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Crystal Structure of Tetraaqua(ethylenediamine)nickel(II) Sulfate Dihydrate and of Tetraaqua(2,2′-bipyridyl)nickel(II) Sulfate Dihydrate

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Abstract

The crystal structures of the title compounds, $[Ni(OH_2)_4(en)]\,[SO_4].2H_2O$, (1), and $[Ni(OH_2)_4(bpy)][SO_4].2H_2O$, (2), have been determined by single-crystal X-ray diffraction methods at 295 K, being refined by full matrix least-squares methods to residuals of 0·028, 0·031 for 1852, 4323 independent 'observed' reflections respectively. Crystals of (1) are monoclinic, $C2/c$, a 9·459(4), b 12·192(7), c 12·294(3) Å, β 119·84(4)°, Z 4. In the cation, Ni–N is 2·061(2) Å; Ni–O (*trans* to O, N respectively) are 2·106(2), 2·063(2) Å. Instead of being enlarged above 90° as predicted from repulsion theory, the angle between the pair of oxygen atoms *trans* to nitrogen is diminished, being 87·14(7)°. Crystals of (2) are triclinic, $P\bar{1}$, a 11·476(5), b 9·351(5), c 7·793(4) Å, α 77·63(4), β 83·52(3), γ 87·40(4)°, Z 2. In the cation, Ni–N are both 2·063(2) Å. Ni–O (*trans* to N, O respectively) are 2·060(2), 2·042(2); 2·080(2), 2·093(2) Å. The short Ni–O distance [2·042(2) Å] is associated with the coordination of a trigonal water molecule.

Introduction

'Octahedral' six-coordinate species of the type NiL_3, where L is the bidentate aliphatic ligand ethylenediamine, or the aromatic 2,2′-bipyridyl, are well characterized structurally.[1–7] Ni–N are typically 2·12–2·14 Å, with no apparent consistent difference between the two species; however, it has been claimed that in the ethylenediamine case, changes in the relative ligand chiralities can bring about small but significant changes within the above range.[8] Similar species of the type NiL_2X_2, by contrast, are

[1] Ul-Haque, M., Caughlan, C. N., and Emerson, K., *Inorg. Chem.*, 1970, **9**, 2421. $[Ni(en)_3]\,[SO_4]$; Ni–N, 2·124(6) Å (chirality, $\Lambda\delta\delta\delta$). (Values given in subsequent references are cited similarly where justified by precision.)
[2] Raston, C. L., White, A. H., and Willis, A. C., *Aust. J. Chem.*, 1978, **31**, 415. $[Ni(en)_3]\,[ClO_4]_2.H_2O$, 2·13 Å, $\Lambda\delta\delta\lambda$.
[3] Cramer, R. E., and Huneke, J. T., *Inorg. Chem.*, 1978, **17**, 365. $[Ni(en)_3]\,[B(Ph)_4]_2.3Me_2SO$, 2·14 Å, $\Lambda\delta\delta\lambda$.
[4] Swink, L. N., and Atoji, M., *Acta Crystallogr.*, 1960, **13**, 369. $[Ni(en)_3]\,(NO_3)_2$, $\Lambda\delta\delta\delta$.
[5] Cramer, R. E., van Doorne, W., and Huneke, J. T., *Inorg. Chem.*, 1976, **15**, 529. $[Ni(en)_3](OAc)_2.2H_2O$, $\Lambda\delta\delta\delta$.
[6] Wada, A., Sakabe, N., and Tanaka, J., *Acta Crystallogr., Sect. B*, 1976, **32**, 1121. $[Ni(bpy)_3][SO_4].7{\cdot}5H_2O$, 2·09 Å.
[7] Finney, A. J., Hitchman, M. A., Kepert, D. L., Raston, C. L., Rowbottom, G. L., and White, A. H., *Aust. J. Chem.*, 1981, **34**, 2177. $[Ni(bpy)_3]\,[SO_4].7{\cdot}5H_2O$, 2·09 Å.
[8] McDougall, G. J., and Hancock, R. D., *J. Chem. Soc., Dalton Trans.*, 1980, 654. $[Ni(OH_2)_4(en)](NO_2)_2$, $2{\cdot}06_5$ Å.

