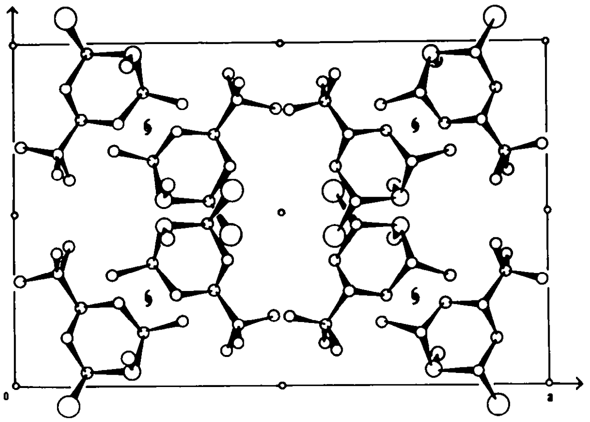


Fig. 3. Projection of the structure along **c**.

tert-Butyl group

Fig. 2 is the Newman projection through C(4)–C(7). The *tert*-butyl group is twisted away from the staggered position by about 10°. This value is greater than for PBCA (6°), BCA (6°), BCA (8°), and CTTH (8 and 6°).

Sulphoxide group

The O atom is axial. C(2)–S and C(6)–S bonds are equal (1·819 Å). The S–O distance is 1·473 Å. All these values are similar to those in other sulphoxides (Robert, 1977).

The crystal packing is governed by van der Waals contacts (Fig. 3).

We thank Dr C. Stora for her help and interest and Dr A. Marquet for providing the samples.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM 360 System. *World List of Crystallographic Computer Programs*, p. 52. Utrecht: Oosthoek.

Altona, C. & Sundaralingam, M. (1970). *Tetrahedron*, **26**, 925–939.

Bory, S., Lett, R., Moreau, B. & Marquet, A. (1973). *C. R. Acad. Sci. Paris, Sér. C*, **276**, 1323–1326.

Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

De Rango, C. Tsoucaris, G., Zelwer, C. & Baudour, J. L. (1964). *Bull. Soc. Sci. Bretagne*, **39**, 155–161.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.

Koningsveld, H. van (1972). *Acta Cryst.* B**28**, 1189–1195.

Mallissard, M., Sicsic, S., Welvart, Z., Chiaroni, A., Riche, C. & Pascard-Billy, C. (1974). *Bull. Soc. Chim. Fr.* pp. 1459–1463.

Robert, F. (1977). *Acta Cryst.* B**33**, 3480–3484.

Acta Cryst. (1977). B**33**, 3487–3491

The Crystal and Molecular Structure of Triaqua[2,6-bis(2′-pyridyl)-4-(2′-pyridinio)-1,3,5-triazine]nickel(II) Bromide Monohydrate

By G. A. Barclay, R. S. Vagg and E. C. Watton

School of Chemistry, Macquarie University, North Ryde, NSW 2113, *Australia*

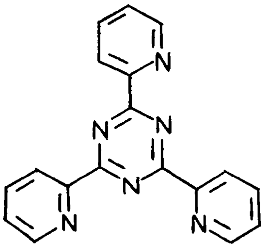
(*Received* 29 *March* 1977; *accepted* 6 *May* 1977)

$[C_{18}H_{13}N_6(H_2O)_3Ni]^{3+}.3Br^-.H_2O$ is monoclinic, space group $P2_1$, with a = 12·06 (4), b = 11·23 (4), c = 8·95 (2) Å, β = 96·5 (2)°, Z = 2. The structure was refined to R 0·069 for 1363 photographic intensities. The Ni atom is at the centre of a distorted octahedron of three water molecules [av. Ni–O 2·07 (2) Å] and three N atoms of the tridentate ligand. The bond from the metal atom to the central triazine ring of the ligand molecule [Ni–N 1·97 (2) Å] is significantly shorter than those to the two outer pyridyl rings [av. Ni–N 2·15 (2) Å]. The N atom of the pyridyl ring which is not coordinated to the Ni atom is protonated; all four aromatic rings of the ligand are coplanar. There is evidence for the existence of a network of hydrogen bonds between the pyridinium ion, the Br^- ions and the water molecules.

