Wesentlich für die Anordnung der Moleküle ist die Lage der drei Kristallwassermoleküle, die über Wasserstoffbrücken die einzelnen Eisen(III)-benzhydroxamat-moleküle untereinander verbinden. Der Abstand zweier über Wasserstoffbrücken verbundenen Sauerstoffatome ist nach Pimentel & McClellan (1960) in Kristallen etwa 2,5 bis 2,9 Å. Im Kristallgitter des Eisen-(III)-benzhydroxamat-Trihydrates liegen eine Reihe von Abständen dieser Grösse zwischen den Sauerstoff- und Stickstoffatomen der Eisen(III)-benzhydroxamat-moleküle und den Kristallwassermolekülen vor. Diese Abstände sind in Fig.2 durch gestrichelte Linien angedeutet. Das Wassermolekül W(1) verbindet das Sauerstoffatom O(11) mit dem Atom N(11) des Benzhydroxamatmoleküls der Nachbarkette und stellt so den Zusammenhalt zwischen den Ketten her. Das Wassermolekül W(2) wurde bei der Bestimmung der Struktur wegen seiner nicht genau festlegbaren Position in zwei um 0,7 Å voneinander entfernte Schwerpunkte gelegt. Es verbindet den zweiten Liganden des in y-Richtung benachbarten Benzhydroxamatmoleküls über das Atom O(12) mit dem Wassermolekül W(3). Das Atom N(12) des Moleküls der Nachbarkette wird durch W(2) ebenfalls mit W(3) verknüpft (vgl. Fig.2). Es ist bemerkenswert, dass die Abstände beider Positionen des Kristallwassers W(2) von W(3) mit 2,73 bzw. 2,74 Å praktisch gleich sind, während die Abstände W(12)–N(12) mit 2,65 und W(12)–O(12) mit 2,96 Å sowie W(22)–N(12) mit 2,80 und W(22)–O(12) mit 2,63 Å deutlich voneinander abweichen. Mit dieser Beobachtung könnte die statistische Anordnung des Kristallwassers W(2) in zwei Positionen erklärbar sein: die Lage W(12) begünstigt die Ausbildung von Wasserstoffbrücken zwischen W(2) und N(12), die Lage W(22) die zwischen W(2) und O(12). Beide Lageschwerpunkte erlauben in gleicher Weise die Ausbildung von Wasserstoffbrücken zum Kristallwasser W(3), das zentral zwischen zwei Molekülen einer Kette liegt. Das Kristallwassermolekül W(3) ist etwa tetraedrisch von Sauerstoffatomen im Abstand 2,7 bis 3,0 Å umgeben und verbindet das Sauerstoffatom O(23) mit dem Sauerstoffatom O(12) des benachbarten Benzhydroxamatmoleküls.

Neben diesen über Kristallwassermoleküle ausgebildeten Wasserstoffbrücken tritt innerhalb der Ketten der Benzhydroxamatmoleküle eine Wasserstoffbrücke zwischen den Atomen N(13) und O(21) auf. Der Abstand zwischen diesen beiden Atomen ist 2,74 Å.

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The Crystal and Molecular Structure of Hexakis(imidazole)nickel(II) Nitrate, $(C_3H_4N_2)_6Ni(NO_3)_2$

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The crystal and molecular structure of hexakis(imidazole)nickel(II) nitrate, $(C_3H_4N_2)_6Ni(NO_3)_2$, was determined by single-crystal X-ray diffraction techniques. This compound crystallizes in the trigonal system, space group $R\bar{3}$. The lattice parameters (hexagonal axes) are $a = 12\cdot353 \pm 0\cdot001$, $c = 14\cdot803 \pm 0\cdot002$ Å, $Z = 3$, $\varrho_o = 1\cdot51$ g.cm⁻³, $\varrho_c = 1\cdot506$ g.cm⁻³. Three-dimensional data were used (905 reflections) and the structure was solved by an analysis of the Patterson map. The complex cation, $(C_3H_4N_2)_6Ni^{2+}$, has 3 point symmetry with the nickel atom at the center of a slightly compressed octahedron of nitrogen atoms. The imidazole rings are planar to within experimental error. The final refinement by a three-dimensional least-squares analysis resulted in an R value $0\cdot071$.

Introduction

Crystals of metal ion coordination complexes frequently contain molecules or ions of high symmetry. The visible and vibrational spectra of these materials reflect this high symmetry and assignments can be made with confidence. From these assignments information on the mutual influence of ligand and metal ion can be

obtained. Selected single crystalline compounds, therefore, can serve as prototypes in the investigation of the interactions between metal ions and ligand molecules.

