60

(c) Organisation de la structure

Le cristal de méthyl-naphtohydroquinone est formé d'empilements des molécules parallèles de direction [010]; la distance entre plans est de 3,55 Å l'inclinaison sur l'axe de la pile est de 38°: le recouvrement moléculaire, s'il est notable, n'intéresse pas tout le noyau naphtalène mais se fait entre cycles benzéniques et noyaux phénols.

C'est un phénomène très voisin de celui mis en évidence dans la naphtohydroquinone; dans le dérivé substitué le recouvrement est modifié de manière à mettre en superposition atome d'oxygène et groupement méthyle d'une part, atome d'oxygène et carbone hybride sp^2 d'autre part (Fig. 5). Cette configuration pourrait expliquer l'intervalle plus important observé entre plans moléculaires (0,07 Å).

Les liaisons hydrogène O-H··· relient, autour des axes hélicoïdaux, deux empilements pour créer des feuillets moléculaires parallèles au plan (001). Les molécules font entre elles un angle de 75° (Fig. 6).

Aucune autre liaison forte n'existe pour assurer la cohésion entre feuillets parallèles distants de c/2 (Fig.7); ceux-ci sont arrangés suivant un close-packing classique pour lequel chaque colonne est entouré de six colonnes identiques.

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The Crystal and Molecular Structure of Diaquobis-(2, 2'-biimidazole)nickel(II) Dinitrate, Ni(C₆H₆N₄)₂(H₂O)₂(NO₃)₂

BY ALAN D. MIGHELL, CURT W. REIMANN AND FLOYD A. MAUER

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

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The crystal and molecular structure of diaquobis-(2,2'-biimidazole)nickel(II) dinitrate, Ni $(C_6H_6N_4)_2(H_2O)_2(NO_3)_2$, was determined by single-crystal X-ray diffraction techniques. This compound crystallizes in the monoclinic system with $a = 10.3925 \pm 0.0004$ Å, $b = 9.6284 \pm 0.0004$ Å, $c = 9.9615 \pm 0.0003$ Å, $\beta = 96.308 \pm 0.003^\circ$, space group $P_{2_1/n}$, $\rho_c = 1.63$ g. cm⁻³, and Z = 2. Three-dimensional data (3151 reflections) were used and the structure solved by the heavy atom method. The Ni $(C_6H_6N_4)_2(H_2O)_2(NO_3)_2$ molecule is centrosymmetric with the nickel atom at the center of an octahedron formed by two water oxygen atoms and four nitrogen atoms. The four coordinating nitrogen atoms, two from each biimidazole molecule, form a parallelogram (3.193×2.711 Å) which is nearly a rectangle. The structure consists of these complex cations linked to one another by nitrate anions which are hydrogen bonded to the coordinated water molecules, and to the N–H groups in the biimidazole molecules. All hydrogen atoms in this structure were located in a difference map. Final refinement of this model by three-dimensional anisotropic least-squares analysis resulted in an *R* value of 5.2%.

Introduction

As part of a program in the investigation of the relationship between the detailed crystallographic environment and the spectra of transition element ions the complex, diaquobis-(2,2'-biimidazole)nickel(II) dinitrate, was prepared. From the chemical composition and preliminary unit cell data, it appeared likely that the nickel ion resides in a tetragonal or lower symmetry crystalline field. The presence of water in this complex, moreover, was taken as an indication that hydrogen bonding was present in the structure. The structure determination of Ni($C_6H_6N_4$)₂(H_2O)₂(NO₃)₂ was undertaken to provide the structural information required for an analysis of the polarized electronic absorption spectrum and to elaborate the details of the hydrogen bonding network.

Experimental

Crystals of Ni($C_6H_6N_4$)₂(H_2O)₂(NO₃)₂ were grown by evaporation of an aqueous solution of Ni(NO₃)₂ and 2,2'-biimidazole. The data for the space group determination and the preliminary cell dimensions were obtained from zero and upper level precession photographs. The observed systematic extinctions led to the assignment of the crystal to the monoclinic space group $P2_1/n$.

Prior to the determination of precise unit-cell dimensions, a single crystal ($\sim 0.4 \times 0.3 \times 0.2$ mm) was mounted on a diffractometer and a rapid survey made of all reflections in the 2θ region greater than 120° with Cu K α ($\lambda = 1.54051$) radiation. Seventeen strong reflections were selected for 2θ measurement. The cell parameters were then refined by least-squares analysis to obtain optimum agreement between observed and calculated 2θ angles. Assuming two molecules of Ni(C₆H₆N₄)₂(H₂O)₂(NO₃)₂ per unit cell and using the refined cell parameters, the X-ray density was calculated to be 1.630 g.cm⁻³. The density obtained by flotation was 1.68 g.cm⁻³. A summary of the crystal data is given in Table 1.

Table 1. Crystal data for $Ni(C_6H_6N_4)_2$ (HOH)₂ (NO₃)₂

Systematic extinctions h0l h+l=2n+10k0 k = 2n+1

The errors in the cell parameters are the standard deviations obtained from a least-squares refinement of these parameters using seventeen experimental 2θ values. The 2θ measurements were taken at 23 ± 2 °C.

For the structure determination, the stationary-crystal stationary-counter method was employed. The crystal was oriented with the b axis coincident with the φ axis. The intensities of all 3151 unique reflections (2165 observed, 986 unobserved) within sin $\theta/\lambda = 0.724$ were measured using molybdenum radiation and a β filter of 0.025 mm thick niobium. Approximately 400 reflections equivalent to those in the above set were measured and it was found that equivalent pairs agreed within counter error. The data thus obtained were corrected for Lorentz and polarization factors. As the linear absorption coefficient for crystalline $Ni(C_6H_6N_4)_2(H_2O)_2(NO_3)_2$ is only 10.5 cm⁻¹, no absorption correction was applied. Additional details on the method of data collection are given in a previous paper (Reimann, Mighell, & Mauer, 1967).

Determination of structure

The chemical composition, density, unit-cell volume, and space group require that the nickel ion lie on a center of symmetry. This conclusion is confirmed by the fact that the observed reflections with an even (h+k+l)were greater, on the average, than those with odd (h+k+l).

To determine the structure, an electron density map was calculated using reflections for which the F_c based upon the nickel atom position satisfied the condition:

$$\frac{1}{2}|F_o| < F_c| < 3/2|F_o|$$
.