Introduction

2,4,6-Tris(2′-pyridyl)-1,3,5-triazine (tpt) (I) has been shown to act primarily as a tridentate ligand, similar to 2,2′,2″-terpyridine, in forming complexes with bivalent Ni (Vagg, Warrener & Watton, 1967), Co (Vagg, Warrener & Watton, 1969; Goodwin, Sylva, Vagg & Watton, 1969) and the lanthanides (Durham, Frost &

Hart, 1969; Kingston, Krankovits, Magee, Watton & Vagg, 1969). However, the coordinated ligand is more versatile than terpyridine, for the uncoordinated N atom of the third pyridyl group remains reactive towards protonation (Collins, Diehl & Smith, 1959; Fraser, Epstein & Macero, 1972; Vagg, Warrener & Watton, 1967) or interaction with a second metal ion (Vagg, Warrener & Watton, 1967, 1969).



tpt

(I)

The use of tpt as a spectroscopic reagent for Fe (Collins, Diehl & Smith, 1959), Co (Janmohamed & Ayres, 1972) and Ru (Embry & Ayres, 1968) has been proposed. It has been reported also that the coordinated ligand is susceptible to hydrolytic attack at the triazine centre under basic conditions (Lerner & Lippard, 1976). Here we report the determination of the structure of a Ni complex with the ligand in the protonated form. A preliminary communication has appeared (Barclay, Vagg & Watton, 1969).

Experimental

The complex crystallizes as amber–green octagonal plates from a warm aqueous solution of the ligand and $NiBr_2$ acidified with HBr.

Crystal data

$C_{18}H_{21}N_6Br_3O_4Ni$, $M_r = 683{\cdot}8$, monoclinic, $a = 12{\cdot}06\,(4)$, $b = 11{\cdot}23\,(4)$, $c = 8{\cdot}95\,(2)$ Å, $\beta = 96{\cdot}5\,(2)°$, $V = 1204{\cdot}3$, $D_m = 1{\cdot}90$ (by flotation), $Z = 2$, $D_c = 1{\cdot}89$ g cm^{-3}, $F(000) = 672$, μ(Cu $K\alpha$) = 7·8 cm^{-1}. Systematic absences: $0k0$ when $k = 2n + 1$, space group $P2_1$ or $P2_1/m$. The estimated standard deviations on unit-cell dimensions were calculated from Weissenberg and oscillation photographs with crystals mounted about the three principal axes and Si powder as an internal standard.

A crystal cut to 0·06 × 0·08 × 0·12 mm (corresponding to the three axial directions) was mounted about **c**. 1005 reflexions were collected from layers $hk0$–5 by the equi-inclination Weissenberg technique on packs of five films. A second crystal 0·10 × 0·12 × 0·13 mm was used to collect 956 reflexions from layers $h0$–$6l$ and, after resetting, 748 from 0–$5kl$. Intensities were read visually. They were corrected for Lorentz–polarization effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation to yield a final data set of 1363 unique reflexions.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962), the Ni and Br atoms being corrected for anomalous dispersion. Isotropic refinement was carried out on an IBM 360/50 computer with *ORFLS* (Busing, Martin & Levy, 1962). Anisotropic refinement was performed on a Univac 1106 computer with programs written by F. S. Stephens.

Structure determination

A solution to the structure was sought in the space group $P2_1$, the Ni atom thereby being assumed to be located neither at an inversion centre nor on a mirror plane. The successful refinement confirmed that choice to be correct. The Ni atom and the three Br^- ions were located from a Patterson synthesis. The complete structure was obtained from a Fourier synthesis phased with these four heavy atoms.

Isotropic refinement was by full-matrix least-squares calculations in which the function minimized was $\Sigma\, w\Delta^2$ with unit weights. Positional and individual isotropic thermal parameters and an overall scale factor were varied; R based on all 1363 reflexions converged to 0·080.

A difference synthesis revealed peaks in the positions expected for the 12 H atoms of the aromatic rings and also between the O atoms and Br^- ions, confirming the presence of hydrogen bonds between these species. An additional peak attributable to a H atom appeared in a position confirming that N(21) was the site of protonation.

