Structural Investigations of Metal–Nitrate Complexes. Part IV.† Crystal and Molecular Structure of Bisaquonitratobispyridinenickel(II), $[Ni(C_5H_5N)_2(NO_3)_2(H_2O)_2]$

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The structure of the title compound has been determined by three-dimensional *X*-ray analysis from diffractometer data. The crystals are monoclinic, space-group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions: $a = 8{\cdot}787$, $b = 11{\cdot}725$, $c = 7{\cdot}548$ Å, $\beta = 106{\cdot}94°$. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final R of 0·044 for 1849 independent reflections. The molecule is a centrosymmetric, six-co-ordinate monomer; the high stability and ease of formation of the crystalline compound may be related to a complex system of intermolecular hydrogen bonding.

UNLIKE the corresponding complexes of zinc(II)[1] and copper(II),[2] anhydrous dinitratobis(pyridine)-nickel(II) has not been reported as a stable crystalline species, although it may be present in dichloromethane solutions containing pyridine and nickel(II) nitrate.[3] It is possible, however, to prepare and isolate the hydrated complex $Ni(py)_2(NO_3)_2,2H_2O$ (py = pyridine) as a crystalline solid. The i.r. spectrum of this latter complex[4] suggests that all the groups are co-ordinated to the nickel, *i.e.* $[Ni(py)_2(NO_3)_2(H_2O)_2]$, but the detailed mode of nitrate co-ordination was not clear. Of the two hydrated nickel(II) nitrates for which the structures are known, $Ni(NO_3)_2,2H_2O$ contains bridging nitrate groups[5] while $Ni(NO_3)_2,4H_2O$ contains unidentate nitrate groups and has a complex system of intermolecular hydrogen bonding in the crystal.[6] The extremely intense diffraction patterns produced by the present complex also suggested a high degree of intermolecular association. Our three-dimensional *X*-ray analysis of this species was carried out to study the effect of both co-ordinated water molecules and another ligand on the detailed nitrate co-ordination.

EXPERIMENTAL

Preparation of Crystals.—Crystals of $Ni(py)_2(NO_3)_2(H_2O)_2$ were prepared from an acetone solution containing stoicheiometric amounts of $Ni(NO_3)_2,2H_2O$ and pyridine. The crystals are blue needles elongated along *a*. To avoid problems of atmospheric decomposition in the *X*-ray beam, the crystals were enclosed in a thin-walled glass capillary.

Crystal Data.—$C_{10}H_{12}NiN_4O_8$, $M = 358{\cdot}9$, Monoclinic, $a = 8{\cdot}787 \pm 0{\cdot}002$, $b = 11{\cdot}725 \pm 0{\cdot}005$, $c = 7{\cdot}548 \pm$

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† Part III, ref. 11.

[1] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *J. Chem. Soc.* (*A*), 1971, 3402.

[2] A. F. Cameron, K. P. Forrest, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 210; *J. Chem. Soc.* (*A*), 1971, 2492.

[3] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 840.

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[6] P. P. Gallezot, D. Weigel, and M. Prettre, *Acta Cryst.*, 1967, **22**, 699.

0·002 Å, $\beta = 106{\cdot}94 \pm 0{\cdot}02°$, $U = 744$ Å^3, $D_m = 1{\cdot}60$, $Z = 2$, $D_c = 1{\cdot}603$, $F(000) = 388$. Space-group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $0k0$ for k odd, $h0l$ for l odd. Mo-K_α X-rays, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 14·0 cm^{-1}.

Crystallographic Measurements.—The unit-cell parameters were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å), and from precession photographs taken with Mo-K_α radiation. These were subsequently adjusted by least-squares refinement of θ, χ, and ϕ setting angles of twelve reflections determined on a Hilger and Watts Y 290 diffractometer.

For the intensity measurements zirconium-filtered molybdenum radiation was used and 2161 reflections were collected by use of the θ—2θ scan technique. Of these some 1849 reflexions were considered observed using the criteria $I \geqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz-polarisation effects but no corrections for absorption were made.