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poorly characterized for the situation X = unidentate ligand; if $X_2 \equiv$ bidentate then more data are available, leading to the conviction from the more precise determinations[9] that in such complexes for both ligands Ni–N is typically 2·09–2·10 Å.[9]* For the situation $NiLX_4$, X = unidentate, very little information is available, a situation which is true generally for metal complexes of this type, in spite of its potential value, for example, in assisting our understanding of mechanistic pathways in ligand exchange procedures, and particularly for the case X = H_2O appropriate to aqueous solution. The results already available suggest that it is not to be expected that bond lengths appropriate to ML_3 species, for example, will be immediately transferable to the M–L distances in the context of the MLX_4 situation because of electron-pair repulsion effects, changes in ligand charge, *cis*- and *trans*-effects in bonding, and effects consequent upon the bulk of the ligands. In this context, therefore, we considered it to be of interest to examine the geometries of the species $[NiL(H_2O)_4]^{2+}$ for the above pair of bidentate ligands for which the electronic structure, stereochemistry and hydrogen bonding potential of the nitrogen ligand are very different, and, accordingly, report the structure determination of the title compounds, $[Ni(OH_2)_4(en)]\,[SO_4].2H_2O$, (1), and $[Ni(OH_2)_4(bpy)]\,[SO_4].2H_2O$, (2). [In the course of this work, the structure determination of the nitrate analogue of (1) became available,[8] providing a useful basis for comparison of the identical cation in two different crystal lattices.]

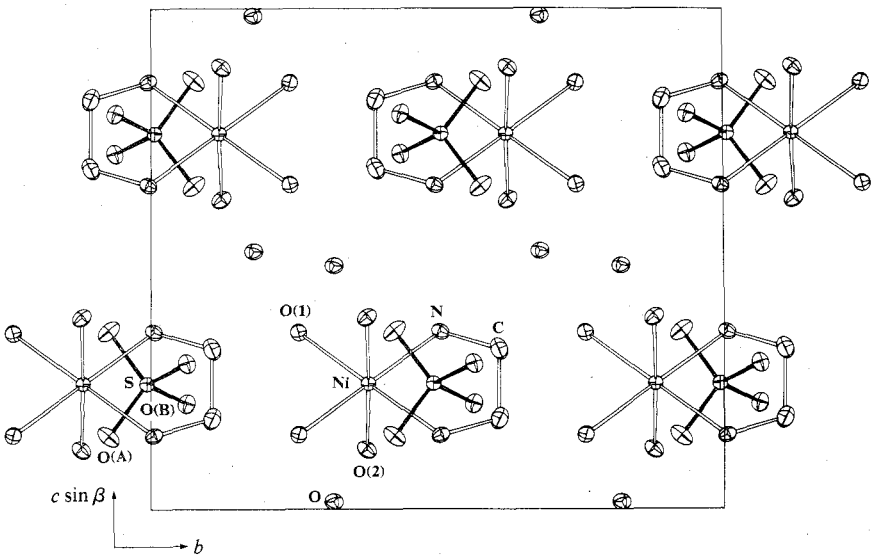

Fig. 1. Unit cell contents of (1) projected down *a*; 20% thermal ellipsoids are shown for the non-hydrogen atoms.

$[Ni(OH_2)_4(en)]\,[SO_4].2H_2O$, (1), readily crystallizes as pale blue prisms from an aqueous solution of hydrated nickel sulfate and the ligand in stoichiometric amounts.

* Ref.[7] In $[Ni(bpy)_2(O_2N)]\,[NO_3]$, the Ni–N value of $2{\cdot}04_2$ Å is anomalously short, presumably in consequence of the very small 'bite' of the nitrite ligand.

[9] E.g. Joung, K. O., O'Connor, C. J., Sinn, E., and Carlin, R. L., *Inorg. Chem.*, 1979, **18**, 804. $[Ni_2(en)_4Cl_2]\,Cl_2$, $2{\cdot}08_8$ Å.