Final anisotropic refinement was carried out with H atoms kept in these positions. Owing to the large number of parameters (289) it was necessary to use block matrices. The four matrices contained (1) the overall scale factor and thermal parameter, and the parameters for (2) the three Br^- ions, (3) the uncoordinated pyridyl ring and (4) the coordinated pyridyl and triazine rings and the Ni coordination sphere together with the lattice water molecule. The weighting scheme was $w = (8{\cdot}80 - 0{\cdot}07|F_o| + 0{\cdot}002|F_o|^2)^{-1}$. Reflexions for which $|F_c| < 0{\cdot}5|F_o|$ were omitted from the refinement, which was terminated when the maximum shift in any parameter was $<0{\cdot}25\sigma$. 1327 reflexions were included in the last cycle. A final difference synthesis showed maximum positive electron densities of 0·7 e Å^{-3} near the heavy atoms. The final R based on all 1363 reflexions was 0·069 and R'

$[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0·085. Atomic coordinates are given in Table 1.*

Table 1. *Final atomic coordinates (fractional,* × 10^4 *for heavy atoms,* × 10^3 *for hydrogen atoms) with estimated standard deviations in parentheses*

	x	*y*	*z*
Ni	8157 (3)	1975 (4)	728 (4)
Br(1)	4651 (2)	5000	7343 (3)
Br(2)	9250 (2)	4257 (3)	6836 (3)
Br(3)	1896 (2)	2966 (3)	670 (3)
O(1)	9652 (13)	1877 (20)	2041 (20)
O(2)	8637 (16)	3703 (17)	144 (19)
O(3)	7833 (13)	301 (15)	1585 (18)
O(4)	3077 (17)	299 (17)	106 (23)
N(1)	6702 (15)	2006 (19)	−530 (17)
N(2)	5624 (16)	1601 (18)	−2816 (21)
N(3)	4754 (17)	2393 (20)	−767 (20)
N(11)	8567 (17)	1198 (21)	−1367 (23)
N(21)	2776 (16)	2374 (18)	−2521 (18)
N(31)	7058 (15)	2738 (20)	2156 (20)
C(1)	6630 (19)	1611 (20)	−1950 (24)
C(2)	4753 (19)	1986 (22)	−2260 (26)
C(3)	5771 (18)	2427 (24)	4 (26)
C(11)	7677 (19)	1147 (24)	−2454 (24)
C(12)	7714 (21)	666 (24)	−3860 (28)
C(13)	8745 (28)	301 (30)	−4257 (35)
C(14)	9632 (27)	322 (23)	−3082 (33)
C(15)	9542 (20)	810 (26)	−1718 (26)
C(21)	3670 (18)	2005 (18)	−3185 (20)
C(22)	3586 (19)	1689 (23)	−4680 (27)
C(23)	2454 (23)	1764 (30)	−5457 (26)
C(24)	1645 (23)	2140 (30)	−4854 (32)
C(25)	1731 (17)	2507 (22)	−3372 (28)
C(31)	5942 (19)	2859 (24)	1554 (26)
C(32)	5113 (20)	3372 (25)	2232 (31)
C(33)	5332 (26)	3705 (26)	3734 (33)
C(34)	6471 (24)	3633 (24)	4427 (25)
C(35)	7305 (23)	3091 (27)	3527 (28)
H(12)	688	61	−432
H(13)	887	0	−541
H(14)	1054	2	−342
H(15)	1020	118	−109
H(*P*21)	288	258	−121
H(22)	430	142	−535
H(23)	233	170	−676
H(24)	83	214	−516
H(25)	109	279	−290
H(32)	438	319	202
H(33)	458	417	390
H(34)	665	394	550
H(35)	797	356	373
H(*W*11)	1040	204	172
H(*W*12)	998	121	248
H(*W*21)	878	380	−67
H(*W*22)	804	398	−45
H(*W*31)	789	−38	103
H(*W*32)	706	30	174
H(*W*41)	365	12	42
H(*W*42)	302	85	64

Discussion

Bond lengths and angles are given in Table 2. A perspective drawing of the $[Ni(H_2O)_3(tpt.HBr)]^{2+}$ unit showing the labelling is given in Fig. 1 (Johnson, 1965). Fig. 2 shows the packing of the non-hydrogen atoms with the proposed hydrogen bonds; the donor–acceptor distances are given in Table 3.