As part of a program in the structural and spectroscopic investigation of transition-metal complexes, crystals of hexakis(imidazole)nickel(II) nitrate, $(C_3H_4N_2)_6Ni(NO_3)_2$, (hereafter called $Im_6Ni(NO_3)_2$) were grown and preliminary measurements were carried out on them. The visible spectrum indicates that the ligand field about the nickel(II) ion is octahedral. The space group determination shows that these crystals belong in either the $R3$ or $R\bar{3}$ trigonal space group. The structure determination of $Im_6Ni(NO_3)_2$ was undertaken to furnish the structural information required for an analysis of the visible and vibrational spectra.

Experimental

Crystals of $Im_6Ni(NO_3)_2$ were grown by evaporation of an aqueous solution of $Ni(NO_3)_2$ and imidazole. Crystal symmetry and approximate cell parameters were obtained from zero and upper level precession photographs. The crystal belongs to the trigonal system and reflections with $-h+k+l \neq 3n$ (hexagonal indexing) are systematically absent. Of the five possible space groups consistent with these extinctions, three ($R32$, $R\bar{3}m$, and $R3m$) were ruled out, as no symmetry lines were found on the precession photographs taken with the [001] as the precession axis. Of the two remaining space groups $R3$ and $R\bar{3}$, the latter was assigned on the basis of the complete structure determination.

To determine precise unit-cell parameters, the 2θ angles of 48 lines of a powder pattern were measured with a diffractometer using powdered tungsten as a calibrating substance. The approximate cell parameters obtained from the precession photographs were then refined by least-squares analysis to obtain the best agreement between the 48 calculated and observed 2θ angles. A summary of the crystal data is given in Table 1.

Table 1. *Crystal data for* $(C_3H_4N_2)_6Ni(NO_3)_2$
based upon hexagonal indexing

$a = b = 12\cdot353 \pm 0\cdot001$ Å*	Space group $= R\bar{3}$ (No.148)
$c = 14\cdot803 \pm 0\cdot002$ Å	$Z = 3$
$\gamma = 120°$	$\varrho_o = 1\cdot51$ g.cm^{-3}
	$\varrho_c = 1\cdot506$ g.cm^{-3}

Systematic extinctions
$-h+k+l \neq 3n$

* Standard deviations based on least-squares refinement of powder data.

Intensity data were obtained with Cu $K\alpha$ radiation from multiple-film integrated Weissenberg photographs. The crystal was rotated about one of the rhombohedral axes rather than about the threefold axis. With this rotation axis, equivalent reflections, in general, appear on different levels with different Lorentz factors. Thus the scale factors between levels were determined experimentally and the intensities of a large number of weak reflections could be measured accurately. Of the nine levels measured, the first eight were recorded by using the equi-inclination method and the ninth by using an arbitrary μ-angle within the recording range of the camera.

All the reflections recorded on the films were measured and averaged to obtain a set of 905 unique reflections of which 63 were 'observed as zero'. In general three reflections were averaged to obtain the intensity of each unique reflection. About two thirds of the data were measured on a densitometer. Weak reflections were estimated by eye against a calibrated intensity scale. The data were corrected for Lorentz and polarization factors. No absorption correction was applied, however, as the linear absorption coefficient of this compound is small (~ 16 cm^{-1} for Cu $K\alpha$), and the crystal used was cube-like with a side of about $0\cdot3$ mm. A sphere having the same linear absorption coefficient and a diameter equal to the average of the side of the cube and the diagonal would have a $\mu R = 0\cdot3$. For this μR, the absorption coefficient would vary only 4% over the entire range of θ.

Determination and refinement of the structure

As indicated in Table 1, there are three molecules of $Im_6Ni(NO_3)_2$ per hexagonal unit cell. If the centrosymmetric space group $R\bar{3}$ is assumed, the positions of the nickel atoms must have symmetry $\bar{3}$ and those of the nitrogen atoms in the nitrate groups symmetry 3. Therefore the structure is completely specified by the coordinates of the atoms in one imidazole ring, by the z coordinate of the nitrogen atom in one nitrate group, and by the coordinates of one of the oxygen atoms.

In order to determine the structure, a three-dimensional Patterson map was calculated using the complete set of observed data. As the nickel atom is the only heavy atom in the structure, three nickel-light atom vector sets gave the largest peaks in the map. Peaks near the origin were identified as imidazole ring atoms by the spatial relationships between them. The atom closest to the origin was labelled as a nitrogen atom. The second nitrogen atom was tentatively assigned on the basis of peak size. An electron-density Fourier synthesis with phases determined by the previously identified atoms was then calculated. The nitrate group was readily located in this synthesis.