$[Ni(OH_2)_4(bpy)]\,[SO_4].2H_2O$, (2), was obtained by the slow evaporation at 80° of an aqueous ethanol solution comprising equimolar quantities of hydrated nickel sulfate and the ligand.

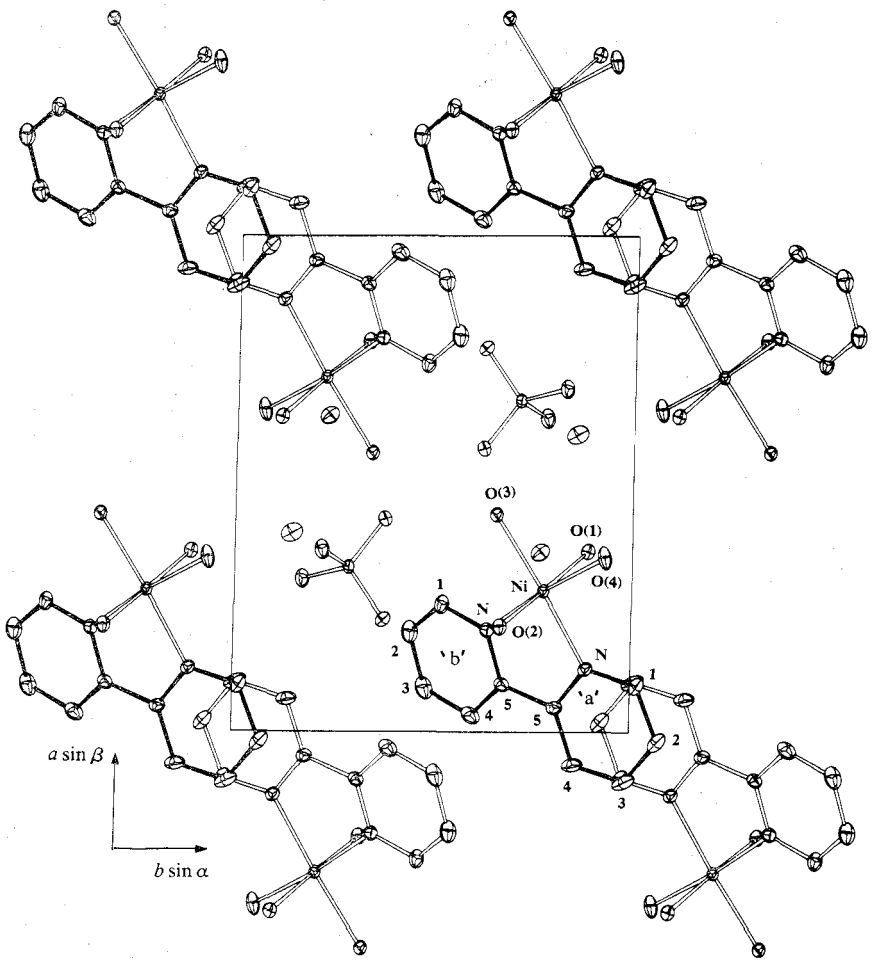

Fig. 2. Unit cell contents of (2) projected down *c*.

Crystallography

Crystal data.—(1): $C_2H_{20}N_2NiO_{10}S$, M 322·7, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a 9·459(4), b 12·192(7), c 12·294(3) Å, β 119·54°, U 1238(1) Å^3, D_c ($Z = 4$) 1·73, D_m 1·72(1) g cm^{-3}. $F(000)$ 680. μ_{Mo} 16·7 cm^{-1}. $2\theta_{max}$ 60°, N, N_0 2248, 1852. R, R' 0·028, 0·040. Specimen: 0·18 by 0·20 by 0·30 mm (prism).