Structure Determination and Refinement.—Since the density indicated $Z = 2$, and also the data were observed to be systematically weak when $k + l = 2n$, it was thought that the nickel atoms would occupy crystallographic special positions. This was confirmed by a three-dimensional Patterson synthesis, and an electron-density calculation with the initial phasing appropriate to the nickel atom revealed all the other non-hydrogen atom positions. Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0·27. During these preliminary calculations an overall isotropic vibration parameter, U_{iso} (0·05 Å^2), was assigned to the atoms.

The least-squares refinement of positional, thermal, and scale parameters converged after 9 cycles, when R was 0·044 and $R' (= \Sigma w\Delta^2/\Sigma wF_o^2)$ was 0·003. After cycle (5), a difference Fourier synthesis was calculated which revealed positions for all the hydrogen atoms. In subsequent cycles these were refined using isotropic temperature factors (for details of the refinement see Table 1).

TABLE 1

Course of refinement

Cycles	Parameters refined	Final R	Final R'
(1)—(3)	x, y, z, U_{iso} for Ni, N, O, C; one overall scale-factor K_k, unit weights, full-matrix	0·1003	0·0121
(4)—(5)	x, y, z, U_{iso} for Ni, N, O, C; one overall scale-factor, weighting scheme adjusted, full-matrix	0·0934	0·0106
(6)	x, y, z, U_{iso} for Ni, N, O, C, H; one overall scale-factor, weighting scheme adjusted, full-matrix	0·0879	0·0094
(7)—(9)	x, y, z, U_{ij} (i, j = 1, 2, 3) for Ni, N, O, C; x, y, z, U_{iso} for H; one overall scale-factor, small adjustments to weighting scheme, full-matrix	0·0444	0·0030

In all refinement cycles, a weighting scheme of the form: $\sqrt{w} = [\{1 + \exp\,[-p_1(\sin\theta/\lambda)]^2\}/(1 + p_2|F_o| + p_3|F_o|^2)]^{\frac{1}{2}}$ was applied to the data. Initially the p parameters were chosen to give unit weight to all reflections, but they were varied in later cycles as indicated by a $|F_o|$ and ($\sin\theta/\lambda$) analysis of $\Sigma w\Delta^2$. The final values are p_1 50, p_2 0·01, and p_3 0·001.

At the conclusion of the refinement a difference synthesis and final electron-density distribution were calculated. These revealed no errors in the structure.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 7. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20272 (3 pp., 1 microfiche).*

Fractional co-ordinates of all non-hydrogen atoms are given in Table 2 and anisotropic thermal parameters in Table 3. The positions of the hydrogen atoms and their isotropic thermal parameters are given in Table 4.

TABLE 2

Atom positions (fractional co-ordinates)

	x/a	y/b	z/c
Ni	0·00000(0)	0·00000(0)	0·00000(0)
C(1)	0·3525(5)	−0·0331(3)	0·1484(6)
C(2)	0·4998(5)	−0·0853(4)	0·2003(6)
C(3)	0·5082(5)	−0·2019(4)	0·1701(7)
C(4)	0·3693(5)	−0·2597(3)	0·0908(7)
C(5)	0·2264(4)	−0·2012(3)	0·0449(6)
O(1)	0·0731(3)	0·1101(2)	0·2289(3)
O(2)	0·1464(4)	−0·0183(2)	0·4465(4)
O(3)	0·1438(3)	0·1607(2)	0·5159(3)
O(4)	0·1069(3)	0·1200(2)	−0·1239(4)
N(1)	0·1209(3)	0·0819(2)	0·3982(4)
N(2)	0·2162(3)	−0·0891(2)	0·0726(4)

TABLE 3

(*a*) Anisotropic temperature factors (Å^2) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Ni	0·027	0·017	0·022	0·000	0·000	0·000
C(1)	0·036	0·030	0·046	−0·005	0·023	−0·006
C(2)	0·036	0·039	0·059	−0·008	0·017	−0·007
C(3)	0·035	0·040	0·066	0·004	0·023	0·013
C(4)	0·040	0·028	0·078	−0·008	0·021	0·009
C(5)	0·031	0·031	0·048	−0·009	0·015	−0·004
O(1)	0·051	0·026	0·022	−0·001	0·013	0·005
O(2)	0·058	0·024	0·041	0·012	0·026	0·017
O(3)	0·054	0·025	0·026	−0·012	0·015	−0·004
O(4)	0·045	0·024	0·028	−0·001	0·028	−0·012
N(1)	0·030	0·023	0·026	0·001	0·016	0·001
N(2)	0·032	0·024	0·031	−0·004	0·018	−0·004