The trial model of the structure was refined by full-matrix least-squares analysis (Busing, Martin & Levy, 1962). The quantity minimized was $\Sigma w(F_o - F_c)^2$ with the weighting scheme $w = 1$ for $F_o < 50$ and $w = 50/F_o$ for $F_o > 50$. The scattering factors used in the calculations are those given in *International Tables for X-ray Crystallography* (1962) for neutral nickel, nitrogen, carbon, and hydrogen atoms and for the singly negative oxygen atom. After three cycles of isotropic refinement, the residual factor ($R = \Sigma ||F_o| - |F_c||/$

$\Sigma|F_o|$) based on 842 observed non-zero reflections was 0·14. Two cycles of anisotropic refinement on all atoms except hydrogen were then carried out and the R value reduced to 0·08.

Further refinement was now attempted including the hydrogen atoms in the imidazole rings. The coordinates for these atoms were calculated by assuming that (i) the hydrogen atoms lie in the plane of the imidazole ring, (ii) each hydrogen atom is equidistant from the two atoms adjacent to the atom to which the hydrogen is bonded, and (iii) the C–H and N–H distances are 1 Å and 0·9 Å respectively. These positions are consistent with peaks observed in the difference-Fourier synthesis calculated after the anisotropic refinement. Attempts to refine the calculated positions of the hydrogen atoms gave mixed results. The average of the three C–H distances was 0·92 Å, but the position of the fourth hydrogen atom failed to refine. For this reason, in the last refinement the positions of the hydrogen atoms were kept fixed in the assumed positions. The introduction of the hydrogen atoms in this final refinement reduced the R index from 0·080 to 0·071. The final positional and thermal parameters are reported in Tables 2 and 3, respectively.

Table 2. *Atomic coordinates*

	X/a	Y/b	Z/c
Ni	0	0	0
C(1)	0·11284 (36)*	0·27661 (35)	0·05218 (29)
C(2)	0·05169 (58)	0·29097 (50)	0·18665 (42)
C(3)	0·00722 (47)	0·16817 (43)	0·16573 (33)
N(1)	0·04569 (28)	0·16031 (27)	0·08024 (21)
N(2)	0·11699 (39)	0·35709 (33)	0·11360 (32)
N(3)	0	0	0·39155 (38)
O(1)	0·07133 (33)	0·11471 (31)	0·39260 (28)

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

The listing of the calculated and observed structure factors is given in Table 4. It is evident that several of the strongest F_o's are considerably lower than the corresponding F_c's. This effect may be attributed to secondary extinction, as the crystal used for collecting the intensity data was relatively large and the absorption low. If the nine reflections most affected by extinction are excluded, the R value decreases to 0·064.

In order to check the assignment of the non-coordinating nitrogen atom in the independent imidazole ring, the structure was refined with C(2) and N(2) interchanged. After two cycles of refinement, the R index increased from 0·071 to 0·082. This significant increase corroborates the initial assignment of the atoms in the imidazole ring.

As the refinement of the trial model was satisfactory in the centric space group $R\bar{3}$, no further consideration was given to the acentric space group $R3$.

Description

3-Dimensional packing

The crystal structure of $Im_6Ni(NO_3)_2$ consists of discrete Im_6Ni^{2+} complex cations and nitrate anions packed in a hexagonal unit cell as shown in Fig. 1. The closest cation–anion approaches are between ring atoms in the cation and oxygen atoms in the anions and these are indicated in Fig. 1. Each of the three closest approaches involve the pyrrole ($>$N–H) nitrogen atom in an imidazole ring and an oxygen atom in one of the two adjacent nitrate groups. The orientation of the imidazole molecule with respect to this pair of nitrate groups, moreover, is such that the pyrrole hydrogen atom extends even closer toward these oxygen atoms. This orientation of the imidazole ring with respect to a pair of adjacent nitrate groups is consistent with hydrogen bonding. The exact position of the pyrrole hydrogen atom has not been established but if its position as calculated above is approximately correct, it lies significantly closer to O(1) than to O(2) or O(3'). In this case the shortest N–O and H–O distances are consistent with one relatively weak hydrogen bond. Weak hydrogen bonds involving O(2) and O(3'), however, cannot be ruled out.

