Acta Cryst. (1976). B32, 1121

The Crystal Structure of Tris-(2,2′-bipyridyl)nickel(II) Sulphate Hydrate, $[Ni(C_{10}H_8N_2)_3]SO_4.7{\cdot}5H_2O$

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(*Received* 17 *September* 1974; *accepted* 13 *September* 1975)

The crystal structure of $[Ni(bipy)_3]SO_4.7{\cdot}5H_2O$, has been determined by the heavy-atom method and refined by the block-diagonal least-squares method to a final R value of 0·099 using 3752 reflexions measured on a Hilger–Watts four-circle diffractometer. The complex crystallizes in the monoclinic system in space group $C2/c$, with eight formula units per unit cell. Cell parameters are: $a=22{\cdot}703$ (1), $b=13{\cdot}550$ (1), $c=24{\cdot}727$ (1) Å; $\beta=115{\cdot}13$ (2)°. The structure analysis reveals that the complex has an approximate D_3 symmetry, and the pseudo threefold axis of the complex is almost perpendicular to the (001) plane in the crystal.

Introduction

The complexes of transition metal ions with 2,2′-bipyridyl are enantiomeric, and the optical activity of various complexes has been investigated from several different aspects (Bosnich, 1968; Hanazaki & Nagakura, 1969; Ferguson, Hawkins, Kane-Maguire & Lip, 1969). In order to confirm the assignment of electronic transitions, either A_2 or E type transitions, we have measured the single-crystal absorption spectra of tris-(2,2′-bipyridyl)nickel(II) complexes. The analysis of the spectra needs precise crystal structure information, therefore we have attempted the crystal structure analysis of tris-(2,2′-bipyridyl)nickel(II) sulphate heptahydrate.

Experimental

$[Ni(bipy)_3]SO_4.7{\cdot}5H_2O$ was prepared according to von Hein's (1936) method, and crystals were obtained from an aqueous solution at room temperature. The crystal structure belongs to a monoclinic system and the space group is $C2/c$, which is in agreement with the results of Jacobs & Speeke (1954). The crystal data are given in Table 1.

Table 1. *Crystal data*

$Ni(C_{10}H_8N_2)_3SO_4.7{\cdot}5H_2O$; F.W.758·3
$a=22{\cdot}703\pm0{\cdot}001$, $b=13{\cdot}550\pm0{\cdot}001$
$c=24{\cdot}727\pm0{\cdot}001$ Å, $\beta=115{\cdot}13\pm0{\cdot}02°$ at 20 °C
$V=6887{\cdot}0$ Å^3, $D_m=1{\cdot}457$, $D_x=1{\cdot}462$ g cm^{-3}
$Z=8$
Systematic absences: hkl: $h+k=2n+1$, $h0l$: $l=2n+1$
Monoclinic $C2/c$, $F(000)=3176$
Mo $K\alpha$ ($\lambda=0{\cdot}71069$ Å), $\mu=7{\cdot}2$ cm^{-1}

A crystal was formed into a spherical shape with a diameter of about 0·2 mm. The intensity data were measured on a Hilger–Watts four-circle diffractometer

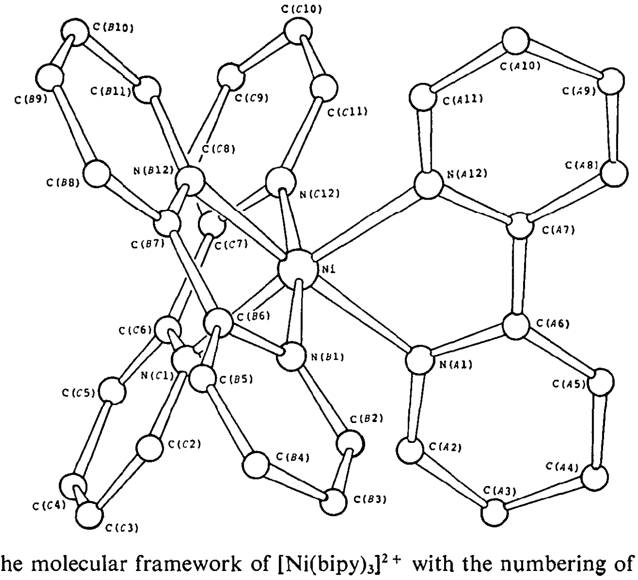

Fig. 1. The molecular framework of $[Ni(bipy)_3]^{2+}$ with the numbering of atoms.

with Zr filtered Mo $K\alpha$ radiation at 20°C using θ–2θ step-scan technique. The scan rates were 2 s step^{-1}, 0·02° step^{-1} and 60 steps reflexion^{-1}. A total of 5606 data were collected within $\theta = 26°$, and corrected for Lorentz and polarization factors; however, absorption and extinction corrections were not applied.

Determination of the structure and refinement

The heavy-atom vectors were easily found in a Patterson map and positions of non-hydrogen atoms in the complex ion and the S atom were obtained from minimum function maps. A Fourier synthesis was performed after three cycles of the block-diagonal least-squares refinement with isotropic thermal factors, and all the remaining atoms except the H atoms could be found. There are eight positions which are assigned to O atoms of water molecules, one of which, however, is on the twofold axis. This means that the number of positions of water molecules in an asymmetric unit is seven and a half, a number larger than the seven reported by von Hein (1936). Then, two cycles of least-squares refinement were carried out with occupancies of water molecules as variables by using block-diagonal approximation. However, no significant deviation from unity could be found, so it was concluded that the

Table 2. *Final fractional atomic coordinates* (× 10^4), *thermal parameters* (× 10^4) *and their standard deviations*

