by slow evaporation. The crystal density D_m was measured by flotation.

Crystal data

$[Ni(SO_4)(C_6H_{17}N_3)(H_2O)_2].H_2O$
$M_r = 340.04$
Triclinic
$P\bar{1}$
$a = 7.242 (3)$ Å
$b = 8.454 (3)$ Å
$c = 12.230 (6)$ Å
$\alpha = 74.53 (3)°$
$\beta = 74.15 (3)°$
$\gamma = 78.64 (3)°$
$V = 688.0 (5)$ Å^3
$Z = 2$
$D_x = 1.642$ Mg m^{-3}
$D_m = 1.63$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 7.5–15°$
$\mu = 1.591$ mm^{-1}
$T = 293 (2)$ K
Parallelepiped
0.44 × 0.24 × 0.12 mm
Light blue

Data collection

$R3m/V$ diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.653$, $T_{max} = 0.784$
2135 measured reflections
2047 independent reflections
1801 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0320$
$\theta_{max} = 23.54°$
$h = -8 \rightarrow 0$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
2 standard reflections monitored every 100 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0246$
$wR(F^2) = 0.0579$
$S = 0.947$
2044 reflections
255 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.6850P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.411$
$\Delta\rho_{max} = 0.238$ e Å^{-3}
$\Delta\rho_{min} = -0.276$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ni	0.19412 (5)	0.06399 (4)	0.28971 (3)	0.02152 (12)
S	−0.25827 (9)	0.26314 (8)	0.30796 (6)	0.0249 (2)
O1	−0.1116 (3)	0.1365 (2)	0.3590 (2)	0.0293 (4)
O2	−0.4441 (3)	0.2568 (3)	0.3956 (2)	0.0386 (5)
O3	−0.1964 (3)	0.4264 (2)	0.2800 (2)	0.0420 (5)
O4	−0.2761 (3)	0.2206 (3)	0.2028 (2)	0.0376 (5)
O5	0.4906 (3)	−0.0164 (3)	0.2314 (2)	0.0334 (5)
O6	0.2448 (3)	0.0918 (3)	0.4465 (2)	0.0324 (5)
O7	0.4214 (4)	0.3143 (3)	0.6229 (2)	0.0563 (7)
N1	0.1461 (4)	−0.1787 (3)	0.3796 (2)	0.0329 (6)
N2	0.1406 (3)	0.0495 (3)	0.1336 (2)	0.0285 (5)
N3	0.2384 (4)	0.3117 (3)	0.2292 (2)	0.0297 (6)
C1	0.1260 (6)	−0.3045 (4)	0.3209 (4)	0.0499 (9)
C2	0.0370 (5)	−0.2310 (4)	0.2183 (3)	0.0453 (8)
C3	0.1606 (5)	−0.1214 (4)	0.1185 (3)	0.0417 (8)
C4	0.2486 (5)	0.1550 (4)	0.0271 (3)	0.0394 (8)
C5	0.2126 (5)	0.3368 (4)	0.0281 (3)	0.0452 (8)
C6	0.3143 (5)	0.3837 (4)	0.1045 (3)	0.0391 (8)

Table 2. *Selected geometric parameters* (Å, °)

Ni—N3	2.084 (2)	S—O1	1.491 (2)
Ni—N2	2.088 (2)	N1—C1	1.481 (4)
Ni—N1	2.099 (3)	N2—C3	1.479 (4)
Ni—O5	2.104 (2)	N2—C4	1.483 (4)
Ni—O6	2.127 (2)	N3—C6	1.475 (4)
Ni—O1	2.171 (2)	C1—C2	1.497 (5)
S—O3	1.460 (2)	C2—C3	1.509 (5)
S—O4	1.468 (2)	C4—C5	1.510 (5)
S—O2	1.474 (2)	C5—C6	1.504 (5)
N3—Ni—N2	93.49 (10)	O4—S—O2	109.96 (12)
N3—Ni—N1	169.98 (10)	O3—S—O1	109.21 (12)
N2—Ni—N1	96.22 (10)	O4—S—O1	108.41 (12)
N3—Ni—O5	91.63 (10)	O2—S—O1	107.59 (12)
N2—Ni—O5	90.81 (9)	S—O1—Ni	131.76 (11)
N1—Ni—O5	90.70 (10)	C1—N1—Ni	122.7 (2)
N3—Ni—O6	83.87 (10)	C3—N2—C4	110.4 (2)
N2—Ni—O6	177.14 (9)	C3—N2—Ni	114.2 (2)
N1—Ni—O6	86.37 (10)	C4—N2—Ni	114.9 (2)
O5—Ni—O6	90.36 (9)	C6—N3—Ni	122.0 (2)
N3—Ni—O1	90.69 (9)	N1—C1—C2	112.9 (3)
N2—Ni—O1	91.31 (9)	C1—C2—C3	114.0 (3)
N1—Ni—O1	86.62 (10)	N2—C3—C2	113.2 (3)