Complex cation and nitrate anion

The structure of the complex cation is shown in Fig. 2. As the nickel atom lies on a threefold axis and a center of symmetry ($\bar{3}$ point symmetry), the coordination polyhedron is completely specified by one nickel-nitrogen distance and by one nitrogen–nickel–nitrogen angle. Moreover, the six imidazole rings are crystallographically equivalent and the unique bond distance and angles in imidazole are included in Fig. 2. The co-

Table 3. *Anisotropic thermal parameters*

The general anisotropic temperature factor has the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
NI	531 (14)	531 (14)	383 (7)	265 (7)	0	0
C(1)	465 (32)	398 (30)	452 (21)	192 (26)	−37 (20)	−57 (20)
C(2)	1244 (65)	703 (46)	659 (33)	349 (45)	249 (37)	−272 (32)
C(3)	901 (46)	584 (38)	424 (22)	300 (35)	170 (26)	−87 (23)
N(1)	447 (26)	339 (25)	319 (15)	199 (20)	−31 (15)	−52 (15)
N(2)	804 (39)	343 (29)	735 (27)	170 (27)	121 (26)	−141 (22)
N(3)	622 (50)	622 (50)	266 (25)	311 (25)	0	0
O(1)	749 (33)	537 (29)	812 (26)	205 (26)	−55 (23)	2 (21)

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

Table 4. *Observed and calculated structure factors*

H,K,0

3	0	617	646
6	0	668	649
9	0	212	193
12	0	158	153
1	1	1241	1581
4	1	199	-84
7	1	523	534
10	1	271	247
2	2	951	1000
5	2	629	649
8	2	247	240
11	2	200	196
3	3	0	81
6	3	420	427
9	3	727	759
1	4	484	503
4	4	418	431
7	4	471	458
10	4	260	259
2	5	1078	1095
5	5	672	671
8	5	527	529
3	6	655	707
6	6	424	415
9	6	102	91
1	7	735	722
4	7	511	495
7	7	223	194
2	8	35	39
5	8	103	88
3	9	0	-2
6	9	276	283
1	10	333	327
4	10	236	229
2	11	195	198

H,K,1

1	0	726	707
4	0	437	-322
7	0	859	786
10	0	133	-135
13	0	28	20
2	1	1615	-2092
5	1	354	353
8	1	112	127
11	1	274	270
0	2	522	564
3	2	95	-14
6	2	103	119
9	2	117	82
12	2	187	187
-2	3	930	963
1	3	1129	1230
4	3	416	423
7	3	135	-103
10	3	302	303
-1	4	439	-308
2	4	842	836
5	4	407	382
8	4	198	181
11	4	109	134
-3	5	1170	1256
0	5	1235	1241
3	5	1134	1154
6	5	78	-88
9	5	222	218
-2	6	616	618
-5	6	110	142
1	6	1069	1056
4	6	320	303
7	6	0	11
-1	7	785	773
-4	7	549	545
2	7	396	370
5	7	245	-226
8	7	25	-28
-3	8	406	-338
-6	8	465	457
0	8	538	532
3	8	77	-94
6	8	198	183
-2	9	163	-163
-5	9	269	242
-8	9	251	268
1	9	28	-12
4	9	145	144
-1	10	68	71
-4	10	29	-41
-7	10	585	576
2	10	331	337
5	10	267	293
-3	11	57	63
-6	11	95	114
0	11	255	249
3	11	0	-13
-2	12	267	244
-5	12	64	56
-8	12	0	34
-11	12	433	441
-1	13	0	8
-4	13	185	187
-7	13	242	247
-10	13	145	133
-3	14	170	183
-6	14	95	82
-9	14	249	268
-5	15	138	163
-8	15	0	3

H,K,2

2	0	760	611
5	0	198	262
8	0	713	681
11	0	32	-10
0	1	1267	1917
3	1	649	706
6	1	885	868
9	1	177	-163
12	1	177	185
1	2	56	137
4	2	78	146
7	2	612	613
10	2	289	276
2	3	212	-133
5	3	694	666
8	3	336	314
11	3	160	153
-3	4	1005	1114
0	4	291	-198
3	4	317	317
6	4	452	466
9	4	531	531
-2	5	1418	1592
1	5	229	228
4	5	641	648
7	5	41	39
10	5	183	151
-1	6	168	174
-4	6	1363	1491
2	6	340	334
5	6	148	127
8	6	138	130
-3	7	26	89
-6	7	867	818
0	7	130	-87
3	7	328	333
6	7	64	-87
-2	8	166	161
-5	8	818	776
1	8	158	181
4	8	236	238
7	8	226	224
-1	9	297	289
-4	9	350	336
-7	9	391	375
2	9	357	354
5	9	331	344
-3	10	0	25
-6	10	756	742
-9	10	217	202
0	10	612	666
3	10	289	309
-2	11	388	387
-5	11	96	92
-8	11	251	242
1	11	433	423
4	11	158	173
-1	12	97	83
-4	12	501	499
-7	12	288	268
-10	12	183	-169
2	12	148	137
-3	13	293	314
-6	13	294	306
-9	13	0	-44
-12	13	82	-98
0	13	126	126
-2	14	147	135
-5	14	31	33
-8	14	283	284
-11	14	183	207
-4	15	105	126
-7	15	112	92
-10	15	178	191