The anisotropic temperature factors are expressed in the form: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{31}hl)]$.
The isotropic thermal parameters are estimated by approximating the thermal ellipsoids to spheres of the same volume.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}	$B_{\rm iso}$
Ni	1596 (1)	615 (1)	2409 (1)	17 (1)	39 (1)	15 (1)	0 (1)	−1 (1)	14 (1)	2·9
N(*A*1)	2517 (4)	42 (6)	2964 (4)	19 (2)	47 (5)	21 (2)	−8 (6)	−4 (5)	16 (4)	3·6
C(*A*2)	2672 (6)	−458 (8)	3482 (5)	34 (4)	50 (7)	19 (2)	2 (8)	9 (7)	12 (5)	4·4
C(*A*3)	3315 (6)	−731 (9)	3851 (5)	25 (3)	67 (8)	22 (3)	10 (9)	7 (8)	0 (5)	4·8
C(*A*4)	3805 (6)	−481 (10)	3676 (6)	25 (4)	83 (11)	28 (3)	4 (10)	4 (10)	10 (5)	5·6
C(*A*5)	3648 (5)	23 (9)	3144 (6)	20 (3)	70 (9)	34 (4)	0 (8)	−9 (9)	15 (5)	5·1
C(*A*6)	2985 (5)	277 (7)	2786 (5)	22 (3)	39 (6)	22 (3)	−14 (7)	−13 (6)	23 (5)	3·5
C(*A*7)	2778 (5)	835 (7)	2222 (5)	18 (3)	27 (3)	20 (3)	8 (6)	−2 (6)	16 (4)	2·8
C(*A*8)	3198 (5)	1033 (9)	1955 (5)	25 (3)	66 (8)	23 (3)	−19 (8)	−15 (8)	29 (5)	4·1
C(*A*9)	2957 (6)	1553 (9)	1417 (5)	34 (4)	67 (9)	25 (3)	−2 (9)	−16 (8)	28 (6)	5·1
C(*A*10)	2312 (6)	1873 (9)	1162 (6)	42 (5)	63 (9)	28 (4)	−2 (10)	7 (8)	41 (7)	5·2
C(*A*11)	1908 (6)	1612 (9)	1451 (5)	33 (4)	68 (9)	21 (3)	4 (9)	10 (8)	27 (5)	4·7
N(*A*12)	2143 (4)	1094 (6)	1965 (4)	23 (3)	45 (6)	19 (2)	−1 (6)	4 (5)	21 (4)	3·5
N(*B*1)	1753 (4)	1921 (6)	2895 (4)	22 (3)	43 (6)	15 (2)	1 (6)	−4 (5)	16 (4)	3·3
C(*B*2)	2276 (6)	2104 (8)	3411 (5)	33 (4)	57 (8)	19 (3)	−33 (8)	−19 (7)	16 (5)	4·3
C(*B*3)	2327 (6)	2971 (10)	3738 (5)	35 (4)	73 (10)	23 (3)	−20 (10)	−21 (8)	20 (6)	5·3
C(*B*4)	1812 (6)	3645 (9)	3527 (5)	40 (5)	65 (9)	25 (3)	−35 (10)	−27 (8)	29 (6)	5·1
C(*B*5)	1263 (6)	3456 (8)	2984 (5)	41 (5)	44 (7)	27 (3)	−2 (8)	−12 (7)	39 (6)	4·6
C(*B*6)	1260 (6)	2586 (8)	2689 (5)	29 (4)	47 (7)	24 (3)	−5 (7)	2 (7)	32 (5)	3·9
C(*B*7)	721 (5)	2318 (8)	2103 (4)	19 (3)	51 (7)	19 (3)	5 (7)	13 (6)	20 (4)	3·3
C(*B*8)	210 (5)	2967 (9)	1808 (5)	22 (3)	67 (9)	28 (3)	9 (8)	16 (8)	22 (5)	4·6
C(*B*9)	−280 (6)	2683 (9)	1253 (6)	32 (4)	55 (8)	32 (4)	14 (9)	18 (8)	38 (6)	4·7
C(*B*10)	−232 (6)	1763 (10)	1010 (5)	30 (4)	90 (11)	30 (4)	7 (10)	17 (9)	31 (6)	5·5
C(*B*11)	303 (5)	1145 (9)	1352 (5)	22 (3)	77 (9)	20 (3)	−4 (8)	12 (7)	10 (4)	4·5
N(*B*12)	765 (4)	1430 (6)	1881 (4)	19 (2)	39 (5)	16 (2)	−6 (2)	−2 (5)	19 (4)	2·9
N(*C*1)	1157 (4)	−112 (6)	2884 (4)	18 (2)	46 (6)	16 (2)	−6 (6)	−6 (5)	14 (3)	3·2
C(*C*2)	1133 (5)	228 (8)	3387 (5)	29 (4)	65 (8)	20 (3)	3 (8)	−1 (7)	23 (5)	4·5
C(*C*3)	965 (6)	−394 (10)	3759 (5)	31 (4)	97 (11)	23 (3)	21 (10)	19 (8)	25 (5)	5·4
C(*C*4)	800 (6)	−1389 (9)	3583 (5)	29 (4)	70 (9)	22 (3)	2 (9)	7 (8)	22 (5)	4·7
C(*C*5)	805 (5)	−1711 (8)	3054 (5)	20 (3)	59 (8)	28 (3)	−3 (3)	4 (8)	20 (5)	4·4
C(*C*6)	985 (5)	−1068 (8)	2712 (4)	14 (3)	53 (7)	19 (3)	−1 (6)	4 (6)	11 (4)	3·4
C(*C*7)	1000 (5)	−1341 (8)	2141 (4)	17 (3)	45 (7)	18 (3)	1 (7)	6 (6)	11 (4)	3·3
C(*C*8)	752 (6)	−2239 (8)	1862 (6)	27 (4)	46 (7)	30 (4)	1 (8)	−6 (8)	20 (6)	4·7
C(*C*9)	776 (6)	−2455 (9)	1320 (6)	31 (4)	74 (10)	29 (4)	6 (9)	−24 (9)	24 (6)	5·3
C(*C*10)	1064 (6)	−1753 (10)	1084 (5)	28 (4)	79 (10)	20 (3)	22 (9)	−15 (8)	9 (5)	4·8
C(*C*11)	1321 (6)	−882 (9)	1398 (5)	35 (4)	74 (9)	19 (3)	9 (9)	−17 (7)	20 (5)	4·9
N(*C*12)	1288 (4)	−694 (6)	1923 (3)	18 (2)	49 (6)	17 (2)	−3 (6)	−6 (6)	14 (3)	3·4
S	4283 (2)	739 (2)	900 (2)	41 (1)	55 (2)	29 (1)	−9 (3)	−10 (2)	46 (2)	4·7
O(*S*1)	3835 (6)	−45 (8)	846 (6)	73 (6)	86 (8)	81 (6)	−69 (10)	−55 (10)	118 (10)	8·1
O(*S*2)	3941 (5)	1578 (7)	540 (6)	57 (5)	77 (9)	69 (5)	36 (9)	20 (9)	90 (8)	7·5
O(*S*3)	4773 (4)	396 (7)	705 (4)	35 (3)	92 (8)	35 (3)	15 (7)	−9 (7)	46 (5)	5·7
O(*S*4)	4582 (7)	1110 (9)	1504 (5)	96 (7)	116 (11)	32 (3)	−41 (13)	−29 (9)	75 (8)	8·1
O(*W*1)	3306 (5)	1433 (10)	4929 (5)	43 (4)	177 (14)	50 (4)	56 (11)	−26 (11)	7 (6)	10·0
O(*W*2)	1904 (6)	1668 (10)	4647 (5)	47 (5)	131 (13)	38 (4)	−32 (12)	3 (11)	26 (7)	8·5
O(*W*3)	2434 (7)	3593 (13)	107 (5)	67 (6)	330 (23)	41 (4)	81 (18)	63 (15)	48 (7)	12·6
O(*W*4)	1802 (7)	−150 (11)	292 (5)	76 (6)	204 (17)	40 (4)	97 (15)	35 (12)	39 (7)	11·2
O(*W*5)	4472 (5)	4547 (8)	34 (5)	57 (4)	120 (10)	56 (4)	−8 (10)	−3 (10)	69 (7)	9·0
O(*W*6)	630 (4)	2468 (7)	191 (4)	42 (3)	88 (8)	33 (3)	0 (8)	9 (7)	15 (5)	7·1
O(*W*7)	4582 (5)	1169 (7)	4944 (4)	54 (4)	92 (7)	35 (3)	7 (8)	9 (7)	46 (5)	7·3
O(*W*8)	5000	72 (13)	2500	92 (11)	114 (16)	47 (6)	0	0	−6 (12)	11·4