(2): $C_{10}H_{20}N_2NiO_{10}S$, M 418·7, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 11·476(5), b 9·351(5), c 7·793(4) Å, α 77·63(4), β 83·52(3), γ 87·40(4)°, U 811(1) Å^3, D_c ($Z = 4$) 1·71, D_m 1·68(1) g cm^{-3}. $F(000)$ 436. μ_{Mo} 13·0 cm^{-1}. $2\theta_{max}$ 60°, N, N_0 4781, 4323. R, R' 0·031, 0·046. Specimen: 0·55 by 0·50 by 0·12 mm.

Structure determination.—Unique data sets were measured to a preset $2\theta_{max}$ limit by using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode; T was 295 K and the diffractometer was equipped with a monochromatic Mo Kα radiation source. N independent reflections were obtained, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least-squares

refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; for the hydrogen atoms x, y, z, $U_{\text{isotropic}}$ [(1), not (2)] were refined; in (2), U_{iso} were included at constrained estimates. Residuals R, R' are quoted at convergence, reflection weights being $[\sigma^2(F_o)+0\cdot0005(F_o)^2]^{-1}$. Computation used the X-RAY 76 program system[10] implemented by S. R. Hall on a Perkin–Elmer 3240 computer. Neutral atom scattering factors were used, all except hydrogen being corrected for anomalous dispersion (f', f'').[11] Material deposited comprises structure factor amplitudes, thermal parameters and hydrogen atom geometries.* Non-hydrogen atom numbering is shown in the cell diagrams (see Figs 1–3); atom coordinates are given in Tables 1, 2 and derivative geometries in the Tables 3–8.

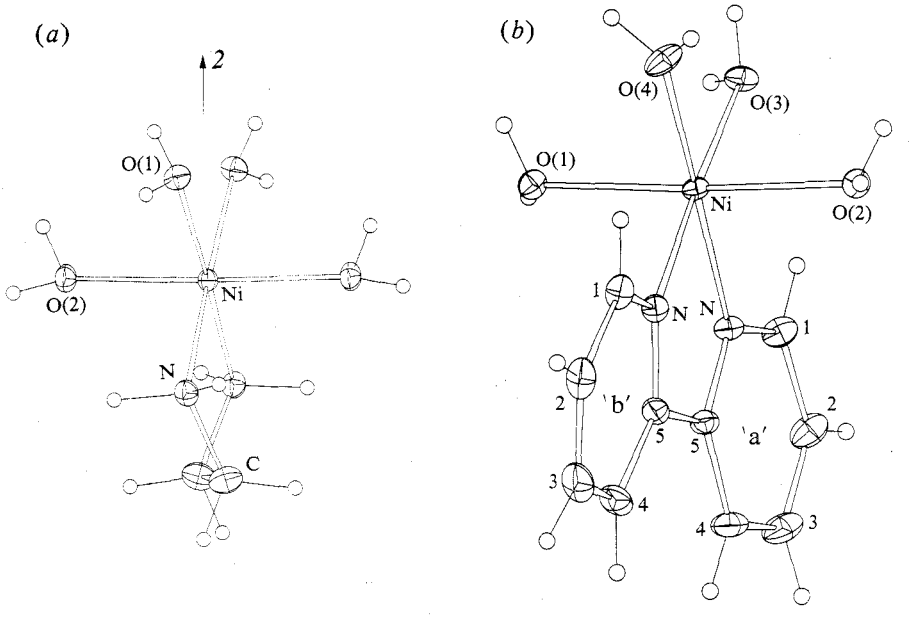

Fig. 3. (*a*) The cation of (1); hydrogen atoms have an arbitrary radius of 0·1 Å. (*b*) The cation of (2).