H,K,3

0	0	412	-274
3	0	234	-125
6	0	116	134
9	0	353	348
12	0	188	167
1	1	837	979
4	1	70	23
7	1	585	562
10	1	110	94
13	1	85	107
-1	2	1455	1801
2	2	745	777
5	2	17	21
8	2	682	672
11	2	313	308
0	3	1187	1439
3	3	460	481
6	3	789	800
9	3	381	346
-2	4	1265	1498
1	4	1488	1518
4	4	828	796
7	4	389	379
10	4	164	176
-1	5	926	893
-4	5	575	-484
2	5	792	763
5	5	427	445
8	5	217	201
-3	6	1214	1240
0	6	387	397
3	6	639	637
6	6	192	-187
9	6	177	194
-2	7	300	313
-5	7	667	-561
1	7	346	317
4	7	151	131
7	7	216	205
-1	8	771	750
-4	8	430	452
-7	8	0	-1
2	8	314	264
5	8	83	64
-3	9	88	107
-6	9	574	584
0	9	306	284
3	9	370	361
6	9	219	220
-2	10	115	115
-5	10	505	513
-8	10	549	554
1	10	326	316
4	10	0	8
-1	11	358	367
-4	11	333	342
-7	11	254	243
-10	11	212	189
2	11	0	-12
-3	12	353	347
-6	12	368	372
-9	12	106	92
0	12	46	48
-2	13	45	55
-5	13	249	240
-8	13	551	569
-11	13	158	162
-1	14	0	28
-4	14	250	263
-7	14	182	181
-10	14	239	260
-6	15	77	58
-9	15	142	109

H,K,4

1	0	1061	-1076
4	0	658	701
7	0	618	629
10	0	161	145
13	0	110	114
2	1	343	338
5	1	328	358
8	1	344	292
11	1	135	115
0	2	560	506
3	2	519	525
6	2	642	595
9	2	78	52
12	2	110	118
-2	3	816	-730
1	3	635	599
4	3	177	193
7	3	522	517
10	3	62	23
-1	4	1195	1192
2	4	613	611
5	4	131	118
8	4	66	-49
-3	5	1119	1165
0	5	136	141
3	5	160	-112
6	5	68	-57
9	5	120	110
-2	6	710	659
-5	6	363	368
1	6	236	228
4	6	[illegible]	93
7	6	203	[illegible]
-1	7	247	[illegible]
-4	7	258	295
2	7	371	382
5	7	50	-48
-3	8	560	525
-6	8	133	152
0	8	47	-39
3	8	425	451
6	8	146	142
-2	9	78	-75
-5	9	684	679
-8	9	332	332
1	9	348	354
4	9	194	191
-1	10	335	331
-4	10	471	-458
-7	10	0	-43
2	10	396	417
-3	11	22	-22
-6	11	199	182
-9	11	105	104
0	11	351	356
3	11	46	57
-2	12	66	-79
-5	12	281	275
-8	12	138	118
-11	12	88	-119
1	12	232	237
-1	13	58	61
-4	13	66	76
-7	13	287	285
-10	13	189	197
-6	14	82	-101
-9	14	215	195
-12	14	127	163
-5	15	68	77
-8	15	183	167