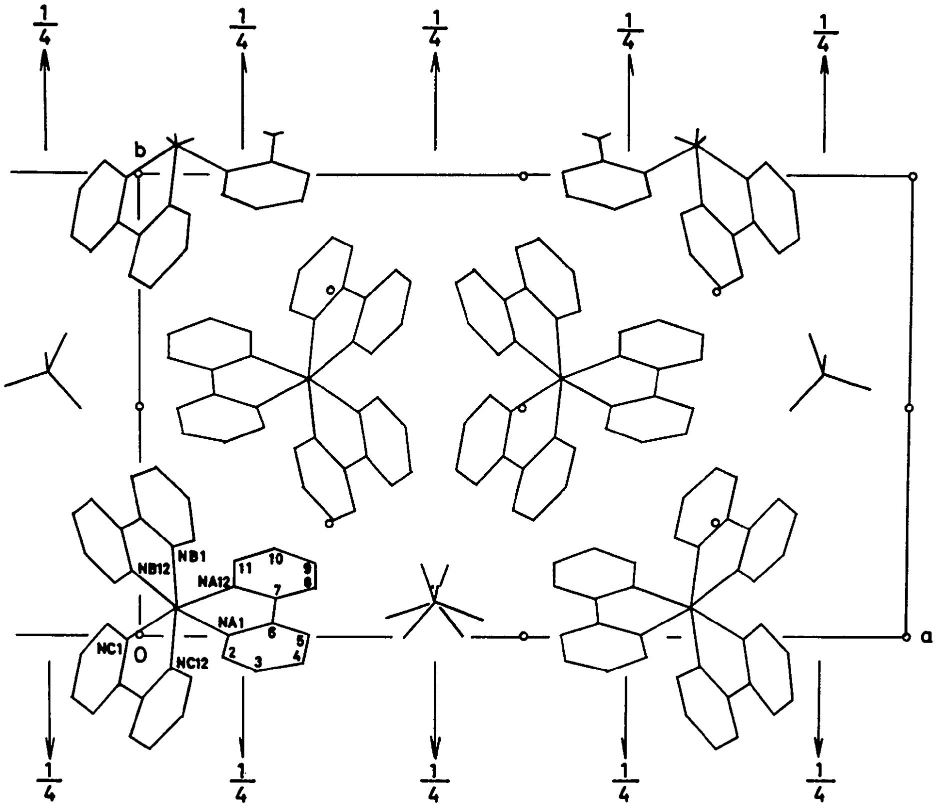

Fig. 2. The arrangements of $[Ni(bipy)_3]^{2+}$ and $SO_4^=$ ions projected onto the (001) plane.

number of molecules of water of crystallization is 7·5 per complex.