Table 1. Atom coordinates for (1)

Atom	x	y	z	Atom	x	y	z
Ni	0	0·38039(2)	1/4	C	0·0577(3)	0·6071(2)	0·3194(2)
O(1)	0·1629(2)	0·2578(1)	0·3519(1)	H(CA)	−0·039(4)	0·616(2)	0·349(3)
H(1A)	0·153(3)	0·205(2)	0·315(2)	H(CB)	0·145(4)	0·678(2)	0·344(3)
H(1B)	0·257(4)	0·275(2)	0·389(3)	S	0	−0·00674(4)	1/4
O(2)	0·0797(2)	0·3771(1)	0·1177(1)	O(A)	−0·1148(2)	−0·0751(1)	0·1447(1)
H(2A)	0·063(4)	0·320(2)	0·074(3)	O(B)	0·0929(2)	0·0637(1)	0·2100(1)
H(2B)	0·181(4)	0·392(2)	0·129(3)	O	0·5150(2)	0·3205(1)	0·0144(1)
N	0·1565(2)	0·5052(1)	0·3533(1)	H(A)	0·477(3)	0·353(2)	0·050(2)
H(NA)	0·200(3)	0·493(2)	0·422(3)	H(B)	0·497(4)	0·359(2)	−0·040(3)
H(NB)	0·248(3)	0·511(2)	0·340(2)				

* Copies are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

[10] 'The X-RAY System—Version of March, 1976' Technical Report, TR-446, Computer Science Center, University of Maryland, U.S.A. (Ed. J. M. Stewart).

[11] 'International Tables for X-Ray Crystallography' (Eds J. A. Ibers and W. C. Hamilton) Vol. 4 (Kynoch Press: Birmingham 1974).

Table 2. Atom coordinates for (2)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0·28453(1)	0·77849(2)	0·22527(2)	C(4b)	0·0338(2)	0·6028(2)	0·6524(3)
O(1)	0·3640(1)	0·8890(1)	0·3843(1)	H(4b)	−0·039(2)	0·632(2)	0·682(3)
H(1A)	0·444(2)	0·891(2)	0·368(3)	C(3b)	0·0881(2)	0·4840(2)	0·7538(3)
H(1B)	0·346(2)	0·966(2)	0·368(3)	H(3b)	0·044(2)	0·442(3)	0·858(4)
O(2)	0·2124(1)	0·6709(1)	0·0540(2)	C(2b)	0·2008(2)	0·4451(2)	0·7012(2)
H(2A)	0·239(2)	0·696(3)	−0·038(3)	H(2b)	0·245(2)	0·365(3)	0·772(4)
H(2B)	0·218(2)	0·589(3)	0·082(3)	C(1b)	0·2572(2)	0·5237(2)	0·5449(2)
O(3)	0·4382(1)	0·6577(1)	0·2063(2)	H(1b)	0·341(2)	0·495(3)	0·494(3)
H(3A)	0·428(2)	0·574(2)	0·200(3)	N(b)	0·2059(1)	0·6393(1)	0·4457(2)
H(3B)	0·493(2)	0·688(2)	0·115(3)				
O(4)	0·3505(1)	0·9314(1)	0·0123(2)		Anion		
H(4A)	0·359(2)	1·010(3)	0·009(3)	S	0·33210(3)	0·28708(3)	0·16904(5)
H(4B)	0·641(2)	1·085(3)	0·071(4)	O(A)	0·2262(1)	0·3770(1)	0·1395(2)
N(a)	0·1270(1)	0·8884(1)	0·2636(2)	O(B)	0·4290(1)	0·3769(1)	0·1934(2)
C(1a)	0·0935(2)	1·0166(2)	0·1667(2)	O(C)	0·3673(1)	0·2195(1)	0·0162(2)
H(1a)	0·152(2)	1·075(2)	0·081(3)	O(D)	0·3089(1)	0·1709(1)	0·3299(2)
C(2a)	−0·0202(2)	1·0720(2)	0·1889(3)				
H(2a)	−0·037(2)	1·179(3)	0·103(3)		Lattice water molecules		
C(3a)	−0·1008(2)	0·9924(3)	0·3127(3)	O(5)	0·6381(1)	0·2303(2)	0·2462(2)
H(3)	−0·175(2)	1·033(3)	0·309(4)	H(5A)	0·640(2)	0·208(3)	0·345(3)
C(4a)	−0·0667(2)	0·8613(2)	0·4153(3)	H(5B)	0·581(2)	0·273(3)	0·238(3)
H(4a)	−0·121(3)	0·799(3)	0·494(4)	O(6)	0·5992(1)	0·8575(2)	0·3526(2)
C(5a)	0·0489(1)	0·8131(2)	0·3887(2)	H(6A)	0·631(2)	0·833(3)	0·440(4)
C(5b)	0·0962(1)	0·6795(2)	0·4985(2)	H(6B)	0·607(2)	0·786(3)	0·317(4)