H,K,5

2	0	977	1075
5	0	852	858
8	0	293	290
11	0	149	128
0	1	1292	1609
3	1	683	701
6	1	724	699
9	1	448	419
1	2	956	943
4	2	250	276
7	2	858	854
10	2	115	113
-1	3	1074	1115
2	3	716	723
5	3	471	476
8	3	624	608
11	3	0	26
-3	4	602	585
0	4	1118	1081
3	4	308	-229
6	4	650	640
9	4	106	87
-2	5	720	647
1	5	294	285
4	5	292	267
7	5	382	355
-1	6	103	-31
-4	6	60	68
2	6	268	273
5	6	456	446
8	6	302	300
-3	7	1183	1161
-6	7	99	136
0	7	486	482
3	7	232	221
6	7	256	251
-2	8	635	598
-5	8	158	146
1	8	94	90
4	8	386	396
-1	9	238	242
-4	9	387	369
-7	9	438	421
2	9	553	577
5	9	18	-28
-3	10	232	214
-6	10	304	308
-9	10	210	211
0	10	457	455
3	10	125	133
-2	11	417	421
-5	11	822	845
-8	11	78	-90
1	11	222	219
-1	12	147	154
-4	12	352	354
-7	12	538	563
-10	12	211	178
2	12	124	161
-3	13	50	55
-6	13	361	352
-9	13	253	262
-2	14	37	32
-5	14	213	224
-8	14	241	233
-11	14	143	144
-7	15	91	102

H,K,6

0	0	428	-347
3	0	167	-88
6	0	146	145
9	0	157	132
12	0	269	270
1	1	74	-84
4	1	698	700
7	1	388	384
10	1	273	257
-1	2	45	27
2	2	335	328
5	2	391	391
8	2	95	95
11	2	123	100
0	3	1114	1124
3	3	541	549
6	3	296	291
9	3	0	-90
-2	4	301	290
1	4	603	609
4	4	19	4
7	4	327	300
10	4	126	-142
-1	5	583	577
-4	5	802	738
2	5	335	380
5	5	242	228
-3	6	104	133
0	6	1109	1093
3	6	40	49
6	6	129	122
-2	7	798	772
-5	7	341	-275
1	7	379	375
4	7	113	121
7	7	142	142
-1	8	37	52
-4	8	290	258
-7	8	256	289
2	8	94	84
5	8	242	[illegible]
-3	9	0	[illegible]
-6	9	199	[illegible]
0	9	222	227
3	9	210	198
-2	10	455	[illegible]
-5	10	0	[illegible]
-8	10	182	[illegible]
1	10	222	218
4	10	84	-104
-1	11	108	97
-4	11	131	116
-7	11	253	237
-10	11	303	305
2	11	140	141
-3	12	182	-188
-6	12	517	554
-9	12	342	35[illegible]
0	12	188	200
-2	13	17	0
-5	13	60	59
-8	13	34	69
-11	13	252	268
-4	14	63	67
-7	14	146	144
-10	14	107	93
-9	15	0	59

H,K,7

1	0	88	149
4	0	1019	979
7	0	246	242
10	0	172	170
2	1	170	211
5	1	947	952
8	1	130	121
11	1	220	194
0	2	335	397
3	2	800	746
6	2	481	476
9	2	0	-33
-2	3	894	891
1	3	0	32
4	3	41	64
7	3	297	268
10	3	45	-17
-1	4	872	827
-3	5	312	335
2	4	178	-127
5	4	337	338
0	5	110	127
3	5	147	142
6	5	275	251
-2	6	372	371
-5	6	723	701
1	6	304	280
4	6	184	157
-1	7	192	162
-4	7	532	489
2	7	329	-336
5	7	410	434
-3	8	364	359
-6	8	175	155
0	8	130	147
3	8	316	327
6	8	99	103
-2	9	353	354
-5	9	235	-236
-8	9	368	400
1	9	369	387
4	9	221	243
-1	10	477	491
-4	10	426	426
-7	10	315	307
2	10	153	160
-3	11	212	196
-6	11	423	427
-9	11	176	185
0	11	153	146
-2	12	110	107
-5	12	147	147
-8	12	82	101
-11	12	194	170
-1	13	110	138
-4	13	18	-22
-7	13	164	164
-10	13	95	105
-3	14	0	-93
-6	14	152	156
-9	14	42	-14

H,K,8

2	0	829	808
5	0	549	530
8	0	280	238
11	0	296	305
0	1	208	246
3	1	572	558
6	1	85	81
9	1	213	199
1	2	915	922
4	2	674	655
7	2	195	194
-1	3	997	969
2	3	384	377
5	3	244	235
-3	4	514	485
0	4	298	317
3	4	604	625
6	4	568	573
-2	5	297	308
1	5	422	388
4	5	331	330
-1	6	701	663
-4	6	0	36
2	6	150	124
5	6	195	185
-3	7	329	299
-6	7	190	-201
0	7	253	237
3	7	196	184
-2	8	308	315
-5	8	0	-9
1	8	216	214
4	8	380	415
-1	9	660	692
-4	9	475	462
-7	9	308	288
2	9	24	7
5	9	107	130
-3	10	639	659
-6	10	171	146
-9	10	479	456
0	10	84	91
3	10	34	20
-2	11	256	268
-5	11	250	258
-8	11	459	465
1	11	0	13
-1	12	125	117
-4	12	67	55
-7	12	187	160
-10	12	240	253
-3	13	47	60
-6	13	241	267
-9	13	116	123
-5	14	0	[illegible]
-8	14	52	[illegible]