The Ni atom is at the centre of a distorted octahedron of one triazine and two pyridyl N atoms and the O atoms of three water molecules. The fourth water molecule and the Br^- ions are dispersed throughout the crystal in the hydrogen-bonding network indicated. The two coordinated pyridyl rings and

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Ni–N(1)	1·97 (2)	Ni–O(1)	2·04 (2)
Ni–N(11)	2·18 (2)	Ni–O(2)	2·11 (2)
Ni–N(31)	2·12 (2)	Ni–O(3)	2·08 (2)
N(1)–C(1)	1·34 (2)	N(1)–C(3)	1·35 (3)
N(2)–C(1)	1·36 (3)	N(2)–C(2)	1·29 (3)
N(3)–C(2)	1·41 (3)	N(3)–C(3)	1·34 (3)
N(11)–C(11)	1·37 (3)	N(11)–C(15)	1·32 (3)
N(21)–C(21)	1·35 (3)	N(21)–C(25)	1·40 (3)
N(31)–C(31)	1·40 (3)	N(31)–C(35)	1·29 (3)
C(31)–C(32)	1·35 (3)	C(32)–C(33)	1·39 (4)
C(33)–C(34)	1·44 (4)	C(34)–C(35)	1·49 (4)
C(21)–C(22)	1·38 (3)	C(22)–C(23)	1·37 (4)
C(23)–C(24)	1·33 (4)	C(24)–C(25)	1·38 (4)
C(11)–C(12)	1·37 (3)	C(12)–C(13)	1·39 (4)
C(13)–C(14)	1·41 (4)	C(14)–C(15)	1·35 (4)
C(1)–C(11)	1·48 (3)	C(2)–C(21)	1·46 (3)
C(3)–C(31)	1·46 (3)		
O(1)–Ni–O(2)	86·7 (7)	O(1)–Ni–O(3)	85·9 (7)
O(2)–Ni–O(3)	171·9 (6)	O(1)–Ni–N(1)	177·8 (8)
O(1)–Ni–N(11)	101·7 (7)	O(1)–Ni–N(31)	104·2 (7)
O(2)–Ni–N(1)	95·4 (7)	O(2)–Ni–N(11)	93·4 (7)
O(2)–Ni–N(31)	89·2 (7)	O(3)–Ni–N(1)	92·0 (7)
O(3)–Ni–N(11)	91·5 (7)	O(3)–Ni–N(31)	89·2 (7)
N(1)–Ni–N(11)	77·8 (7)	N(1)–Ni–N(31)	76·2 (6)
N(11)–Ni–N(31)	154·0 (7)	Ni–N(1)–C(1)	120 (1)
Ni–N(1)–C(3)	122 (1)	Ni–N(11)–C(11)	113 (1)
Ni–N(11)–C(15)	129 (1)	Ni–N(31)–C(31)	117 (1)
Ni–N(31)–C(35)	127 (2)		
N(1)–C(1)–C(11)	116 (2)	N(1)–C(3)–C(31)	115 (2)
C(1)–C(11)–N(11)	113 (2)	C(3)–C(31)–N(31)	111 (2)
C(1)–C(11)–C(12)	122 (2)	C(3)–C(31)–C(32)	122 (2)
N(2)–C(2)–C(21)	120 (2)	N(3)–C(2)–C(21)	116 (2)
C(2)–C(21)–C(22)	121 (2)	C(2)–C(21)–N(21)	117 (2)
C(1)–N(1)–C(3)	119 (2)	N(1)–C(1)–N(2)	120 (2)
C(1)–N(2)–C(2)	119 (2)	N(2)–C(2)–N(3)	124 (2)
C(2)–N(3)–C(3)	114 (2)	N(3)–C(3)–N(1)	124 (2)
N(11)–C(11)–C(12)	124 (2)	C(11)–C(12)–C(13)	118 (2)
C(12)–C(13)–C(14)	115 (2)	C(13)–C(14)–C(15)	123 (2)
C(14)–C(15)–N(11)	121 (2)	C(15)–N(11)–C(11)	118 (2)
N(21)–C(21)–C(22)	122 (2)	C(21)–C(22)–C(23)	116 (2)
C(22)–C(23)–C(24)	124 (2)	C(23)–C(24)–C(25)	120 (2)
C(24)–C(25)–N(21)	117 (2)	C(25)–N(21)–C(21)	120 (1)
N(31)–C(31)–C(32)	127 (2)	C(31)–C(32)–C(33)	119 (2)
C(32)–C(33)–C(34)	118 (2)	C(33)–C(34)–C(35)	117 (2)
C(34)–C(35)–N(31)	123 (2)	C(35)–N(31)–C(31)	116 (2)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32741 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the triazine ring are coplanar (Table 4, plane 1). The uncoordinated pyridyl ring (Table 4, plane 2) is turned slightly out of the plane of the rest of the molecule owing to the attraction of H(*P*21) to Br(3). The angle between these two planes (5·0°) is of little physical significance and the tpt molecule may be thought of as being completely planar (Table 4, plane 3).