As nickel contributes to reflections only if (h+k+l)is even, two images of the structure related by a mirror normal to **b** appeared in the electron density map. An internally consistent image was identified in this map based upon the assumptions of octahedral coordination about the nickel atom and of the planar configuration of the biimidazole molecule. Another Fourier synthesis was then calculated with phases determined from the chosen image. The mirror image structure present in the initial electron density map was thus obliterated and the resulting map contained a chemically reasonable structure.

Refinement

Full-matrix isotropic least-squares refinement on all atoms except hydrogen was carried out on the tentative model. In this refinement scattering factors for neutral nickel, carbon, nitrogen, hydrogen and singly negative oxygen were used and these were obtained from International Tables for X-ray Crystallography (1962). The quantity minimized in this refinement was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme w = 1 for $|F_o| < 35$ and $w = 35/|F_o|$ for $|F_o| > 35$. Reflections for which the net number of counts observed did not exceed zero by at least twice the standard deviation were designated as unobserved, and assigned a value for the net number of counts equal to one standard deviation. These 986 unobserved reflections were given zero weight in the refinement unless the value of F_c exceeded that of F_o . Those reflections for which this occurred were given unit weight. As a result of this refinement the agreement factor, R, where $R = \sum (|F_o| - |F_c|) / \sum F_o$ based upon 2165 observed reflections refined to a value of 0.099.

The model was next refined by full-matrix anisotropic least-squares analysis and the R value decreased to 0.064. A difference $(F_o - F_c)$ synthesis was then calculated and this map contained well defined peaks outside the periphery of the biimidazole rings and near the coordinated oxygen atoms. Bond angle analysis indicated that these peaks are consistent with hydrogen atom positions. Bond length calculations showed that the average C-H, N-H and O-H distances were 0.96 Å, 0.84 Å and 0.75 Å respectively. Although these distances are shorter than the accepted internuclear separations, they are consistent with X-ray bond distances involving hydrogen atoms; e.g. Brown (1967), Marsh (1959). Including the hydrogen atoms in the final structure factor calculation reduced the Rvalue from 0.064 to 0.052. For this calculation each hydrogen atom was assigned an isotropic temperature factor of 4.5. The final atomic coordinates, anisotropic thermal parameter and structure factors are presented in Tables 2, 3 and 4 respectively.

	<i>x</i> / <i>a</i>	y/b	z/c
Ni	0.5	0.5	0.2
O(1)	0.31801 (23)	0.43983 (24)	0.55393 (23)
O(2)	0.31232 (36)	0.18766 (33)	0.72223(27)
O(3)	0.35130 (27)	0.36334 (28)	0.84930 (27)
O(4)	0.35373 (32)	0.15832 (32)	0.93547 (27)
N(1)	0.40924 (26)	0.56615 (28)	0.31128 (26)
N(2)	0.35612 (28)	0.50783 (35)	0.09800 (25)
N(3)	0.46857 (30)	0.21324 (31)	0.19424 (29)
N(4)	0.50687 (27)	0.31509 (27)	0.39273 (26)
N(5)	0.33891 (30)	0.23627 (33)	0.83471 (30)
C(1)	0.35548 (35)	0.67919 (38)	0.24190 (36)
C(2)	0.32214 (37)	0.64400 (44)	0.11050 (38)
C(3)	0.40814 (30)	0.46529 (34)	0.22124 (30)
C(4)	0.45982 (31)	0.33166 (32)	0.26413 (31)
C(5)	0.52222 (40)	0.11414 (39)	0.28181 (42)
C(6)	0.54461 (37)	0.17799 (36)	0.40416 (38)
H(1)	0.3374 (44)	0.7730 (50)	0.2826 (45)
H(2)	0.2883 (45)	0.6960 (47)	0.0378 (45)
H(3)	0.3413 (45)	0.4576 (47)	0.0334 (75)
H(4)	0.4433 (45)	0.2022 (48)	0.1134 (45)
H(5)	0.5343 (44)	0.0212 (48)	0.2632 (46)
H(6)	0.5836 (44)	0.1428 (49)	0.4899 (44)
H(7)	0.3278 (45)	0.4003 (52)	0.6127 (46)
H(8)	0.2862 (46)	0.5131 (51)	0.5719 (46)

Table 2. Atomic coordinates*

* The numbers in parentheses are standard deviations in the last significant figures.

Discussion

The only crystallographic constraint on the Ni(C₆H₆N₄)₂(H₂O)₂(NO₃)₂ molecule is that it must have a center of symmetry. The asymmetric unit, therefore, comprises half a nickel ion, one biimidazole molecule, one water molecule and one nitrate anion. The crystal structure consists of discrete, centrosymmetric complex cations, Ni(C₆H₆N₄)₂(H₂O)²⁺₂, joined by hydrogen bonding *via* their O-H and N-H groups to the nitrate anions. This cation with the unique coordination distances and angles is shown in Fig. 1. The packing arrangement and the distances between atoms connected by hydrogen bonds are shown in Fig. 2.

The basal plane

In order to describe the details of the structure of $Ni(C_6H_6N_4)_2(H_2O)_2(NO_3)_2$, we will utilize the rigorous plane defined by the coordinating nitrogen atoms [N(1)N(1')N(4)N(4')] as a reference plane. This plane, which passes through the nickel ion, hereafter will be referred to as the basal plane. The structure of $Ni(C_6H_6N_4)_2(H_2O)_2(NO_3)_2$ may now be considered in terms of the orientation of the various groups (water, nitrate, biimidazole) with respect to the basal plane (Table 5).

The coordinated water molecules

The water molecules lie above and below the basal plane. The nickel oxygen direction is virtually normal to the basal plane making an angle of 88.6° with it. The plane of the water molecule was found to make an



Fig. 1. The $Ni(C_6H_6N_4)_2(HOH)_2^{2+}$ cation. Unique bond distances and angles are indicated.