H,K,9

0	0	612	-542
3	0	651	622
6	0	263	255
9	0	380	383
1	1	112	129
4	1	748	[illegible]
7	1	260	-250
10	1	288	156
-1	2	246	-194
2	2	622	582
5	2	249	246
8	2	0	-34
0	3	142	127
3	3	349	335
6	3	196	185
-2	4	248	245
1	4	0	18
4	4	178	150
7	4	0	-37
-1	5	248	220
-4	5	146	185
2	5	504	495
5	5	70	-68
-3	6	101	111
0	6	73	-89
3	6	0	12
-2	7	243	239
-5	7	313	319
1	7	49	42
4	7	311	334
-1	8	267	278
-4	8	289	294
-7	8	161	143
2	8	220	216
-3	9	456	459
-6	9	65	75
0	9	264	260
3	9	140	123
-2	10	187	176
-5	10	0	12
-8	10	371	361
1	10	110	-127
-1	11	102	92
-4	11	22	-31
-7	11	0	28
-10	11	150	139
2	11	0	53
0	12	0	14
-3	12	65	56
-6	12	73	-107
-9	12	122	140
-5	13	39	-44
-8	13	19	-16

H,K,10

1	0	669	658
4	0	661	659
7	0	108	102
10	0	175	174
2	1	944	899
5	1	481	473
8	1	288	252
0	2	570	579
3	2	343	317
6	2	0	-42
-2	3	541	543
1	3	467	471
4	3	417	385
7	3	262	239
-1	4	188	-159
2	4	338	311
5	4	264	210
-3	5	61	49
0	5	0	29
3	5	220	200
6	5	347	332
-2	6	271	247
-5	6	314	286
1	6	147	126
4	6	164	147
-1	7	146	146
-4	7	469	443
2	7	464	472
5	7	262	301
-3	8	564	546
-6	8	468	452
0	8	314	309
3	8	301	316
-2	9	375	387
-5	9	373	363
-8	9	352	336
1	9	0	5
4	9	123	153
-1	10	176	175
-4	10	385	389
-7	10	107	110
2	10	31	35
-3	11	267	267
-6	11	23	8
-9	11	155	163
0	11	31	17
-2	12	171	195
-5	12	176	187
-8	12	109	118
-11	12	105	98
-4	13	62	85
-7	13	39	51

H,K,11

2	0	264	242
5	0	132	133
8	0	156	135
0	1	490	457
3	1	494	497
6	1	86	94
9	1	245	235
1	2	368	338
4	2	272	291
7	2	0	-65
-1	3	42	-33
2	3	180	174
5	3	182	188
8	3	91	101
-3	4	20	45
0	4	220	210
3	4	279	282
6	4	0	-14
-2	5	189	-198
1	5	507	510
4	5	0	-23
-1	6	261	254
-4	6	198	180
2	6	490	507
5	6	230	236
-3	7	271	276
-6	7	464	487
0	7	270	267
3	7	179	198
-2	8	259	261
-5	8	335	334
1	8	262	276
4	8	0	2
-1	9	0	5
-4	9	196	179
-7	9	122	101
2	9	38	-29
-3	10	118	121
-6	10	0	-11
-9	10	125	102
0	10	28	-13
-2	11	102	86
-5	11	40	54
-8	11	148	143
-4	12	59	72
-7	12	41	35

H,K,12

0	0	442	446
3	0	329	304
6	0	391	397
9	0	58	-28
1	1	297	280
4	1	239	216
7	1	105	100
-1	2	475	488
2	2	45	-28
5	2	137	144
8	2	142	149
0	3	0	17
3	3	198	97
6	3	70	-84
-2	4	136	-150
1	4	214	184
4	4	281	258
7	4	140	45
-1	5	0	98
-4	5	225	217
2	5	293	176
5	5	132	118
-3	6	267	272
0	6	316	308
3	6	183	176
-5	7	590	610
-2	7	60	67
1	7	328	332
4	7	0	26
-1	8	42	-13
-4	8	151	131
-7	8	295	312
2	8	120	122
-3	9	60	74
-6	9	164	179
0	9	58	70
-2	10	25	37
-5	10	94	92
-8	10	104	93
-4	11	148	146
-7	11	74	85
-5	12	0	28