Table 3. Non-hydrogen atom distances (Å) and angles (degrees) for (1)

Primed atoms are related by the twofold symmetry axis. For the coordinated water molecules, O(1)–H(1A,B) are 0·77(3), 0·79(3); O(2)–H(2A,B), 0·85(3), 0·91(4) Å. ∠H–O–H are 109(3), 96(3)° respectively. Ni–O(1)–H(1A,B) are 114(2), 116(2)° and Ni–O(2)–H(2A,B), 119(3), 129(2)°

Feature	Atoms	Distance	Atoms	Angle	Atoms	Angle
Cation	Ni–O(1)	2·063(2)	N–Ni–O(1)	94·03(7)	O(1)–Ni–N(1′)	177·9(5)
	Ni–O(2)	2·106(2)	N–Ni–O(2)	93·83(8)	O(1)–Ni–O(1′)	87·14(6)
	Ni–N	2·061(2)	N–Ni–N′	84·84(7)	O(1)–Ni–O(2′)	87·90(7)
	N–C	1·484(3)	N–Ni–O(1′)	177·9(2)	O(2)–Ni–O(2′)	177·8(2)
	C–C	1·500(3)	N–Ni–O(2′)	87·78(8)	Ni–N–C	106·6(1)
			O(1)–Ni–O(2)	90·53(6)	N–C–C	108·6(2)
Anion	S–O(A)	1·467(2)	O(A)–S–O(B)	109·78(10)	O(A)–S–O(B′)	108·81(10)
	S–O(B)	1·477(2)	O(A)–S–O(A′)	110·69(10)	O(A)–S–O(B′)	108·95(10)

Table 4. Metal atom environment for (2)

The second entry in each matrix is the central atom peripheral atom distance (Å); other entries are the angles subtended at the central atom by the relevant peripheral atoms

Atom	r_{Ni-L}	O(2)	O(3)	O(4)	N(a)	N(b)
O(1)	2·080(2)	176·7(2)	87·43(6)	87·93(6)	91·89(5)	90·68(6)
O(2)	2·093(2)		90·81(6)	89·31(7)	90·08(6)	92·23(6)
O(3)	2·060(2)			89·26(6)	175·4(2)	96·09(5)
O(4)	2·042(2)				95·27(6)	174·4(2)
N(a)	2·063(2)					79·37(5)
N(b)	2·063(2)					

Table 5. Sulfur environment for (2)

The second entry in each matrix is the central atom peripheral atom distance (Å); other entries are the angles subtended at the central atom by the relevant peripheral atoms

Atom	r_{S-O}	O(B)	O(C)	O(D)
O(A)	1·458(1)	110·56(8)	109·81(9)	109·33(8)
O(B)	1·476(2)		108·90(8)	108·77(8)
O(C)	1·474(2)			109·45(8)
O(D)	1·480(1)			

Table 6. Hydrogen contacts, H···O < 2 Å, for (1)

Transformation of the asymmetric unit: i $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$; ii $(1-x, y, \frac{1}{2}-z)$; iii $(\frac{1}{2}-x, \frac{1}{2}-y, \bar{z})$; iv $(\frac{1}{2}+x, \frac{1}{2}+y, z)$

Atoms	r(H···O) (Å)	N,O–H···O (deg)
H(NB)···O(B^{i})	1·99(3)	163(2)
H(1B)···O^{ii}	1·96(3)	177(4)
H(2A)···O^{iii}	1·96(3)	166(4)
H(2B)···O(2^{iv})	1·89(4)	177(3)

Table 7. Hydrogen contacts, H···O < 2 Å, for (2)

Transformation of the asymmetric unit: i $(x, 1+y, z)$; ii $(1-x, 1+y, \bar{z})$; iii $(1-x, 1-y, 1-z)$