Table 3. Anisotropic therma	l parameters*†
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	10 ⁵ β ₁₁	10 ⁵ β ₂₂	10 ⁵ \beta_{33}	$10^{5}\beta_{12}$	$10^{5}\beta_{13}$	$10^{5}\beta_{23}$
Ni	705 (5)	628 (5)	590 (5)	92 (5)	42 (4)	-15(5)
O(1)	890 (23)	850 (26)	944 (26)	85 (20)	129 (20)	101 (21)
O(2)	2435 (51)	1516 (44)	880 (28)	246 (38)	-275(30)	-268(29)
O(3)	1254 (32)	947 (30)	1236 (33)	-154 (25)	262 (26)	-68(25)
O(4)	1963 (43)	1536 (40)	1030 (30)	-752(33)	-379(28)	394 (28)
N(1)	782 (25)	819 (30)	771 (27)	134 (22)	67 (20)	38 (23)
N(2)	935 (27)	1256 (37)	699 (24)	-13(30)	-61(20)	59 (29)
N(3)	1033 (32)	951 (33)	919 (3 1)	- 28 (26)	119 (25)	-288(26)
N(4)	859 (27)	739 (28)	787 (27)	38 (22)	87 (21)	-58(22)
N(5)	1066 (32)	1046 (36)	841 (31)	- 157 (27)	38 (25)	24 (27)
C(1)	903 (35)	1009 (40)	1001 (38)	175 (30)	88 (2 9)	135 (32)
C(2)	949 (38)	1363 (50)	966 (39)	74 (35)	-50(30)	307 (36)
C(3)	672 (27)	997 (37)	670 (28)	-65(24)	73 (22)	20 (25)
C(4)	740 (30)	764 (33)	763 (30)	-18(24)	110 (24)	-131(25)
C(5)	1174 (43)	868 (39)	1384 (49)	156 (33)	162 (36)	-227(36)
C(6)	978 (37)	815 (36)	1167 (41)	161 (30)	60 (31)	-59(31)

* The general anisotropic temperature factor has the form $\exp \left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$. † The numbers in parentheses are standard deviations in the last significant figures. Table 4. Observed and calculated structure factors

The columns are l, $10F_o$ and $10F_c$, respectively. Unobserved reflections are indicated with a *.