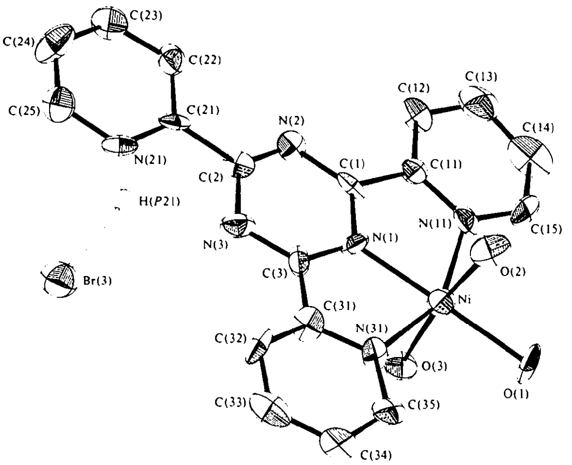


Fig. 1. A perspective drawing of the $[Ni(H_2O)_3(tpt.HBr)]^{2+}$ unit and labelling of the atoms. Thermal ellipsoids are scaled to include 50% probability.

Table 3. *Proposed hydrogen bonds* (Å)*: donor–acceptor distances are given, with estimated standard deviations in parentheses*

Bond		Acceptor at	
1	N(21)–H(*P*21)···Br(3)	(x,y,z)	3·23 (3)
2	O(1)–H(*W*11)···Br(3)	$(1+x,y,z)$	3·33 (4)
3	O(1)–H(*W*12)···Br(2)	$(2-x,y-\frac{1}{2},1-z)$	3·33 (3)
4	O(2)–H(*W*21)···Br(2)	$(x,y,z-1)$	3·19 (3)
5	O(2)–H(*W*22)···O(4)	$(1-x,\frac{1}{2}+y,-z)$	2·73 (3)
6	O(3)–H(*W*31)···Br(3)	$(1-x,y-\frac{1}{2},-z)$	3·35 (4)
7	O(3)–H(*W*32)···Br(1)	$(1-x,y-\frac{1}{2},1-z)$	3·26 (3)
8	O(4)–H(*W*41)···Br(1)	$(1-x,y-\frac{1}{2},1-z)$	3·38 (3)
9	O(4)–H(*W*42)···Br(3)	(x,y,z)	3·38 (4)

Details of the coordination of the Ni atom are given in Table 2. The two N–Ni–N angles [av. 77·0 (7)°] appear to be a compromise between an angle of 90° required by the Ni atom and one of 60° preferred by the undistorted planar ligand. This effect is again evidenced by the inward bending of the two coordinated pyridyl groups; the average of the four internal C–C–N angles is 114 (2)°. In addition the bond from the metal to the central triazine N atom [Ni–N 1·97 (2) Å] is significantly shorter than those of the two outer pyridyl rings [av. Ni–N 2·15 (2) Å]. These three forms of distortion are found also in related complexes of 2,2′,2″-terpyridine (Einstein & Penfold, 1966; Goldschmied & Stephenson, 1970; Maslen, Raston & White, 1974).