Atoms	r(H···O) (Å)	O–H···O (deg)	Atoms	r(H···O) (Å)	O–H···O (deg)
H(1A)···O(6)	1·79(2)	169(3)	H(3B)···O(C^{ii})	1·93(2)	159(2)
H(1B)···O(D^{i})	1·92(2)	176(3)	H(4A)···O(C^{i})	1·98(3)	174(3)
H(2B)···O(A)	1·94(2)	176(3)	H(5B)···O(B)	1·99(3)	174(3)
H(3A)···O(B)	1·86(2)	171(2)	H(6A)···O(D^{iii})	1·98(3)	163(3)

Table 8. Bipyridyl non-hydrogen geometry for (2)

The two values in each entry are for sections a, b. Coordinated water molecule geometry (molecules 1–4 respectively): O(n)–H(nA,B): 0·91(2), 072(2); 0·74(2), 0·75(2); 0·81(2), 0·90(2); 0·74(3), 0·69(3) Å. ∠H–O–H: 104(2); 110(3); 103(2); 112(3)°. Ni–O(n)–H(nA,B): 116(2), 111(2); 111(2), 113(2); 113(2), 119(1); 127(2), 120(2)°

Atoms	Distances (Å)	Atoms	Angles (degrees)
N–C(1)	1·338(2), 1·341(2)	Ni–N–C(1)	126·4(1), 126·2(1)
N–C(5)	1·348(2), 1·343(2)	Ni–N–C(5)	114·3(1), 114·5(1)
C(1)–C(2)	1·389(3), 1·388(3)	C(1)–N–C(5)	119·0(1), 119·0(1)
C(2)–C(3)	1·376(3), 1·370(3)	N–C(1)–C(2)	121·7(2), 122·1(2)
C(3)–C(4)	1·380(3), 1·385(3)	C(1)–C(2)–C(3)	119·1(2), 119·1(2)
C(4)–C(5)	1·388(2), 1·396(2)	C(2)–C(3)–C(4)	119·6(2), 119·5(2)
C(5)–C(5)	1·474(2)	C(3)–C(4)–C(5)	118·4(2), 118·7(2)
		C(4)–C(5)–N	122·1(1), 121·7(1)
		C(4)–C(5)–C(5)	122·7(1), 122·6(1)
		N–C(5)–C(5)	115·1(1), 115·7(1)

Discussion

Compound (1)

As expected, the structure determination shows the unit cell contents to comprise $[Ni(OH_2)_4(en)]^{2+}$ cations and $[SO_4]^{2-}$ counterions, one half of each, with one molecule of water, comprising the asymmetric unit of the structure (Fig. 1). Since cation and anion both lie about crystallographic twofold axes, the stoichiometry of the salt is that of the dihydrate. A number of close interspecies hydrogen contacts are observed (Table 5). The sulfate geometry is normal and the cation water molecules pseudo-tetrahedral (rather than trigonal) with angle sums between the bonded atoms at the oxygen being 339(6) and 344(6)°.

The determination of the cation geometry is more precise than that of the nitrate salt and offers some interesting points of comparison (nitrate parameters[8] are *italicized*):

(i) In both structures, the Ni–N distances [2·061(2); *2·058(6)*, *2·073(6)* Å] are reduced well below the values of 2·12–2·14 Å determined for various $[Ni(en)_3]^{2+}$ compounds.

(ii) Whereas in the nitrate salt the Ni–O distances are very consistent [*2·079(5)–2·093(4)* Å], those of the present determination are of two types: 2·063(2) Å, *trans* to the nitrogen, and 2·106(2) Å, *trans* to itself; the latter distance is appreciably longer than the Ni–O distances observed in $[Ni(OH_2)_6]^{2+}$ cations.[4] Electron pair repulsion theory considerations[5] are in agreement with the observation, and also with the closing of the O–Ni–O *trans* angle from 180°, away from the bidentate ligand, as observed in both structures.