0+0+L 2 357 -3 4 364 3 5 52 - 5 165 1 10 188 1 12 100 14 42 1+0+L 1 711 6	-11 79 65 10.0.1 48 9 0 71 54 2 157 66 4 50 93 6 99 25 8 47 -2 120 -4 203 -5 103 98 -6 47	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	56 57 50 -22 1362 1677 373 511 127 -127 368 380 132 123 348 352 134 -127 239 - 127 239 - 16 300 16	-6 87 - -7 64 -8 48 -9 130 1 -10 3; -11 77 -12 37 - 9,-1,L 0 133 1 1 3 1 2 129 1	6 1 22 19 1 19 2 10 3 11 4 5 6 7 6 8 6 9 20 10	-2.L 249 234 105 87 105 -104 314 325 190 194 39 37 202 277 27+ 10 66 61 299 -16	0 12 7 4 5 6 7 8 9 0	23+ 18 29 -30 344 342 216 210 27+ -16 153 149 2923 177 176 30+ 16 88 81	-10 1 2 3 4 5 7 -1	37* -2 2,-2,L 123 113 32* -4 33 15 33* -18 106 102 36* 6 52 57 39* -2 32* -29	-8 -9 -10 -11 -2 -13 -14 4 0 2	288 21 28+ 2 78 31+ - 86 - 36+ - 39+ 2 3,L 163 11 206 22 30 -	87 2 14 3 73 4 84 6 21 7 34 8 10 -1 65 -2 -3 25 -4	110 11 37 3 144 15 73 -8 64 6 32+ 1 70 7 36+ -1 46 3 28+ 28+ 77 7 71 7 214 21	5 -R 9 -9 10 -10 14 -11 7 -12 5 4 2 6 0 3 1 5 4 2 9 3	108 82 89 34 55 2,-4,L 327 67 562 196	115 80 -14 88 54 322 42 566 1 -184	0 156 1 238 2 27. 3 196 4 28. 5 173 6 111 7 68 8 45 9 75 10 36. 11 28.	-150 224 -22 35 178 -111 75 43 78 3 24	C 555 1 384 -1 384 -2 555 -3 394 -4 52 0,-5, 1 331 2 502 3 211 4 55	44 - 6 - 3 48 - 37 35 -1 338 492 208 88
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	114 -12 -13 L -14 143 91 94 0 13 1 169 2 74 3 52 4 121 5 20 6	115 121 35 -0 10 41 4,-1,L 317 315 276 265 174 175 318 306 140 -140 164 105 71 70 128 128	3 103 - 4 4 142 1 5 29* 6 82 7 31* 8 69 9 36* - 10 38* -1 141 1 -2 139 1 -3 28* -4 127 1 -5 52 - -5 52 - -5 77 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	115 112 33* C 33* -22 854 858 144 -147 30 -38 454 462 309 -297 275 280 265 -5 52 -47 104 103	1121234367890112	35* -0 38* 39 2C1 -193 7C2 682 123 122 197 196 69 -71 109 106 41 39 97 97 64 -67 80 75 36 24	-2 -3 -5 -6 -7 -8 -1 0 12	64 69 31- 19 91 99 3310 34- 26 3310 34- 26 34- 26 34- 26 34- 26 34- 26 34- 26 34- 26	345678901123123	474 4 219 2. 72 93 93 114 1 314 76 36* 110 572 5 86	82 -5 23 -6 85 -7 95 -8 61 -9 72 -10 19 -11 -2 -12 76 15 1 98 52 D 84 1 52 D	32 -2 157 15 30+ -1 32+ -1 32+ -1 32+ -1 34+ -2 34+ -2 10,-2,L 24+ 1 123 11	0 4 5 6 7 8 9 10 10 10 10 10 10 10 10 10 10 10 10 10	304 245 275 135 107 45 121 37 46 38 151 185 136	305 -21 -280 -138 107 -138 -13	1 183 2 51 3 180 4 20 5 184 6 20 5 184 7 182 0 45 1 72 2 37+	176 -50 177 -22 171 15 165 90 63 -31 51 7	5 284 6 137 7 243 8 79 9 108 10 310 11 89 12 36 13 57 1,-5, C 348	289 127 243 -A0 98 • 25 R9 • -14 46 +L 340
2,0,L 2 101 1 4 657 6 5 276 2 8 28 - 10 353 3 12 101 14 58 -2 94 - -4 134 1 -6 172 1 -8 499 4	12,0, 06 0 120 61 2 112 51 4 346 25 6 98 45 -2 45 92 -4 37 55 -6 59 92 -8 36 30 76 13,0, 57	L 8 114 10 110 11 37 12 86 13 39 -1 55 -2 69 -3 3 -4 3 -5 L -5 -7	32 8 159 210 5 -62 161 98 35• -16 52 84 750 729 21• -11 150 187 24 -11 275 270 32 18 261 345	-7 29 -8 78 -9 32 -0 121 1 -11 36 -12 36 10,-1,L 0 29 1 197 1 2 56 3 60	1 -11 1 -12 -5 -13 29 -14 13 6 2 0 1 6 2 18 35 4 57 5	154 148 33• 5 61 60 38• 1 ,-2,L 264 251 276 -263 470 465 515 -512 695 686 226 224	-13	3A* 11 100 -98 290 282 100 -98 111 110 27* 3 312 305 51 46 142 141 32 30	3 -1 -2 -3 -5 -7 -8 1	B9 63 49 -47 55 54 72 71 34= 17 35= -11 73 65 36= -7 51 52 39= 3 4,-2,L 4	-6 -7 -8 -10 -11 -12 -13	156 -1 302 2 172 1 161 1 92 - 104 1 300 - 135 1 340 - 52	44 3 90 5 69 5 69 6 7 04 8 204 9 217 -1 217 -2 -49 -3 -5 -6	60 5 31• 1 117 12 35• 5 36• -2 51 4 110 11 133 -4 201 20 35 4 36• 8 47 -5	5 -5 1 -6 1 -7 6 -8 2 -10 5 -11 3 -12 2 -13 5 -13 5 -13 6 0 0	143 249 29 207 28- 136 31- 90 37- 3,-4,L	186 248 33 204 -19 130 5 79 -30	0 175 1 27- 2 180 3 77 4 148 5 51 6 51 7 44 8 56 9 30- 1 81 1	170 -22 180 74 147 -39 63 -46 102 -23 61	1 87 2 408 3 166 4 291 4 129 6 48 7 28 8 284 9 53 10 54 11 33 12 94 13 39 -1 217	- H6 406 - 160 297 133 287 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 133 297 134 297 134 297 134 297 134 297 134 297 134 297 297 297 297 297 297 297 297
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-1 1140 100	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	27 3 36 4 50 8 50 8 9 L 10 11 563 12 ~765 -1 746 -2 ~290 -3	23• -12 23• 9 2>• 21 1CH 110 19 -49 220 239 1C9 116 67 75 3•• 6 17 55 64 79 850 935 22• -6	-6 31- -9 50 -10 36 -11 40 11,-1,L 0 173 1 1 33 2 85 3 30- 4 83 5 32-	-5 -650 -712 -859 $-9-10-1270$ -1322 $-1481-1$ $373-1$ 0	371 370 33 26 181 183 86 70 114 108 300 -9 122 122 359 12 359 50 -2+L 95 -92	-11 -12 -13 0 1 2 3 4 5 6	34+ 23 36+ -1 98 97 82+L 188 182 86 -78 210 196 116 -108 159 154 46 -45 111 108	1 2 3 4 5 6 7 8 9 10 11 12	384 365 118 124 288 295 106 108 416 416 72 68 310 308 79 73 141 135 3030 81 75 333	-1 -2 -3 -5 -6 -7 -8 -10 -11 -12 -13	67 227 2 130 -1 381 3 64 - 132 1 27• 175 1 43 - 31• - 94 37•	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3 j+ 84 9 37+ 30+ 4 ju+ - 30+ 2 31 -3 1 93 20 31 -3 193 20 31+ -2 34 4 3 j+ -2 37+ -2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	399 21. 514 22. 240 240 240 27. 83 30. 142 34. 48	387 -11 494 4225 50 228 -3 82 18 138 -23 -23 -23 -23	0 28+ 1 64 2 64 3 47 4 20+ 5 114 6 47 7 74 8 25+ 3 47 1 187 2 20+	-4 77 71 47 -2 122 -58 90 4 64 159 -11	2:-5: 0 33 1 169 2 50 3 142 4 206 5 213 6 48 7 170 8 86 9 160 10 31	-32 168 465 -199 213 52 164 -88 158