* These are the values of U_{ij} in the expression: $\exp\,[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

(*b*) Mean estimated standard deviations (10^3 Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Ni	0·2	0·2	0·2	0·0	0·0	0·0
C	2	2	2	3	3	3
O	2	1	1	2	2	2
N	1	1	1	2	2	2

Table 5 contains bonded distances, valence angles, and intramolecular and intermolecular distances. The estimated standard deviations recorded in Tables 2—5 were derived from the inverse of the least-squares, normal-equation matrix, and are best regarded as minimum values. A number of planes were calculated for portions of the molecular framework (Table 6).

The atomic numbering scheme is shown in Figure 1 and the packing arrangement of the molecule in the unit cell is given in Figure 2.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 4

Hydrogen positions * (fractional co-ordinates) and isotropic temperature factors (Å^2)

	x/a	y/b	z/c	U_{iso}
H(1)[C(1)]	0·3424(54)	0·0507(41)	0·1670(63)	0·014(12)
H(2)[C(2)]	0·5991(55)	−0·0363(41)	0·2581(64)	0·019(11)
H(3)[C(3)]	0·6139(69)	−0·2401(51)	0·2084(78)	0·038(15)
H(4)[C(4)]	0·3629(61)	−0·3348(47)	0·0552(73)	0·037(10)
H(5)[C(5)]	0·1293(48)	−0·2348(34)	−0·0101(54)	0·016(9)
H(6)[O(4)]	0·0834(50)	0·1234(38)	−0·2419(65)	0·017(10)
H(7)[O(4)]	0·1092(65)	0·1841(51)	−0·0990(77)	0·040(15)

* Hydrogens are bonded to atoms shown in square brackets.