The final refinement was carried out by a block-diagonal least-squares method with anisotropic thermal parameters for all atoms, using 3752 observed F_o with $3\sigma(F_o) < F_o$. Weights for these data were taken as unity and the conventional R index converged to 0·099.* Since no large peaks were found in difference Fourier maps at this stage, no attempt was made to locate the H atoms. Table 2 shows the final atomic coordinates and anisotropic thermal parameters with their estimated standard deviations.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968).

Results and discussion

The $[Ni(bipy)_3]^{2+}$ complex has an approximate point group D_3 symmetry, where the Λ isomer is illustrated in Fig. 1 with the numbering of atoms.

The bond lengths and angles are listed in Table 3 with their estimated standard deviations. The mean value of bond distances between the Ni and N atom is 2·089 (4) Å and is in good agreement with the corresponding value of 2·090 Å in $[Ni(phen)_3]^{2+}$ (Frenz & Ibers, 1972), but it is slightly longer than the value of

Table 3. *Intramolecular bond lengths* (Å) *and angles* (°)

Ni——N(*A*1)	2·103 (7)
-N(*A*12)	2·082 (11)
-N(*B*1)	2·082 (8)
-N(*B*12)	2·095 (7)
-N(*C*1)	2·082 (10)
-N(*C*12)	2·090 (8)
N(*A*1)—C(*A*2)	1·36 (1)
-C(*A*6)	1·35 (1)
C(*A*2)—C(*A*3)	1·40 (2)
C(*A*3)—C(*A*4)	1·40 (2)
C(*A*4)—C(*A*5)	1·39 (2)
C(*A*5)—C(*A*6)	1·43 (1)
C(*A*6)—C(*A*7)	1·48 (1)
C(*A*7)—C(*A*8)	1·40 (2)
-N(*A*12)	1·35 (1)
C(*A*8)—C(*A*9)	1·39 (2)
C(*A*9)—C(*A*10)	1·39 (2)
C(*A*10)-C(*A*11)	1·43 (2)
C(*A*11)-N(*A*12)	1·35 (1)
N(*B*1)-C(*B*2)	1·35 (1)
-C(*B*6)	1·36 (1)
C(*B*2)—C(*B*3)	1·40 (2)
C(*B*3)—C(*B*4)	1·40 (2)
C(*B*4)—C(*B*5)	1·41 (1)
C(*B*5)—C(*B*6)	1·39 (2)
C(*B*6)—C(*B*7)	1·49 (1)
C(*B*7)—C(*B*8)	1·39 (1)
-N(*B*12)	1·34 (1)
C(*B*8)—C(*B*9)	1·41 (1)
C(*B*9)—C(*B*10)	1·41 (2)
C(*B*10)-C(*B*11)	1·42 (2)
C(*B*11)-N(*B*12)	1·34 (1)
N(*C*1)-C(*C*2)	1·35 (2)
-C(*C*6)	1·37 (1)
C(*C*2)—C(*C*3)	1·41 (2)
C(*C*3)—C(*C*4)	1·42 (2)
C(*C*4)—C(*C*5)	1·38 (2)
C(*C*5)—C(*C*6)	1·39 (2)
C(*C*6)—C(*C*7)	1·47 (2)
C(*C*7)—C(*C*8)	1·39 (1)
-N(*C*12)	1·34 (2)
C(*C*8)—C(*C*9)	1·40 (2)
C(*C*9)—C(*C*10)	1·41 (2)
C(*C*10)-C(*C*11)	1·40 (2)
C(*C*11)-N(*C*12)	1·35 (2)
S——O(*S*1)	1·44 (1)
-O(*S*2)	1·45 (1)
-O(*S*3)	1·46 (1)
-O(*S*4)	1·44 (1)

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* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31397 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3 (*cont.*)