6 150 1 H 27; 2 10 104 1 17 45 -2 354 2 -4 590 5 -6 287 2 -8 177 2 -10 218 2 -12 54 -14 38* 5,0,L	50 5 402 72 6 287 C6 7 211 45 8 29 97 10 29* 88 11 135 78 17 32* 20 13 36* 1,-1,	399 - 4 282 -5 215 -6 -8 -7 -5 -8 -3 -9 130 -10 11 -11 -37 -12 -36 -13 -14	252 310 e1 -57 213 246 128 -130 e4 94 46 52 59 63 50 48 59 63 50 48 59 63 50 48 59 63 50 48 59 63 50 40 37+ -22 46 40 57+ -22	6 62 7 36. 8 38. -1 34 - -2 118 1 -3 30. -5 31. -5 31. -6 87 -7 52 - -8 34. -9 36. -10 51	60 1 -6 2 38 3 11 5 12 6 95 7 15 8 10 8 11 37 12 66 13 12	26 -3 138 132 136 144 209 -294 393 389 43 -36 43 -36 43 -36 43 -36 57 27C 266 60 59 34* 1 55 55 55 55	7 9011- 	91 88 12C 127 34* -2 4C 48 38* -9 65 -74 104 101 224 222 145 141 73 -72 16C 162 76 75 47 -74	13	75 65 34(-3,L 782 75; 54 -64 633 631 167 16; 284 284 284 28 271 27; 26. 26 26. 26	0 1 2 3 4 5 6 7 8 9 0	81 352 3 150 -1 214 2 163 1 282 2 39 - 66 74 174 1	-10 1 65 44 0 43 1 19 2 56 3 78 4 5 5 60 6 64 -1 24 -2 -2 -2 -2	38+ - 21-3+L 32+ 5 54 5 31+ 5 31+ 5 31+ 5 31+ 5 31+ 5 31+ 7 31+ 7 31	3 5 1 1 2 1 3 8 4 9 5 3 7 8 8 9 9	271 232 345 204 - 107 134 236 - 98 47	247 215 201 201 201 -1 146 -1 258 105 97	1 194 2 29 3 30 7 97 8 1 3 24 3 24 1 80 10,-4,1 0 123	197 1 90 -24 97 41 27 -23 74 :20 -	11 88 12 38 13 14 -1 674 -2 124 -3 214 -4 109 -5 399 -6 20 -7 36 -8 43 -9 240 10 30 -	80 17 42 655 -108 216 112 405 27 43 240 -19
1 245 2 3 437 4 5 186 2 7 156 -1 9 166 1 13 143 1 -3 264 2 -5 100 1 -7 28. -9 209 2 -1 3 6	74 + AA 738 2 6c7 738 2 6c7 76 4 742 164 4 742 164 4 742 169 5 41 69 4 296 123 7 217 759 8 175 750 9 80 113 10 154 154 17 87 154 12 3 56	66 0 673 1 -141 2 763 3 -44 4 293 5 215 6 168 7 -81 4 151 9 -18 10 -81 11 -81 12	2*• -72 317 305 60 -60 51F 495 162 -154 240 238 67 66 122 133 29• -10 48 50 22• 20 25• 32 38• -7	12,-1,1 0 32* 1 77 2 32* 3 115 1 4 34* 5 57 6 37* 7 59 -1 112 1 -2 31* -3 32*	$\begin{array}{c} -2 \\ -3 \\ -3 \\ -4 \\ 79 \\ -5 \\ -6 \\ -6 \\ -6 \\ 11 \\ -7 \\ 31 \\ -8 \\ 64 \\ -9 \\ 10 \\ -7 \\ 10 \\ +3 \\ -11 \\ 12 \\ -12 \\ 23 \\ -14 \end{array}$	57 59 539 527 222 227 428 418 177 170 187 176 82 -74 201 197 32 -35 150 149 32* -C 66 58 39* -31	-10 -1: -12 0 1 2 3 4 5 6	122 130 35• 22 63 50 9,-2+L 29• -40 183 178 53 50 28• -4 35 -44 136• -13 36• -13	9 10 11 12 13 -1 -5 -5 -5 -7 -8	28* - 229 222 31* 14 50 5(41 19 313 322 380 ~37 518 53 164 18 200 19 73 -7 92 8		47 38• - 52 110 -1 169 1 143 -1 273 2 49 222 2 75 - 112 1 31+ 33•	30 -4 16 -5 54 -6 07 -7 67 -8 40 -9 67 41 1 23 67 0 17 1 33 2 20 3	34+ 22 34+ 22 34+ 26 34+ 20 34+ 20	2 11 1 12 1 2 -1 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	34+ 65 99 365 517 75 250 27+ 131 60 76 32+	-14 -14 -14 -14 -14 -14 -12 -14 -12 -14 -14 -14 -14 -14 -14 -14 -14	11+ 12+ 12+ 12+ 12+ 12+ 12+ 12+	41 -1 111 -1 49 -1 127 -7 44 -24 50 -4; 50 -16 124 10 96	11 55 12 35 13 72 5,-5, 1 469 1 160 2 279 3 90 4 202 5 178 6 230 7 200	49 -2 57 L 476 280 -76 207 128 -202
-13 68 2,522 6 4 66 5 154 10 41 12 88 -2 52 -4 151 12 88 -2 52 -4 151 -2 52 -4 151 -2 52 -4 151 -2 52 -4 151 -2 52 -4 151 -2 52 -4 151 -2 52 -4 151 -4 151 	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	289 286 453 466 313 315 279 -/66 153 154 153 154 153 154 153 154 153 154 17 28+ -2 155 152 31+ 17 12+ 32 20 8 67 71	-4 44 - -5 33 -6 33 -7 57 -8 36 -9 36 13,-1,L 0 90 1 45 2 60 3 37 9 7	46 33 4 -7 0 0 17 1 27 2 3 64 6 36 7 84 7 84 9	93 94 214 -4 32 30 95 103 262 260 244 15 296 296 41 49 99 94 84 -98	7 H 4 10 - 1 - 2 - 3 - 5 - 5 - 7 - 8 - 4	85 98 34• -27 68 78 38• -0 28• 36 54 6C 350 348 93 100 10^ 106 41 -46 76 82 30• -11 92 95	-4 -10 -11 -12 -13 -14 0 1 2 3	131 12: 165 15: 38 -21 93 8' 360 65 5' 9,-3,L 51 5: 380 37' 275 -29 527 53	-12 -13 -13 -13 -13 -13 -12 -13 -12 -13 -12 -13 -12 -13 -13 -13 -13 -13 -13 -13 -13 -13 -13	35. 61 7,-3,1 139 1 191 -1 356 7 105 123 1 29 192 1 30.	6 4 71 5 -1 -2 -3 30 -4 81 -5 81 -5 92 -7 26 92 -7 26 95 -8 0	38+ 44 39+ 7 34+ -4 70 71 35+ -18 8, 97 36+ 27 37+ 10 37+ -6 +, -3,L 38+ 15	-12 -13	67 37+ 258 264 97 334 147 162 160 -: 88	65	2:+ 56 25+ 48 11,-4,0 20+ 25 86 51 33+ 51	-26 72 -1 1 43 1 -7 - 71 - 71 - 71 - 95 - 24 - 24 -	8 120 9 37 10 84 11 35 12 240 1 240 2 210 3 86 4 322 5 108 6 192 7 100 8 165	12; 35 79
-6 51 -9 161 -10 114 -12 75 7.0.0 1 227 3 354 5 211 7 207 9 122	39 -13 35 159 -14 38 65 2,-14 36 65 2,-14 169 7 500 1 169 219 7 144 345 3 37 209 2 144 133 37 209 4 143 37 144 343 7 4 143 37	15 16 16 163 163 163 163 10	7,-1,L 279 269 117 110 342 327 45 -65 184 177 27* 12 1CU 97 41 31 5C7 206	4 ~ 0 5 388 -1 49 -2 348 -3 348 -4 35 -5 358 -6 68 -7 388 -8 53 141.L	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	108 109 33. 9 36 43 302 290 728 727 117 118 492 485 217 -211 341 336 86 -83 257 256 28- 5	-10 -11 -12	34+ -25 52 56 38+ 2 10,-2.L 214 215 29+ -6 36 13 149 152 31+ -42 64 69	45 67 89 10 11 12 1-2 -3	54 -4 500 49 28 2 217 21 95 -9 107 9 85 7 95 9 34• 2 50 5 145 13 208 -20 55 59	3 9 3 9 5 10 11 3 -2 3 -5 6 -6 -8 -9	43 33+ 72 37+ 134 -1 270 2 36 238 2 41 - 75 82 90 30+	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	37+ -4 3n+ -9 52 44 37+ -8 37+ 38 37+ 38 80 80 -4+L 240 240 240 240 241 352	4 10 11 -1 -3 -4 -5 -7 -9	29. 120 33. 57 38. 289 114 53 167 167 158 109 32	-26 6 137 1 -15 -1 54 -2 '' -3 255 -4 115 -5 166 -6 -57 -7 157 -8 114 -9 29	30+ 30+ 124 80 73 21+ 48 30+ 49 30+ 49	-4 - 39 -1 131 -1 -83 -1 66 -1 -16 49 -23 69 21 48 -10	4 42 0 73 1 33* 2 58 3 38* 4,-5,1 0 86 1 566 2 54 3 95	-39 65 -21 55 -7 1 78 505 -48 110 -1