O5—Ni—O1	176.75 (8)	N2—C4—C5	113.9 (3)
O6—Ni—O1	87.63 (8)	C6—C5—C4	114.8 (3)
O3—S—O4	110.98 (13)	N3—C6—C5	111.8 (3)
O3—S—O2	110.59 (12)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N2—H(N2*A*)···O4	2.24 (2)	3.075 (3)	161 (3)
N3—H(N3*B*)···O3	2.24 (3)	3.048 (3)	155 (3)
O5—H(O5*A*)···O4^{i}	1.91 (4)	2.763 (4)	172 (4)
O6—H(O6*B*)···O2^{i}	1.90 (3)	2.724 (3)	167 (3)
O7—H(O7*B*)···O2^{i}	2.05 (3)	2.823 (4)	153 (4)
N1—H(N1*B*)···O6^{ii}	2.28 (3)	3.131 (3)	172 (3)
O6—H(O6*A*)···O1^{ii}	1.87 (3)	2.711 (3)	159 (4)
O7—H(O7*A*)···O3^{iii}	1.97 (4)	2.791 (4)	165 (4)
N1—H(N1*A*)···O7^{iv}	2.37 (3)	3.111 (4)	144 (3)
O5—H(O5*B*)···O7^{iv}	1.88 (3)	2.741 (3)	175 (4)

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

Table 4. *A comparison of* Ni—N(*primary/secondary*) *distances* (Å) *and* N(*primary*)—Ni—N(*primary*) *bond angles* (°) *in octahedral* Ni^{II}–*triamine complexes*

	Ni—N(pr.)	Ni—N(sec.)	N(pr.)—Ni—N(pr.)
Ni(dpt)$_2$-(ClO$_4$)$_2$*	2.12 (2)–2.17 (2)	2.22 (2)–2.23 (2)	175.5 (3)–176.9 (3)
[Ni(dpt)(H$_2$O)$_2$-(SO$_4$)].H$_2$O†	2.084 (2)–2.099 (3)	2.088 (2)	170.0 (1)
[Ni(dien)$_2$]-(NCS)$_2$‡	2.096 (1)–2.134 (1)	2.110 (1)	92.6 (1)
[Ni(NCO)$_2$-(terpy)(H$_2$O)]§	2.152 (2)–2.165 (2)	2.047 (3)	154.8 (1)
[Ni(bamp)$_2$]-Cl$_2$.1.67H$_2$O¶	2.128 (3)–2.168 (3)	2.001 (3)–2.025 (3)	157.1 (1)–159.1 (1)

* Biagini & Cannas (1970).

† This work.

‡ dien = diethylenetriamine; Mukherjee *et al.* (1994).

§ terpy = 2,2′:6′,2″-terpyridine; Cortes *et al.* (1988).

¶ bamp = 2,6-bis(aminomethyl)pyridine; Bonhote, Ferigo, Stoeckli-Evans & Marty (1993).

The metal position was obtained from a Patterson synthesis and the remaining non-H atoms were located by successive Fourier difference syntheses. The structure was refined on F^2 by full-matrix least squares with anisotropic displacement parameters for non-H atoms. All H atoms were clearly visible in a difference map computed in the final stage of refinement and refined isotropically. All calculations were performed using a VAX 3400 computer at the Computer Center, Indian Association for the Cultivation of Science.

Data collection: *SHELXTL* (Sheldrick, 1985*b*). Cell refinement: *SHELXTL*. Data reduction: *SHELXTL*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93. Program(s) used for geometric calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(2,2′-bipyridine)zinc(II) Perchlorate

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Abstract

The crystal structure of tris(2,2′-bipyridine)zinc(II) perchlorate, $[Zn(C_{10}H_8N_2)_3](ClO_4)_2$, has been established by X-ray crystallography. The Zn^{II} atom is coordinated by three chelating 2,2′-bipyridine ligands in a highly distorted octahedral arrangement with Zn—N bond lengths ranging from 2.135 (2) to 2.172 (3) Å.

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