N(A1)—Ni———N(A12)	79·0 (4)
-N(B1)	93·3 (3)
-N(B12)	169·7 (3)
-N(C1)	92·2 (3)
-N(C12)	93·4 (3)
N(A12)-Ni———N(B1)	92·5 (4)
-N(B12)	95·0 (4)
-N(C1)	168·9 (3)
-N(C12)	95·1 (4)
N(B1)—Ni———N(B12)	78·5 (3)
-N(C1)	94·8 (3)
-N(C12)	170·6 (4)
N(B12)-Ni———N(C1)	94·6 (4)
-N(C12)	95·5 (3)
N(C1)—Ni———N(C12)	78·4 (4)
Ni———N(A1)—C(A2)	126 (1)
-C(A6)	114 (1)
C(A2)—N(A1)—C(A6)	120 (1)
N(A1)—C(A2)—C(A3)	122 (1)
C(A2)—C(A3)—C(A4)	119 (1)
C(A3)—C(A4)—C(A5)	120 (1)
C(A4)—C(A5)—C(A6)	119 (1)
N(A1)—C(A6)—C(A5)	121 (1)
-C(A7)	117 (1)
C(A5)—C(A6)—C(A7)	123 (1)
C(A6)—C(A7)—C(A8)	123 (1)
-N(A12)	115 (1)
C(A8)—C(A7)—N(A12)	122 (1)
C(A7)—C(A8)—C(A9)	118 (1)
C(A8)—C(A9)—C(A10)	120 (1)
C(A9)—C(A10)-C(A11)	118 (1)
C(A10)-C(A11)-N(A12)	121 (1)
Ni———N(A12)-C(A7)	115 (1)
-C(A11)	125 (1)
C(A7)—N(A12)-C(A11)	120 (1)
Ni———N(B1)—C(B2)	125 (1)
-C(B6)	116 (1)
C(B2)—N(B1)—C(B6)	119 (1)
N(B1)—C(B2)—C(B3)	122 (1)
C(B2)—C(B3)—C(B4)	119 (1)
C(B3)—C(B4)—C(B5)	120 (1)
C(B4)—C(B5)—C(B6)	117 (1)
N(B1)—C(B6)—C(B5)	123 (1)
-C(B7)	114 (1)
C(B5)—(CB6)—C(B7)	123 (1)
C(B6)—C(B7)—C(B8)	121 (1)
-N(B12)	116 (1)
C(B8)—C(B7)—N(B12)	123 (1)
C(B7)—C(B8)—C(B9)	119 (1)
C(B8)—C(B9)—C(B10)	119 (1)
C(B9)—C(B10)-C(B11)	118 (1)
C(B10)-C(B11)-N(B12)	122 (1)
Ni———N(B12)-C(B7)	115 (1)
-C(B11)	126 (1)
C(B7)—N(B12)-C(B11)	120 (1)
Ni———N(C1)—C(C2)	125 (1)
-C(C6)	115 (1)
C(C2)—N(C1)—C(C6)	119 (1)
N(C1)—C(C2)—C(C3)	122 (1)
C(C2)—C(C3)—C(C4)	118 (1)
C(C3)—C(C4)—C(C5)	119 (1)
C(C4)—C(C5)—C(C6)	120 (1)
N(C1)—C(C6)—C(C5)	122 (1)
-C(C7)	115 (1)
C(C5)—C(C6)—C(C7)	124 (1)
C(C6)—C(C7)—C(C8)	122 (1)
-N(C12)	116 (1)
C(C8)—C(C7)—N(C12)	122 (1)
C(C7)—C(C8)—C(C9)	119 (1)
C(C8)—C(C9)—C(C10)	118 (1)
C(C9)—C(C10)-C(C11)	120 (1)
C(C10)-C(C11)-N(C12)	121 (1)
Ni———N(C12)-C(C7)	115 (1)
-C(C11)	125 (1)
C(C7)—N(C12)-C(C11)	120 (1)
O(S1)—S———O(S2)	110·4 (7)
-O(S3)	109·9 (7)
-O(S4)	111·0 (9)
O(S2)—S———O(S3)	109·2 (8)
-O(S4)	104·9 (7)
O(S3)—S———O(S4)	111·3 (8)

2·062 Å in $[Ni(bipy)(H_2O)_2]$ (Tedenac & Phillippot, 1974). This difference is small but apparent, and it may occur because of the repulsive force between bipyridyl ligands. However, there is no significant difference in the structure of bipyridyl groups in $[Ni(bipy)_3]^{2+}$ compared with other complexes; $[V(bipy)_3]$ (von Albrecht, 1963), $[Co(bipy)_2(NO_3)]^{2+}$ (Reimann, Zocchi, Mighell & Santoro, 1971), $[Cu(bipy)_2tu\,(ClO_4)_2]$ (Ferrari, Corradi, Fava, Palmieri, Nardelli & Pelizzi, 1973), $[Cu(bipy)(NO_2)_2]$ (Stephens, 1969), $[Ni(bipy)(H_2O)_2]$ (Tedenac & Phillippot, 1974), namely bond lengths C–N 1·35, C–C 1·40 and C–C′ (connecting two pyridyl groups) 1·48 Å are in agreement within experimental error. These values agree with the corresponding value of bipyridyl molecules having different configurations; 2,2′-bipyridyl.2ICl and 2,2′-bipyridyl.2IBr (Soled & Carpenter, 1974) and the 2,2′-bipyridyl molecule (Merritt & Schroeder, 1956).

The equations of least-squares planes for six pyridyl groups are calculated and deviations of each atom from the planes are listed in Table 4. The planarity of each pyridine ring is fairly good but two pyridyl groups in the bipyridyl ligand are twisted with respect to each other in the right-handed screw direction (*S* configuration) in the *Λ* isomer. The twist angles were estimated as 6·8° (ligand *A*), 5·8° (ligand *B*) and 10·9° (ligand *C*),

Table 4. *Least-squares planes and the deviations from their respective planes for pyridyl groups; x, y and z′ are coordinates in* Å *along a, b and c* axes*

$-0{\cdot}0757x+0{\cdot}8695y+0{\cdot}4880z'-3{\cdot}0845=0$					
N(A1)	0·007	C(A2)	−0·002	C(A3)	−0·003
C(A4)	0·004	C(A5)	0·000	C(A6)	−0·006
$0{\cdot}0395x+0{\cdot}8588y+0{\cdot}5109z'-3{\cdot}6482=0$					
C(A7)	0·021	C(A8)	−0·005	C(A9)	−0·015
C(A10)	0·018	C(A11)	−0·003	N(A12)	−0·017
$-0{\cdot}7227x-0{\cdot}4693y+0{\cdot}5074z'-1{\cdot}3860=0$					
N(B1)	0·000	C(B2)	0·006	C(B3)	−0·010
C(B4)	0·008	C(B5)	−0·002	C(B6)	−0·003
$-0{\cdot}7882x-0{\cdot}4127y+0{\cdot}4567z'-1{\cdot}3102=0$					
C(B7)	−0·006	C(B8)	0·001	C(B9)	0·008
C(B10)	−0·012	C(B11)	0·008	N(B12)	0·001
$0{\cdot}8190x-0{\cdot}2690y+0{\cdot}5068z'-2{\cdot}9675=0$					
N(C1)	0·015	C(C2)	−0·015	C(C3)	0·003
C(C4)	0·009	C(C5)	−0·009	C(C6)	−0·003
$0{\cdot}7455x-0{\cdot}4434y+0{\cdot}4976z'-3{\cdot}2236=0$					
C(C7)	−0·018	C(C8)	0·011	C(C9)	0·003
C(C10)	−0·010	C(C11)	0·005	N(C12)	0·010