(iii) Electron pair repulsion theory also predicts enlargement of the O–Ni–O angle opposite the bidentate ligand above 90°. In the nitrate this angle is *92·5(2)*°; in the present compound it is markedly different [87·14(6)°], presumably in consequence of different lattice forces.

(iv) Of the two coordinated water molecules, $H_2O(2)$ is the one more intimately associated with hydrogen-bonding interactions; this may also assist in accounting for the elongation of Ni–O(2) relative to Ni–O(1).

(v) The ligand carbon atom deviates by 0·313 Å from a plane defined by Ni–N(1)–O(1); the symmetry of the ligand conformation conforms to the crystallographic twofold axis which passes through it.

Compound (2)

As expected, the structure determination shows the unit cell contents to comprise $[Ni(OH_2)_4(bpy)]^{2+}$ cations, $[SO_4]^{2-}$ counterions, one of each in the asymmetric unit with two molecules of water, and no species with intrinsic crystallographically imposed symmetry (Fig. 2). A number of close interspecies contacts are observed (Table 7). The sulfate and bipyridyl geometries are normal. Three of the cation water molecules are pseudo-tetrahedral with angle sums subtended at the oxygen by the bonded atoms being 331, 334, 335(6)°; the fourth, $OH_2(4)$, is trigonal [359(6)°]. The following features of interest in the cation geometry may be noted relative to $[Ni(OH_2)_4(en)]^{2+}$, $[Ni(bpy)_3]^{2+}$, and the polymeric species $\cdots O[Ni(bpy)(OH_2)_2]OSO_2O[Ni(bpy)(OH_2)_2]O.SO_2$.[12]

[12] Tedenac, J.-C., and Philippot, E., *Acta Crystallogr., Sect. B*, 1974, **30**, 2286, 2·062(6) Å.

(i) The Ni–N distances of 2·063(2), 2·063(2) Å are comparable with those observed in the ethylenediamine analogues, making a similar parallel to that observed in Ni–N distances in both $[Ni(en)_3]^{2+}$ and $[Ni(bpy)_3]^{2+}$ species.

(ii) The Ni–O distances *trans* to Ni–N are almost identical [2·080(2), 2·093(2) Å], comparable to those observed in $[Ni(OH_2)_4(en)][NO_3]$ [2·091(5), 2·079(5) Å], but longer than their counterparts in $[Ni(OH_2)_4(en)][SO_4].2H_2O$ [2·063(2) Å] and $[Ni(OH_2)_2(bpy)(SO_4)]$ [2·06(1) Å]; Ni–OH_2, *trans* to each other are shorter, 2·060(2), 2·042(2) Å, in contrast to $[Ni(OH_2)_4(en)][NO_3]$ [2·093(4), 2·088(4) Å] and $[Ni(OH_2)_4(en)][SO_4].2H_2O$ [2·106(2) Å] (the latter possibly influenced by strong hydrogen bonding). Interestingly, Ni–O(4), 2·042(2) Å, is the distance corresponding to the trigonal water molecule and is in keeping with the trend observed elsewhere,[13] that coordinated metal–water distances are shorter in those situations involving trigonal rather than tetrahedral water molecules. The mutually *trans* Ni–O(SO_4) distance in $[Ni(OH_2)_2(bpy)(SO_4)]$ [2·156(6) Å][12] is much longer than in any of the other complexes.

(iii) In keeping with electron pair repulsion theory, the closing of the O–Ni–O *trans* angle to 176·7(2)° away from the bidentate ligand is observed; the angle between the other two oxygen atoms is slightly diminished below 90° [89·26(6)°], contrary to expectations.

(iv) For a least-squares plane defined by N,C(1–5)(a), N,C(1–5)(b), σ is 0·104 Å, with atom deviations 0·033, 0·138, 0·104, −0·053, −0·139, −0·076, −0·144, −0·069, 0·090, 0·136, 0·054, −0·075 Å; the nickel deviation is −0·185 Å, and O(3,4) −0·377, −0·150 Å, indicating a bending of the ligand about the N,N coordination line.

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[13] Healy, P. C., Patrick, J. M., and White, A. H., unpublished data.