There is no significant difference in the three Ni–O distances [av. 2·07 (2) Å]; however, a distortion is evidenced by the O(2)–Ni–O(3) angle of 171·9 (6)°, the Ni–O(2) and Ni–O(3) bonds apparently being pushed away from the coordinated ligand. A similar effect is evident in the hydrolysis product of the Cu^{II} chelate of 2,4,6-tris(2′-pyrimidyl)-1,3,5-triazine (Lerner & Lippard, 1976). The reason is not obvious, although it may be an attempt by the metal atom to retain a symmetrically bonded arrangement given the enforced angular distortion in the two outer Ni–N bonds. The coordination may be described by the perpendicular intersection of the planes containing N(1), N(11), N(31), O(1), Ni and N(1), O(1), O(2), O(3), Ni. These planes (Table 4, planes 4 and 5 respectively) intersect at 89·4°. N(11), N(31), O(2), O(3) and Ni show large deviations from their plane of best fit (Table 4, plane 6) towards a tetrahedral arrangement, so that they cannot be considered as coplanar.

The protonation of N(21) was confirmed by a peak near it [N(21)–H(*P*21) 1·19 Å]. The Br(3)···N(21) distance of 3·23 (3) Å is the smallest in the crystal, and

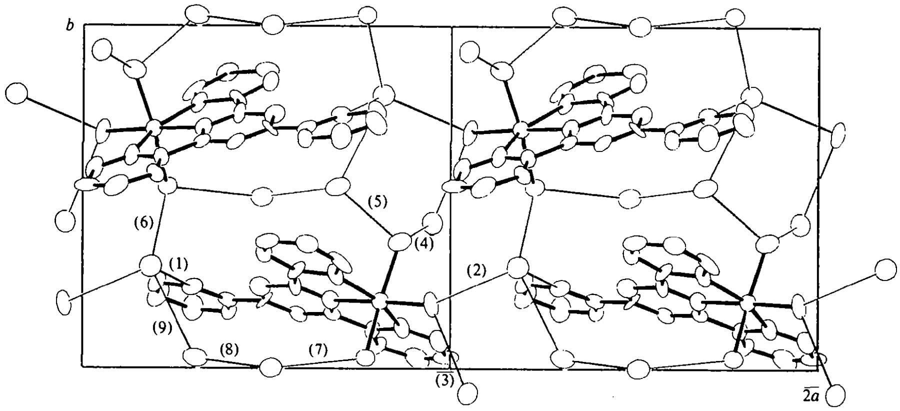


Fig. 2. The contents of the unit cell projected onto (001). Proposed hydrogen bonds are numbered according to details given in Table 3.

Table 4. *Least-squares planes and their equations*

X', Y' and Z' are orthogonal coordinates related to the atomic coordinates X, Y and Z by $X' = X \sin \beta$, $Y' = Y$, $Z' = Z + X \cos \beta$. Deviations (Å) of atoms from the planes are given in square brackets.

Plane 1: C(1), C(2), C(3), N(1), N(2), N(3), C(11), C(12), C(13), C(14), C(15), N(11), C(31), C(32), C(33), C(34), C(35), N(31) $0{\cdot}1998X + 0{\cdot}9117Y - 0{\cdot}3590Z = 4{\cdot}1485$

[N(1), 0·08, N(3) −0·08, C(32) 0·06, C(13) 0·05, C(14) −0·05, C(1) 0·04, C(11) 0·03, N(2) 0·02, C(2), C(15), C(33) −0·02, C(34) 0·01, C(31), C(35), N(11) −0·01, N(31) −0·003, C(3), C(12) −0·001]

Plane 2: C(21), C(22), C(23), C(24), C(25), N(21) $0{\cdot}2039X + 0{\cdot}9393Y - 0{\cdot}2758Z = 3{\cdot}9340$

[C(25) 0·03, N(21) −0·02, C(22) 0·01, C(23), C(24) −0·01, C(21) 0·002]

Plane 3: C(1), C(2), C(3), N(1), N(2), N(3), C(11), C(12), C(13), C(14), C(15), N(11), C(21), C(22), C(23), C(24), C(25), N(21), C(31), C(32), C(33), C(34), C(35), N(31) $0{\cdot}2041X + 0{\cdot}9128Y - 0{\cdot}3539Z = 4{\cdot}1798$