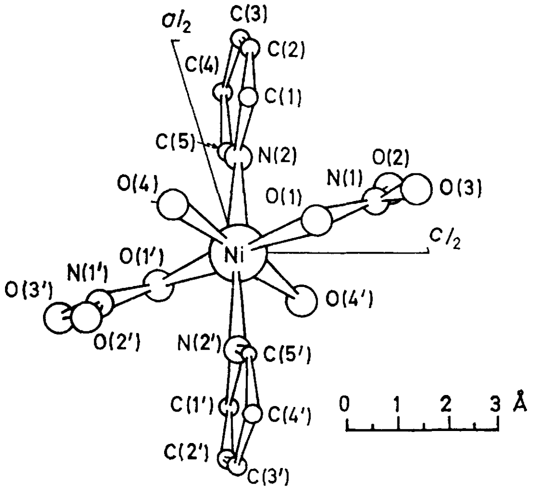


FIGURE 1 A view of the molecule along *b* showing the atomic numbering

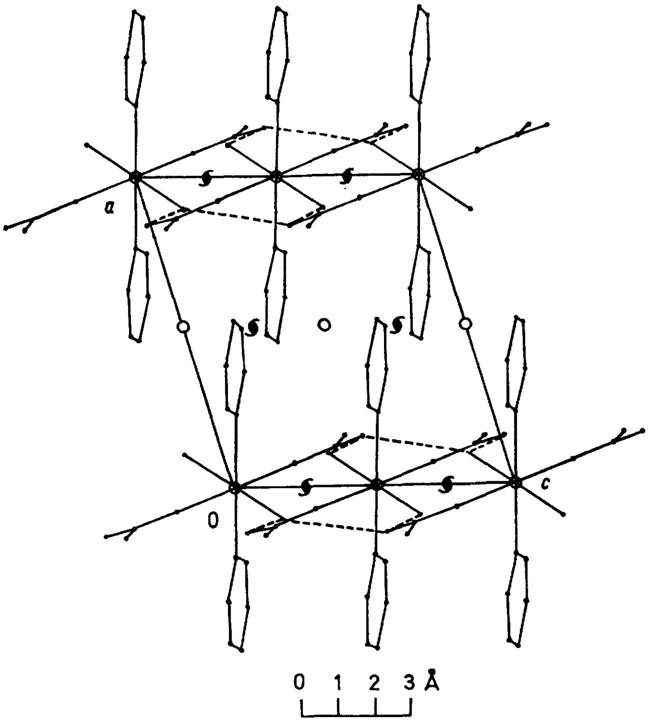


FIGURE 2 The molecular packing viewed along *b*

TABLE 5

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances

Ni–O(1)	2·101(2)	C(4)–C(5)	1·385(5)
Ni–O(4)	2·061(2)	C(5)–N(2)	1·340(4)
Ni–N(2)	2·095(3)	N(1)–O(1)	1·267(3)
C(1)–C(2)	1·377(5)	N(1)–O(2)	1·232(4)
C(1)–N(2)	1·341(5)	N(1)–O(3)	1·258(3)
C(2)–C(3)	1·390(5)	Mean C–C	1·381
C(3)–C(4)	1·375(6)	Mean C–N	1·340
C(1)–H(1)	0·99(5)	C(5)–H(5)	0·90(4)
C(2)–H(2)	1·00(5)	O(4)–H(6)	0·85(5)
C(3)–H(3)	1·00(6)	O(4)–H(7)	0·72(6)
C(4)–H(4)	0·98(6)	Mean C–H	0·97
		Mean O–H	0·78

(*b*) Interbond angles

O(1)–Ni–N(2)	93·11(1)	C(1)–C(2)–C(3)	118·9(4)
O(1)–Ni–O(4)	83·3(1)	C(2)–C(3)–C(4)	118·2(4)
O(1)–Ni–N(2′)	86·9(1)	C(3)–C(4)–C(5)	119·3(4)
O(1)–Ni–O(4′)	96·7(1)	C(4)–C(5)–N(2)	123·0(3)
N(2)–Ni–O(4)	87·7(1)	Ni–O(1)–N(1)	127·0(2)
N(2)–Ni–O(4′)	92·4(1)	O(1)–N(1)–O(2)	121·6(3)
Ni–N(2)–C(1)	120·0(2)	O(1)–N(1)–O(3)	117·4(3)
Ni–N(2)–C(5)	122·9(2)	O(2)–N(1)–O(3)	121·0(3)
C(1)–N(2)–C(5)	117·1(3)	Mean C–C–C	118·8
N(2)–C(1)–C(2)	123·4(3)	Mean C–C–N	123·2
N(2)–C(1)–H(1)	116(3)	C(4)–C(5)–H(5)	121(3)
C(2)–C(1)–H(1)	120(3)	N(2)–C(5)–H(5)	116(3)
C(1)–C(2)–H(2)	117(3)	H(6)–O(4)–H(7)	99(5)
C(3)–C(2)–H(2)	124(3)	O(3′)–O(4)–O(3″)	100·0(1)
C(2)–C(3)–H(3)	121(3)	O(4′)–O(3)–O(4″)	118·9(1)
C(4)–C(3)–H(3)	121(3)	O(4)–H(6)–O(3′)	151(2)
C(3)–C(4)–H(4)	124(3)	O(4)–H(7)–O(3″)	166(2)
C(5)–C(4)–H(4)	117(3)	Mean C–C–H	121
		Mean N–C–H	116

(*c*) Intramolecular distances for non-hydrogen atoms <3·5 Å

Ni · · · C(1)	3·00	O(1) · · · N(2)	3·05
Ni · · · C(5)	3·04	O(2) · · · C(1)	3·28
Ni · · · O(2)	3·24	O(2) · · · O(3)	2·17
Ni · · · N(1)	3·04	O(2) · · · O(4′)	3·02
O(1) · · · C(1)	3·18	O(2) · · · N(2′)	3·17
O(1) · · · C(5′)	3·03	O(4) · · · C(1)	3·09
O(1) · · · O(2)	2·18	O(4) · · · C(5′)	3·30
O(1) · · · O(3)	2·16	O(4) · · · N(1′)	3·39
O(1) · · · O(4′)	3·11	O(4) · · · N(2)	2·88
O(1) · · · N(2′)	2·89	N(1) · · · N(2)	3·46

(*d*) Intermolecular contacts <3·5 Å, including those involved in hydrogen bonding