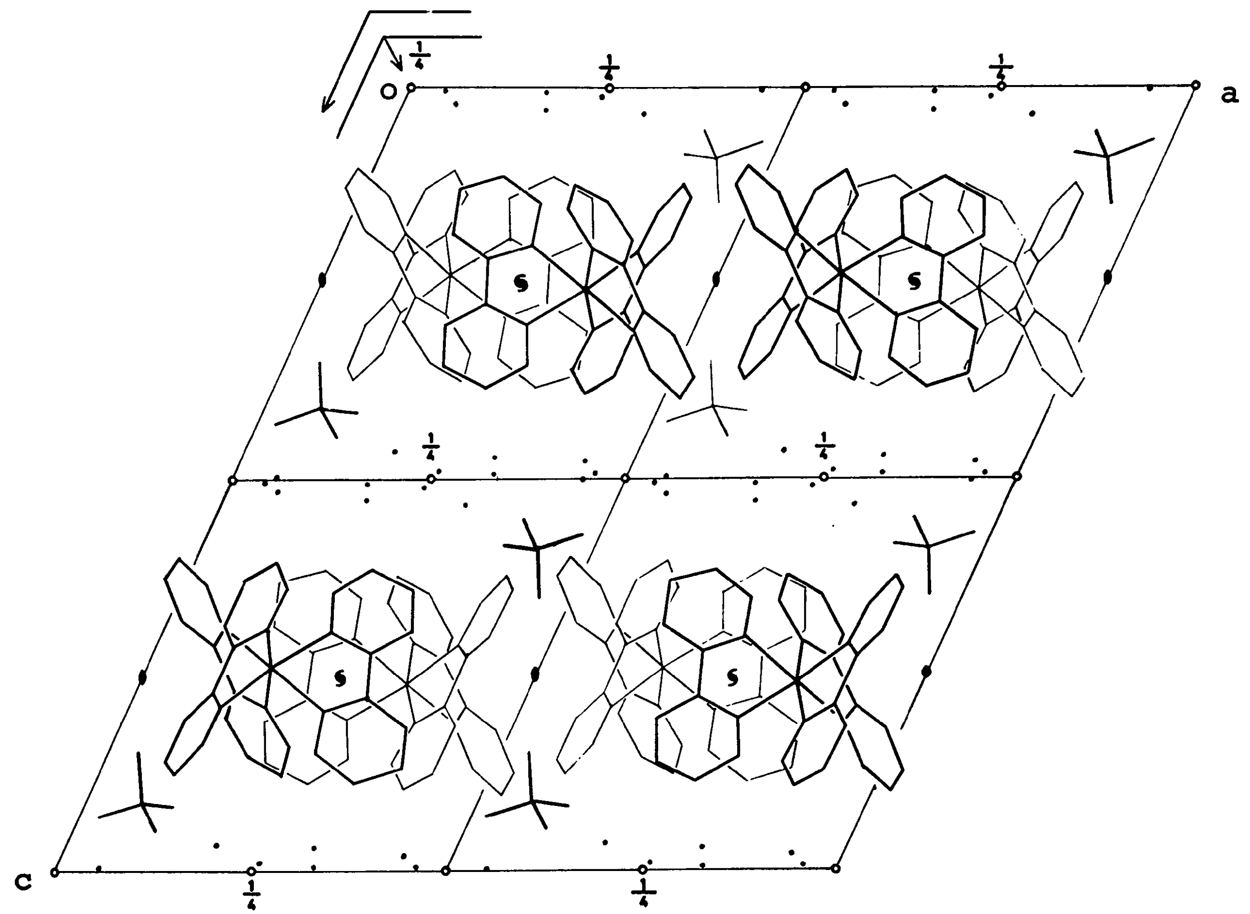

Fig. 3. The crystal structure projected along the *b* axis. Complex ions drawn with heavy lines are lying relatively in a higher part of the unit cell than those drawn with light lines.

respectively, and these are similar to those found in bpyriidyl ligands of foregoing complexes. This twisting is caused by the steric repulsion between non-bonded atoms, for instance, the interatomic distance between H atoms attached to C(*A*5) and C(*A*8) is estimated as 2·1 Å in the planar structure, while in the twisted form it will be 2·7 Å. The interligand non-bonded distances are listed in Table 5 and some of them are within van der Waals contacts. The average value of the distances between N(*A*1) and N(*B*1) and its equivalents is 3·07 Å, while, if the bipyridyl ligands in the Λ isomer form an *R* configuration, this value is estimated to be about 2·97 Å. For this reason the *S* configuration will be more stable than the *R* configuration in the Λ isomer.