11 43 -1 47 -3 269 -5 1-6 -7 7, -9 195 -11 51 -13 44 8.0.L 0 154 2 256		228 10 283 11 9 -7 -1 95 -1 16 -1 1046 - 120 -1 51 - 213 - 463 - -119 -11) 52 57) 54 -10 58 -53 251 241 74 -70 77 -10 77 -10 151 154 728 10 151 154 154 -71 151 139 64 -71 151 139	0 36+ 1 37+ 2 37+ 3 5.) -1 72 -2 36+ -3 36+ -4 37+ -5 50 -6 3++ 15,-1,L	0 -10 12 -11 10 -12 57 -13 52 -14 4 4 0 -8 1 7 3 4	72 -64 31* 6 146 14* 36* -6 61 45 5,-2,L 205 -191 569 563 85 -87 338 333 24* -1	-1 -2 -3 -4 -5 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	51 58 34. 31 3613 49 46 79 78 44 54 161 171 91 -97 130 137 318 61 60 3412 37 33	-4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14	61 - 6 79 - 6 247 24 327 32 27* 47 5 185 19 33* - 82 7 39* -3 3*-3*L	30 2 -11 5 -12 33 6 5 1 0 3 1 0 2 1 3 7	111 : 36 - 77 . 39* 5*-3*L 27* 162 : 93 . 28* 314	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	126 126 128 314 157 157 117 317 117 317 113 109 300 -23 113 109 300 -23 113 20 143 109 300 -23 143 109 144 22 370 -4		113 70 89 35 43 176 176 176 176 172 105	127 -80 95 20 1 50 20 1 50 2 3 4 50 2 3 4 50 2 1 50 2 50 2 50 2 50 2 50 2 50 50 2 50 50 50 50 50 50 50 50 50 50	12,-4,L 87 33+ 34+ 35+ 34+ 35+ 34+ 35+ 35+ 35+ 35+ 35+ 35+ 35+ 35	83 -6 24 11 1 51 1 57 - -39 - -73 - -73 - -73 -	5 198 6 43 7 116 8 299 9 155 0 33* 1 88 2 38* 1 199 2 77 3 167 4 27* 5 221	205 -48 122 -20 163 -20 25 184 72 167 -15
 144 101 56 10 56 2112 60 2112 101 121 101 121 101 121 101 121 101 <l< td=""><td>1-2 -7 16M 1-7 -8 45 55 -9 133 65 -10 148 1-1 148 1-1 148 1-2 -12 33 1-2 -12 33 1-2 -12 33 1-2 -12 33 1-2 -12 33 1-2 -12 -14 -14 1-2 -14 -14 -1</td><td>-235 -235 -235 -199 -22 -235 -7999 -24</td><td>R1.L 118 118 118 118 118 118 1194 118 119 118 118 119 118</td><td>-1 41 -2 45 0,-2,L 1 33 1 435 2 828 3 137 4 400 5 215 - 6 247 7 91</td><td>2 5 54 6 7 8 9 -42 10 437 11 873 12 139 -1 405 -2 205 -3 241 -4 90 -5</td><td>169 18 169 18 165 17 29 30 54 55 32 -2 55 55 32 -2 229 22 229 22 229 22 229 33 339 34 249 -25 354 354 354</td><td>5 -11 5 0 1 5 3 5 5 5 5 5 5 5 5 5 5 5 5 5 7 5 5 5 5</td><td>38 6 11,2,L 3121 167 158 99 96 75 -70 35 37 65 64 68 70 38 4</td><td>0 1 2 3 4 5 6 7 8 9 10 11</td><td>151 14 176 16 339 32 250 -24 207 21 244 -2 360 36 34 -3 142 14 294 -1 136 17 324 -</td><td>678902101 42902101 </td><td>46 97 32+ 48 36+ 29 27+ 263 39 134 46 178 30+</td><td>-44 94 0 5 -17 1 2 59 2 3 -32 4 4 -18 5 1 240 7 2 134 8 -180 10 1 180 10 1</td><td>28 -508 UN 223 UN 223 UN 223 UN 233 UN 23</td><td>- 5 6 7 # 9 0 1 1 - 2 3 4 5 6</td><td>216 1 204 1 324 7 324 7 374 87 - 401 1 203 -1 203 -1 254 2 151 -1</td><td>52 -5 15 -6 -9 -7 104 -8 19 76 13 76 13 74 0 144 30 44 30 44 30 44 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1</td><td>35+ 30+ 37+ 38+ 13+-4+L 36+ 59 26+ 77 38+ 10</td><td>36 - 29 - -17 - -1 -1 -1 -1 -1 -1 -1 -1 -1 -</td><td>537 27+ 8 27+ 9 212 0 46 1 86 2 36+ 3 55 5,-5,1 C 204 1 11</td><td>-14 -221 -35 -83 -21 -48</td></l<>	1-2 -7 16M 1-7 -8 45 55 -9 133 65 -10 148 1-1 148 1-1 148 1-2 -12 33 1-2 -12 33 1-2 -12 33 1-2 -12 33 1-2 -12 33 1-2 -12 -14 -14 1-2 -14 -14 -1	-235 -235 -235 -199 -22 -235 -7999 -24	R1.L 118 118 118 118 118 118 1194 118 119 118 118 119 118	-1 41 -2 45 0,-2,L 1 33 1 435 2 828 3 137 4 400 5 215 - 6 247 7 91	2 5 54 6 7 8 9 -42 10 437 11 873 12 139 -1 405 -2 205 -3 241 -4 90 -5	169 18 169 18 165 17 29 30 54 55 32 -2 55 55 32 -2 229 22 229 22 229 22 229 33 339 34 249 -25 354 354 354	5 -11 5 0 1 5 3 5 5 5 5 5 5 5 5 5 5 5 5 5 7 5 5 5 5	38 6 11,2,L 3121 167 158 99 96 75 -70 35 37 65 64 68 70 38 4	0 1 2 3 4 5 6 7 8 9 10 11	151 14 176 16 339 32 250 -24 207 21 244 -2 360 36 34 -3 142 14 294 -1 136 17 324 -	678902101 42902101 	46 97 32+ 48 36+ 29 27+ 263 39 134 46 178 30+	-44 94 0 5 -17 1 2 59 2 3 -32 4 4 -18 5 1 240 7 2 134 8 -180 10 1 180 10 1	28 -508 UN 223 UN 223 UN 223 UN 233 UN 23	- 5 6 7 # 9 0 1 1 - 2 3 4 5 6	216 1 204 1 324 7 324 7 374 87 - 401 1 203 -1 203 -1 254 2 151 -1	52 -5 15 -6 -9 -7 104 -8 19 76 13 76 13 74 0 144 30 44 30 44 30 44 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1	35+ 30+ 37+ 38+ 13+-4+L 36+ 59 26+ 77 38+ 10	36 - 29 - -17 - -1 -1 -1 -1 -1 -1 -1 -1 -1 -	537 27+ 8 27+ 9 212 0 46 1 86 2 36+ 3 55 5,-5,1 C 204 1 11	-14 -221 -35 -83 -21 -48
1 248 3 82 5 10+ 7 144 9 46 -1 173 -3 20+ -7 132 -9 90	2 2 257 83 3 300 23 4 528 148 5 63 148 5 63 143 204 1 152 7 26 33 8 135 208 9 29 140 10 136 98 12 31	-291 -291 -531 -54 -267 132 -132 -134 -267 -134 -267 -134 -267 -132 -367 -132 -367 -132 -367 -132 -132 -132 -134	. 197 189 R 68 66 9 54 89 0 25* 13 1 57 65 1 121 174 2 104 94 3 222 225 4 27* 13 5 38~ 388	a 149 9 28+ 10 163 11 31+ 12 65 13 35+ 14 64	145 -6 -15 -7 160 -8 23 -9 66 -10 9 -11 57 -12 -13	193 17 107 10 131 -13 114 13 30+ 1 65 6 34+ 52 5	9 -1 7 -2 6 -3 5 -4 2 -5 5 -6 7 -7 9 -8	97 103 3C+ 14 109 105 31+ 13 75 75 35 -42 33+ 40 34+ -15 37+ 42	-12 -3 -4 -5 -7	80 1 38 1 47 3 41 3 105 9 320 31 195 19 436 45 75 -1	04 4 -10 5 -11 6 -12 6 8 3 0 0 6 1	44 33. 64 38. 9,-3,L 142 28.	44 12 -5 13 57 -1 4 -20 -2 3 -3 5 -4 136 -6 7 -7 2		-7 -8 -9 -10 -11 -12 -13	47 58 30* 115 1 3* 78 3**	41 -2 54 -3 21 -4 07 -5 7 -6 78 -7 13	36. 42 30. 70 41 34.	-24 20 3 70 30 40	2 108 3 43 4 125 5 80 6 156 7 42 8 123 9 320 0 86	109 43 131 91 184 -59 146 -13 99