O(1) · · · O(3$^{\text{I}}$)	3·28	O(3) · · · C(2$^{\text{V}}$)	3·36
O(1) · · · O(4$^{\text{II}}$)	3·34	O(3) · · · C(3$^{\text{V}}$)	3·31
O(2) · · · C(4$^{\text{III}}$)	3·25	O(3) · · · O(4$^{\text{II}}$)	2·76
O(2) · · · C(5$^{\text{III}}$)	3·40	O(3) · · · O(4$^{\text{VI}}$)	2·87
O(2) · · · O(2$^{\text{IV}}$)	2·90	O(3) · · · H(6$^{\text{VI}}$)	2·09
O(2) · · · O(3$^{\text{IV}}$)	3·13	O(3) · · · H(7$^{\text{II}}$)	2·06
O(2) · · · N(1$^{\text{IV}}$)	3·01	O(4) · · · N(1$^{\text{I}}$)	3·50

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z:

I $x, \frac{1}{2} - y, -\frac{1}{2} + z$
II $x, \frac{1}{2} - y, \frac{1}{2} + z$
III $x, -\frac{1}{2} - y, \frac{1}{2} + z$
IV $-x, -y, 1 - z$
V $1 - x, -y, 1 - z$
VI $x, y, 1 + z$

DISCUSSION

Our analysis has revealed a centrosymmetric, six-co-ordinate structure, the nickel atom being constrained to lie on a crystallographic centre of inversion (Figure 1). The nitrate groups are unidentate and the nickel–ligand bond lengths [Ni–O(1) 2·101(2), Ni–O(4) 2·061(2), and Ni–N(2) 2·095(2) Å] agree well with reported values in other complexes.[8]

The high stability of the crystals and their ability to produce extremely intense diffraction patterns after relatively short exposure to *X*-rays, had initially led us to expect that within the crystal there existed some form of intermolecular association other than normal van der Waals' contacts. An examination of the crystal packing reveals a complex system of O · · · O hydrogen bonding extending throughout the crystal. Each co-ordinated water molecule is hydrogen bonded to two nitrate groups, one on each of two neighbouring complex molecules, the O · · · O distances being 2·87 and 2·76 Å (Figure 2). Thus each molecule of the complex is hydrogen bonded to its neighbours both through its water and nitrate groupings, giving rise to a total of eight hydrogen bonds per molecule. A similar type of hydrogen bonding is reported in $Ni(NO_3)_2,4H_2O$,[6] in which the O · · · O contacts are 2·80 and 2·91 Å, values very close to those of the present complex although the molecular structures differ in that the nitrate groups of the tetrahydrate salt occupy *cis*-positions, whereas they occupy *trans*-positions in the present bis(pyridine) molecule. A further difference between these two crystal structures is that, in the present complex, the hydrogen bonding is aligned in the *bc* plane, whilst in the tetrahydrate, there is no such regular arrangement.

TABLE 6

Least-squares best planes through the molecule. The equations are in the form $kX' + lY' + mZ' = n$ where X', Y', Z' are co-ordinates in Å. Distances of atoms from planes (Å) are given in square brackets

	k	*l*	*m*	*n*
Plane (1): O(1)—(3), N(1)	0·9468	0·0874	−0·3097	0·2159
[O(1) 0·001, O(2) 0·001, O(3) 0·001, N(1) −0·004, Ni −0·216]				
Plane (2): C(1)—(5), N(2)	0·0933	0·1821	0·9788	−0·0131
[C(1) 0·005, C(2) −0·003, C(3) −0·001, C(4) 0·004, C(5) −0·003, N(2) −0·001, Ni 0·013]				
Plane (3): O(4), H(6)—(7)	0·9745	−0·0118	−0·2240	1·1306
[O(4) 0·0000, H(6) 0·000, H(7) 0·000, Ni −1·13]				