Table 5. *Intramolecular distances* (Å) *less than* 3·6 Å *and their estimated standard deviations*

N(A1)—N(B1)	3·04 (1)	N(A12)-N(B1)	3·01 (1)
-C(B2)	3·14 (2)	-N(B12)	3·08 (1)
-N(C1)	3·02 (1)	-C(C11)	3·22 (1)
-N(C12)	3·05 (1)	-N(C12)	3·08 (1)
C(A2)—C(B2)	3·57 (1)	N(B1)—N(C1)	3·07 (1)
-N(C1)	3·15 (1)	-C(C2)	3·19 (2)
-C(C2)	3·53 (2)	C(B11)-C(C11)	3·56 (2)
C(A11)-C(B11)	3·60 (2)	-N(C12)	3·24 (1)
-N(B12)	3·20 (2)	N(B12)-N(C1)	3·07 (1)
		-N(C12)	3·10 (1)

Table 6. *Intermolecular distances* (Å) *less than* 3·6 Å *and their estimated standard deviatons*

(i)–(i)	
C(A10)-O(W3)	3·60 (2)
-O(W4)	3·37 (2)
C(A11)-O(W6)	3·43 (1)
C(B2)—O(W1)	3·60 (1)
-O(W2)	3·55 (2)
C(B3)—O(W1)	3·52 (2)
-O(W2)	3·31 (2)
C(B10)-O(W6)	3·49 (2)
C(C2)—O(W2)	3·46 (2)
C(C11)-O(W4)	3·49 (2)
(i)–(ii)	
C(B10)-C(C3)	3·53 (2)
-O(W2)	3·44 (2)
C(B11)-C(C3)	3·47 (2)
C(C4)—C(C8)	3·41 (2)
C(C5)—C(C5)	3·52 (1)
(i)–(iii)	
C(A9)—C(C5)	3·47 (2)
C(A10)-C(A3)	3·54 (2)
C(B3)—C(C10)	3·51 (2)
-C(C11)	3·58 (2)
C(B3)—O(W4)	3·48 (2)
C(B4)—C(A8)	3·45 (2)
-O(S1)	3·10 (2)
C(B5)—C(A5)	3·58 (2)
C(B8)—O(W8)	3·46 (2)
O(S2)—C(C4)	3·40 (2)
O(S4)—C(C4)	3·48 (2)
-C(C5)	3·39 (2)
O(W5)-C(C3)	3·52 (2)
O(W6)-C(A3)	3·53 (1)
O(W7)-C(C9)	3·43 (2)
(i)–(iv)	
C(A9)—O(W3)	3·49 (2)
C(A10)-O(W3)	3·48 (2)

Key for molecules

i	x	y	z
ii	$-x$	y	$\frac{1}{2}-z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$

The arrangement of complex ions, sulphate and molecules of water of crystallization are shown in Figs. 2, 3 and 4. The pseudo threefold axis of the complex is nearly vertical to the (001) plane as shown in Fig. 2, where the ions are projected onto the (001) plane. The packing of Λ and Δ enantiomers is shown in Fig. 3 and each isomer is arranged along the *a* axis in a separate layer occupying almost all the half-cell. In Fig. 4, the structure is projected along the *c* axis. The complex ions, drawn with heavy lines, are Δ isomers forming the top layer; the sulphate ions and water molecules make the second layer, where hydrogen-bonds are drawn with broken lines; and the Λ isomers, drawn with light lines, are in the bottom layer. The sulphate ions and water molecules, which form the hydrogen-bonded network between the layers of Δ and Λ isomers, are shown in Fig. 5 with O–O distances and angles. The network is composed of all the water molecules and sulphate ions lying in $z \simeq 0{\cdot}5$ and is connected to the next ones lying in $z \simeq 0{\cdot}0$ and $z \simeq 1{\cdot}0$ by hydrogen-bonds involving the water molecule O(*W*8). All water molecules excepting O(*W*8) are connected to at least three other water molecules by hydrogen-bonds, and so there are no free water molecules. Intermolecular distances less than 3·6 Å are tabulated in Table 6.

All calculations were performed on FACOM 230–60

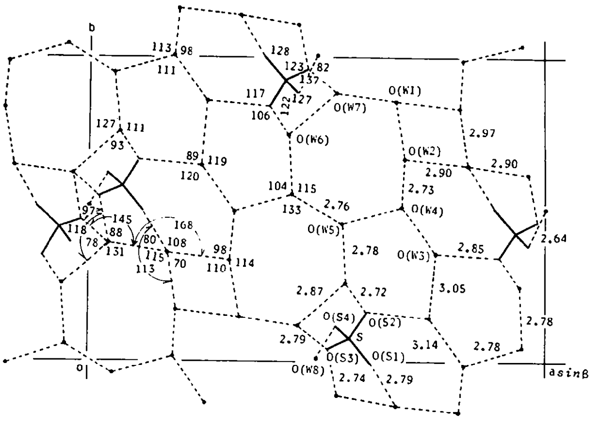

Fig. 5. Sulphate ions and molecules of water of crystallization lying in $z \simeq 0{\cdot}5$. The hydrogen bonds are drawn with broken lines and O–O distances are given in Å and angles in degrees.