Table 4 (cont.)

5	-35 -35 -391 -55 143 -71 143 -71 -144 -71 -146 -71 -71 -71 -71 -71 -71 -71 -71	-4 33* -5 32* -6 76 -7 58 -9 38* 12,-5 0 48 1 118 2 35* 4 38 5 38* -1 55 -2 39	35 13 79 -54 61 -0 +L -42 114 -14 70 8 100 8 100 8 100 -35	8 1 9 10 11 -1 -2 1 -3 -4 -5 1 -5 1 -7 -8 1 -7 -8 1 -7 -7 -8 1 -7 -7 -1 -2 -3 -4 -5 -1 -2 -2 -3 -4 -5 -4 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	20 136 32* -30 48 50 38 -21 49 41 28 177 28 24 28 24 28 24 28 24 28 74 28 24 28 74 28 24 28 74 28 24 28 74 28 24 28 74 29 132 35* -24 60 48	-4 -5 -6 1 -7 -8 -9 11 0 1 2 3 4 5 6 -1	31. 5 32. 2 11.7 115 47 -50 56 60 3829 16,L 33. 2 79 73 34. 4 86 82 35. 2 79 73 34. 5 80 82 35. 20 55 50 50 50 5	2 3 5 1 6 7 1 6 9 9 10 11 -1 2 -2 2 -3 -4 -5 1 -7 1 -7 1 -1 -7 1 -1 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	80 43 80 220 37 -41 56 179 32* -28 32* -28 36* 11 70 73 53 258 06 208 759 -70 19 114 66 -70 19 114 66 -20 66 -20 66 -20	-6 -7 -8 -9 12 3 4 5 -12 -3 -4	53 85 37* 39* 11,-7,L 35* 34* 71 36* 37* 38* 34* 539 05-	-66 - 81 - 20 25 -17 -6 73 -14 32 -7 10 68 -32 84	-10 53 -11 37 5,-6 0 84 1 99 2 26 3 100 4 30 5 186 6 43 7 80 6 43 7 80 6 3 35 9 33 10 45 -1 9	45 -4 -97 96 -0 108 -29 218 -218 89 -218 89 -12 -28 -39 97 -97	0,- 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 9 10 1, 0 1	-9.L 89 89 69 -78 18 122 51 58 36 139 3116 49 150 3320 71 77 45 22 -9.L 27.* 11 48 54	012345671234567	7,-9,L 95 35 78 3,j 77 34- 37- 38- 75 - 152 1 52 1 67 42 99 35- 67 42 99 35- 57- 67 42 35- 57- 67 57- 57- 57- 57- 57- 57- 57- 57	90	4 57 5 56 6 31* 7 70 8 34* 9 9 4,-10 0 194 1 70 2 102 2 102 2 102 2 102 3 63 4 91 5 32* 6 92 7 10* 8 34* 9 7 10* 10* 10* 10* 10* 10* 10* 10*	-63 57 -19 58 13 65 +L 191 57 -65 97 -05 97 -19	-7 -8 012345678-1223	35+ 60 2,-11,1 30+ 74- 38 23- 24- 35+ 65 39+ 14+ 44 1C0	23 56 71 35 82 11 63 -11 63 -11 83 2141 39 103	-3 -4 -5 -6 -7 2 0 1 2 3 4 5 6 -1 -2	51 39 86 35• - 38• -12,L 87 33• 97 35• 79 37• 32• 99	42713 8 81711 4.
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angle of 29° with the basal plane. This angle, assuming tetrahedral coordination about the water molecule, would be 35.26° . Thus, with respect to the oxygen atom, the nickel atom and the two hydrogen atoms occupy, very nearly, three apices of a tetrahedron.