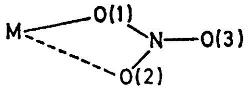
Dihedral angles (°) between planes

Plane (1)—(2)	66
Plane (1)—(3)	8
Plane (2)—(3)	72

An interesting comparison can be made of the detailed mode of nitrate co-ordination in $Ni(py)_2(NO_3)_2(H_2O)_2$ and in the complexes $[Cu(py)_2(NO_3)_2]_2,py$ [2] and $Zn(py)_2(NO_3)_2$.[1] The relevant bond lengths and angles are shown in Table 7. In all these cases the nitrate groups are asymmetrically disposed to the metal atom and the asymmetry can be related to the angle made by the metal and nitrogen atoms with the strongest bound oxygen atom [M–O(1)–N]. It has been suggested [9] that for normal unidentate co-ordination this angle should be close to 110°. This is realised in $Zn(py)_2(NO_3)_2$ [1] in which, although the longer Zn–O contacts are *ca.* 2·75 Å, consideration of the zinc orbitals likely to be employed in the bonding system supports the view that the nitrate groups are unidentate. In $[Cu(py)_2(NO_3)_2]_2,py$,[2] the nitrate groups are not equivalent and while one is expected to be a genuine asymmetric bidentate nitrate group, in the other, the metal–oxygen distance of 2·906 Å can represent at best a very weak interaction. The corresponding long Ni–O distance (3·24 Å) in the present complex is therefore not expected to represent significant interaction. The Ni–O(1)–N(1) valency angle of 127·0(2)° is extended from the normal values found in $Zn(py)_2(NO_3)_2$ as a result of the hydrogen bonding, the nitrate groups being held in a slightly 'extended' attitude by virtue of their close association with neighbouring molecules. The effects of hydrogen bonding are also manifested in the N–O bond lengths and O–N–O bond angles. Polarisation by the nickel atom might have been expected to make the N(1)–O(3) bond shorter than the N(1)–O(1) bond, whereas these bonds are approximately the same length. Similarly, the largest O–N–O angle might otherwise be expected opposite the shortest Ni–O distance, but the hydrogen bonding has also distorted this view.

TABLE 7

Comparison of bond lengths (Å) and angles (°)



	M–O(1)	M–O(2)	N–O(1)	N–O(1)	N–O(3)	M–O(1)–O(2)	M–O(1)–N	M–O(1)–N	O(1)–N–O(2)	O(1)–N–O(3)	O(2)–N–O(3)
$[Cu(py)_2(NO_3)_2]_2,py$ [a]	2·035(6)	2·618(8)	1·327(10)	1·261(11)	1·216(11)	55·3(3)	105·8(5)	80·7(5)	118·1(7)	117·1(8)	124·5(9)
	2·042(6)	2·906(7)	1·364(9)	1·228(10)	1·227(12)	50·0(2)	114·0(5)	76·5(5)	119·0(7)	116·3(8)	124·7(5)
$Zn(py)_2(NO_3)_2$ [b]	2·044(12)	2·758(19)	1·28(2)	1·28(2)	1·27(2)	52·2(5)	110·6(9)	77·0(11)	119·4(16)	120·1(16)	120·5(14)
	2·047(13)	2·754(14)	1·31(2)	1·25(2)	1·25(2)	51·4(5)	112·4(10)	80·1(9)	116·1(13)	120·4(14)	123·5(14)
$Ni(py)_2(NO_3)_2(H_2O)_2$	2·101(2)	3·244(3)	1·267(3)	1·231(4)	1·258(3)	41·7(1)	127·0(2)	69·4(2)	121·6(3)	117·4(3)	121·0(3)

[a] Ref. 2. [b] Ref. 1.

Another feature of interest of the crystal packing is that the aromatic planes of all the pyridine moieties are aligned in one direction throughout the crystal, while the delocalised nickel–nitrate inorganic sheets are all aligned in another direction. A related arrangement has also been found in the trimeric nickel complex

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[8] *Chem. Soc. Special Publ.*, No. 11, 1959; No. 18, 1965.

[9] C. D. Garner, J. Hilton, and S. C. Wallwork, *Acta Cryst.*, 1969, *A*, **25**, (Supplement) *S*104.

$[Ni(\beta\text{-picoline})_2(NO_2)_2]_3$,[10] and it was suggested in the latter case that this was a factor in determining the molecular stability. It is probable that such alignment of delocalised planes is also a factor in the crystal stability of the present compound. This feature is also present in the crystal structures of the two forms of $Cu(\alpha\text{-picoline})_2(NO_3)_2$ [11] and in molecular structure of $[Cu(py)_2(NO_3)_2]_2,py$ [2] although in this latter complex the planes do not extend throughout the crystal. Despite this feature, however, our analysis suggests that the co-ordinated water molecules have played a vital role in the existence of the present complex as a crystalline species, and have contributed to its ease of formation.

The computations were performed on the Glasgow University KDF 9 computer using programs developed by the Glasgow group.

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