[N(21) −0·14, C(23) 0·10, N(3) −0·09, C(22) 0·08, C(32) 0·07, C(14) −0·05, C(13), C(34) 0·04, C(2), C(21), C(25) −0·04, C(24), C(1) 0·03, C(11) 0·02, C(12) −0·02, N(31), C(35) 0·01, N(11), C(15) −0·01, N(1) 0·007, N(2), C(3) −0·004, C(33) −0·003, C(31) −0·001]

Plane 4: N(1), N(11), N(31), O(1), Ni $0{\cdot}2251X + 0{\cdot}9103Y - 0{\cdot}3475Z = 4{\cdot}3595$

[Ni 0·020, N(1) −0·019, O(1) −0·015, N(11), N(31) 0·007]

Plane 5: N(1), O(1), O(2), O(3), Ni $0{\cdot}4212X - 0{\cdot}4035Y - 0{\cdot}8123Z = 3{\cdot}5748$

[O(3) 0·042, O(2) 0·040, O(1) 0·032, N(1) 0·028, Ni 0·022]

Plane 6: N(11), N(31), O(2), O(3), Ni $0{\cdot}8731X - 0{\cdot}0447Y + 0{\cdot}4854Z = 8{\cdot}0714$

[N(31) −0·36, N(11) −0·33, O(3) 0·28, O(2) 0·27, Ni 0·14]

compares with Br(3)···N(3) = 3·87 (3) Å. The latter value confirms that the proton does not bridge with this triazine N atom, in accordance with the weak donor properties of the triazine ring (Johnston, Vagg & Watton, 1977).

All the H atoms of the water molecules are involved in hydrogen bonding. The four H—O—H angles range from 85 to 113° (av. 99°), and the six Ni—O—H angles from 104 to 127° (av. 118°); thus approximately tetrahedral angles are retained about the O atoms. The seven O···Br$^-$ distances (Table 3) vary between 3·19 and 3·38 Å, average 3·32 Å. These distances are comparable with those reported for similar systems (Hamilton & Ibers, 1968).

References

Barclay, G. A., Vagg, R. S. & Watton, E. C. (1969). *Aust. J. Chem.* **22**, 643–645.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Collins, P. F., Diehl, H. & Smith, G. F. (1959). *Anal. Chem.* **31**, 1862–1867.

Durham, D. A., Frost, G. H. & Hart, F. A. (1969). *J. Inorg. Nucl. Chem.* **31**, 571–574.

Einstein, F. W. B. & Penfold, B. R. (1966). *Acta Cryst.* **20**, 924–926.

Embry, W. A. & Ayres, G. H. (1968). *Anal. Chem.* **40**, 1499–1501.

Fraser, F. H., Epstein, P. & Macero, D. J. (1972). *Inorg. Chem.* **11**, 2031–2034.

Goldschmied, E. & Stephenson, N. C. (1970). *Acta Cryst.* B**26**, 1867–1875.

Goodwin, H. A., Sylva, R. N., Vagg, R. S. & Watton, E. C. (1969). *Aust. J. Chem.* **22**, 1605–1611.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*, pp. 166, 221. New York: Benjamin.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–206, 214. Birmingham: Kynoch Press.

Janmohamed, M. J. & Ayres, G. H. (1972). *Anal. Chem.* **44**, 2263–2268.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, revised 1971. Oak Ridge National Laboratory, Tennessee.

Johnston, R. D., Vagg, R. S. & Watton, E. C. (1977). *Inorg. Chim. Acta.* **22**, L37–L38.

Kingston, J. V., Krankovits, E. M., Magee, R. J., Watton, E. C. & Vagg, R. S. (1969). *Inorg. Nucl. Chem. Lett.* **5**, 445–448.

Lerner, E. I. & Lippard, S. J. (1976). *J. Amer. Chem. Soc.* **98**, 5397–5398.

Maslen, E. N., Raston, C. L. & White, A. H. (1974). *J. Chem. Soc. Dalton*, pp. 1803–1807.

Vagg, R. S., Warrener, R. N. & Watton, E. C. (1967). *Aust. J. Chem.* **20**, 1841–1857.

Vagg, R. S., Warrener, R. N. & Watton, E. C. (1969). *Aust. J. Chem.* **22**, 141–152.