The hydrogen atoms of the coordinated water molecules are involved in hydrogen bonding with two ni-



Fig. 2. Projection of the contents of the unit cell for $Ni(C_6H_6N_4)_2(HOH)_2(NO_3)_2$ down the *a* axis. The hydrogen bonding network in relation to the overall structure is shown by dotted lines.



Fig. 3. Orientation of the nitrate groups with respect to a single cation. Hydrogen bonding between the cooordinated water molecules and the nitrate groups is indicated by dotted lines.

Table 5. Angles defining the orientation of the least squares planes of the indicated groups with respect to the basal plane.*

Group	Angle
Nitrate (NO ₃)	22·4°
Nitrate (NO ₃ ⁻)"	14.9
Coordinated water	28.6
Biimidazole†	
Imidazole ring 1 [C(1), C(2), C(3), N(1), N(2)]	3.6
Imidazole ring 2 [C(4), C(5), C(6), N(3), N(4)]	3.6

* Plane defined by nitrogen atoms coordinated to the nickel ion.

 \dagger Ring 1 and ring 2 in biimidazole make an angle of $1\cdot18^{\,\circ}$ with each other.

trate groups. One hydrogen atom, H(8) is bonded to an oxygen atom, O(4), in one nitrate group while the other hydrogen atom, H(7) is involved in a bifurcated hydrogen bond with O(2) and O(3) in a second nitrate group. This situation is depicted in detail in Figs. 3 and 4. These Figures include the hydrogen atom positions which were obtained from the above mentioned difference synthesis.

The biimidazole molecule

The biimidazole molecule consists of two imidazole rings: ring 1 [N(1), N(2), C(1), C(2), C(3)] and ring 2 [N(3), N(4), C(4), C(5), C(6)] bonded through C(3)–C(4). The atoms in each ring were fitted to a plane by leastsquares analysis. Both rings were found to be planar (Table 6) to well within one standard deviation of the atoms normal to the calculated planes. Ring 1 and ring 2 make angles of 3.57° and 3.58° , respectively, with the basal plane. These two rings are nearly coplanar making an angle of 1.18° with each other. The hydrogen atoms were found to lie in the imidazole planes to within two standard deviations of the hydrogen atom positions (Table 6).

Table 6. Distances from the ring atoms to the leastsquares planes of the imidazole rings in biimidazole* These planes were calculated through carbon and nitrogen atom positions, but not hydrogen positions.

Imida	zole ring 1	Imidaz	ole ring 2
	Distance (Å)		Distance (Å)
N(1)	0.0013	C(4)	0.0058
N(2)	-0.0004	C(5)	-0.0017
C(1)	-0.0016	C(6)	0.0021
C(2)	0.0013	N(3)	-0.0067
C(3)	-0.0006	N(4)	-0.0026
H(1)	-0.049	H(4)	-0.017
H(2)	0.040	H(5)	-0.055
H(3)	-0.075	H(6)	0.017

* The equation of the plane in direct space is given by PX+QY+RZ=S. For ring 1, P=9.7173, Q=2.7031, R=3.1677, and S=4.5224. For ring 2, P=9.7803, Q=2.5146, R=3.1569, and S=4.5032.

The crystallographically independent imidazole rings which comprise the biimidazole molecules were found to be nearly superimposable. Bond distances (average $\sigma = 0.0045$ Å) and angles are given in Fig.5. The position of the nickel atom is included in this Figure to emphasize the fact that the exterior angles, N(3)-C(4)-C(3)(130.4°), C(4)-C(3)-N(2)(129.8°), N(4)-C(4)-C(3)(118.6°), and C(4)-C(3)-N(1)(118.7°) are undoubtedly modified by coordination. The importance of resonance in the bonding description of the biimidazole molecule can be inferred from the near coplanarity of the two imidazole rings, from the short C-C single bond which connects these rings and from the relatively narrow range of observed bond distances. The shortest observed distance in each ring is, however, between atoms involved in the classical (C-N) double bond.

The nitrate anion and hydrogen bonding

Although the bond angles in the nitrate group are essentially equal, the N–O bond distances vary significantly, from 1.218 to 1.249 Å. Least-squares plane analysis showed the nitrate group to be planar to well within experimental error.

The orientation of the nitrate groups with respect to a single cation is shown in Fig. 3 and Table 5. In Fig. 3 the nitrate groups above the basal plane are related through the center of symmetry to those below. This Figure shows that four nitrate groups are involved in hydrogen bonding with the two coordinated water molecules within a single cation and that the planes of these nitrate groups are roughly parallel to the basal plane. The two nitrate groups labeled by N(5) and O(4") make angles of $22\cdot4^{\circ}$ and $14\cdot9^{\circ}$, respectively, with the basal plane.

In addition to being hydrogen bonded to water, each nitrate group is also hydrogen bonded to the two N-H groups in a single coordinated biimidazole molecule (Figs. 2,4). Each nitrate anion, then, is associated with three different cations via three distinct

hydrogen bond. Altogether five hydrogen bonds are formed by each nitrate anion.

This involvement in a unique hydrogen bonding situation by each of the oxygen atoms of the nitrate group, moreover, is reflected in the marked variation in the N–O distances in the nitrate group. The oxygen atom involved in the longest of the N–O (1·249 Å) distances participates in two single hydrogen bonds while the oxygen atom involved in the shortest N–O (1·218 Å) distance participates in only half of a bifurcated hydrogen bond.

We would like to acknowledge that most of the computer calculations on this structure were performed with the X-ray 63 system of programs developed at the University of Maryland Computer Science



Fig.4. The nitrate anion and hydrogen bonding. The numbers in parentheses give the distance in ångströms which a given atom lies above or below the plane of the nitrate group.



Fig. 5. The biimidazole molecule. Unique bond distances and angles are indicated. The average standard deviations in bond lengths are as follows: Ni-O, ±0.0025 Å; Ni-N, ±0.0025 Å; N-C, ±0.004 Å; and C-C, ±0.005 Å. The average standard deviation in the bond angles is 0.35°.

Center (1964) and the University of Washington. Programs used in calculating bond distances and angles and in drawing the Figures were written at the National Bureau of Standards.

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