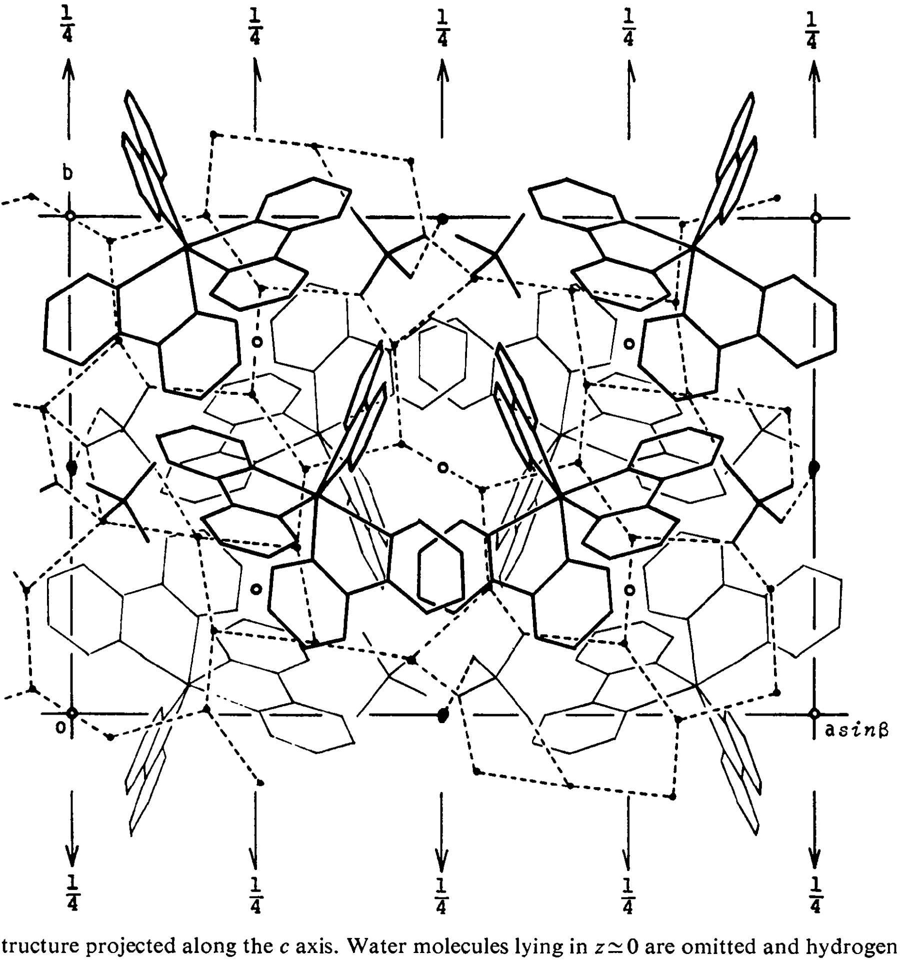

Fig. 4. The crystal structure projected along the *c* axis. Water molecules lying in $z \simeq 0$ are omitted and hydrogen bonds are drawn with broken lines.

computers of the Computing Centres of Nagoya and of Kyoto University using the two programs: *ATLS* (block-diagonal least-squares refinement, by A. Furusaki and others at Kwansei Gakuin University) and *RSDA* 4 [bond lengths and angles, Sakurai (1967)].

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Structure Determination of Pentaaquocopper(II) Tetrafluoroberyllate

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(*Received* 7 *July* 1975; *accepted* 12 *September* 1975)

The crystal and molecular structure of $CuBeF_4.5H_2O$ was determined by single-crystal X-ray analysis. Crystals of $CuBeF_4.5H_2O$ are triclinic, space group $P\bar{1}$. The title compound is isomorphous with $CuSO_4.5H_2O$. Cell parameters are $a=7{\cdot}132$ (1), $b=10{\cdot}674$ (1), $c=5{\cdot}924$ (4) Å, $\alpha=97{\cdot}53$ (3), $\beta=125{\cdot}49$ (5), $\gamma=93{\cdot}94$ (5)°. The unit cell contains two molecular units with Cu atoms on centres of symmetry 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Least-squares refinement resulted in $R=0{\cdot}0197$ and $R_w=0{\cdot}0281$ for 3494 observed reflexions. The Cu atoms are surrounded by four O ($\pm 1{\cdot}96$ Å) and two F atoms ($\pm 2{\cdot}35$ Å) in approximate D_{4h} symmetry. Be is tetrahedrally surrounded by four F atoms ($\pm 1{\cdot}55$ Å). The molecular structure consists of chains of alternating octahedra and tetrahedra along [111]. The octahedra and tetrahedra are coupled *via* F atoms. Special attention is given to corrections for absorption and extinction phenomena. Possibilities such as disorder and the non-centrosymmetric space group are discussed.

Introduction

Crystal structures of several compounds closely related to $CuBeF_4.5H_2O$ have been reported ($CuSO_4.5H_2O$, Beevers & Lipson, 1934; Bacon & Curry, 1962; $MgSO_4.5H_2O$, Baur & Rolin, 1972; $MgCrO_4.5H_2O$, Bertrand, Dusausoy, Protas & Watelle-Marion, 1971). The isomorphism of $CuBeF_4.5H_2O$ with $CuSO_4.5H_2O$ was reported by Tedenac, Granier, Norbert & Cot (1969). Cell constants for $CuBeF_4.5H_2O$ were calculated by Avinens, Cot & Maurin (1970) from Debye–Scherrer photographs. Their reported values ($a=7{\cdot}146$ (3), $b=10{\cdot}685$ (3), $c=5{\cdot}942$ (3) Å, $\alpha=97{\cdot}47$ (3), $\beta=125{\cdot}57$ (3), $\gamma=94{\cdot}00$ (3)°) are in reasonable agreement with our results (Table 1).

The magnetic behaviour of copper ions (Soda & Chiba, 1969) in this structural type is very interesting due to the presence of two different magnetic systems, one being paramagnetic, the other anti-ferromagnetic. A further exploration of the magnetic properties was made by Henkens, Diederix, Klaassen & Poulis (1975) who studied $CuBeF_4.5H_2O$ by means of n.m.r. investigations on Be ($I=1$) and F ($I=\frac{1}{2}$) at about 1 K.

Proton magnetic resonance spectra showed differences between this compound and the sulphate. This prompted us to undertake a detailed crystallographic study. Corrections for absorption and extinction effects were made carefully, to reduce systematic errors. A fairly good solution of the structure in space group $P\bar{1}$ has been determined, which shows no significant deviations from $CuSO_4.5H_2O$, contrary to the evidence from the n.m.r. data. In the discussion, attention is given to possible deviations from the structure presented suggested by the observed anomalous p.m.r. spectra.

Experimental

Crystal data and technical information are collected in Table 1. Preliminary investigations concerning