H,K,13

1	0	576	570
4	0	37	8
7	0	268	259
2	1	301	283
5	1	0	-9
8	1	95	90
0	2	423	437
3	2	105	76
6	2	173	165
-2	3	277	277
1	3	0	-40
4	3	363	359
7	3	138	112
-1	4	311	312
2	4	241	224
5	4	219	216
-3	5	207	194
0	5	470	493
3	5	340	333
6	5	156	184
-2	6	212	198
-5	6	392	397
1	6	321	320
4	6	166	165
-1	7	172	162
-4	7	194	185
2	7	225	225
-3	8	0	20
-6	8	285	265
0	8	142	150
-2	9	105	123
-5	9	200	191
-8	9	79	67
1	9	105	134
-1	10	112	116
-4	10	152	180
-7	10	220	234
-3	11	117	145
-6	11	121	129

H,K,14

5	0	30	26
8	0	0	-10
0	1	73	50
3	1	68	-87
6	1	128	128
1	2	30	-63
4	2	0	-2
-1	3	127	120
2	3	55	47
5	3	199	189
-3	4	39	44
0	4	238	238
3	4	266	270
6	4	38	-10
-2	5	341	-347
1	5	106	119
4	5	161	186
-1	6	142	122
-4	6	189	204
2	6	87	95
-3	7	0	-38
-6	7	175	161
0	7	27	62
3	7	29	47
-2	8	0	-17
-5	8	127	134
1	8	136	122
-1	9	21	23
-4	9	0	17
-6	10	90	99

H,K,15

0	0	222	224
3	0	195	198
6	0	87	72
1	1	278	297
4	1	73	-84
-1	2	69	-84
2	2	144	144
5	2	147	131
0	3	182	194
3	3	199	201
6	3	186	195
-2	4	351	358
1	4	170	162
4	4	229	220
-1	5	306	308
-4	5	202	203
2	5	46	57
-3	6	156	160
0	6	0	28
-2	7	110	95
-5	7	151	155
1	7	99	103
-7	8	136	142
-1	8	50	62
-4	8	199	177
-3	9	103	98

H,K,16

1	0	138	124
4	0	0	17
7	0	68	61
2	1	143	133
5	1	0	6
0	2	30	10
3	2	97	80
-2	3	137	135
1	3	273	284
4	3	103	120
-1	4	223	234
2	4	104	112
-3	5	145	118
-2	6	134	139
-5	6	0	-2
-1	7	84	99
-4	7	133	121
-6	8	102	124

H,K,17

2	0	47	35
5	0	0	4
0	1	55	54
3	1	21	47
1	2	118	107
-1	3	71	73
2	3	128	142
-3	4	150	132
0	4	145	134
-2	5	57	-33
1	5	32	23
-1	6	125	149
-4	6	114	113

H,K,18

3	0	114	113
1	1	82	91
-1	2	111	124
2	2	130	170
0	3	126	137
-2	4	134	165

ordination polyhedron is very nearly a regular octahedron. The cage in which the nickel atom resides may be described as resulting from a 0·04 Å compression along one of the threefold axes of a regular octahedron of nitrogen atoms. In the nitrate anion, the unique N–O distance is $1·239 \pm 0·003$ Å and the nitrogen atom lies 0·014 Å (approximately two standard deviations) from the exact plane defined by the oxygen atoms.

The coordinated imidazole ring

The imidazole ring was found by least-squares analysis to be planar within the standard deviations of the atoms normal to this ring. The results of this analysis are given in Table 5. The nickel atom is approximately coplanar with the centrosymmetrically related pairs of imidazole rings. This configuration establishes that coordination takes place through the pyridine type ($>$N) nitrogen atoms rather than through the pyrrole type ($>$N–H) nitrogen atoms. This conclusion follows from the fact that coordination through the N–H group would result in the formation of a quaternary nitrogen atom with a tetrahedral configuration. If the configuration about the nitrogen atom were tetrahedral the Ni–N bond would make an angle of about 36° with the normal to the imidazole ring. The observed angle of 86° precludes this configuration. The coordination of imidazole to the nickel(II) ion, there-

fore, occurs through the same type of nitrogen atom ($>$N) as does both pyrazole (Reimann, Mighell & Mauer, 1967) and biimidazole (Mighell, Reimann &
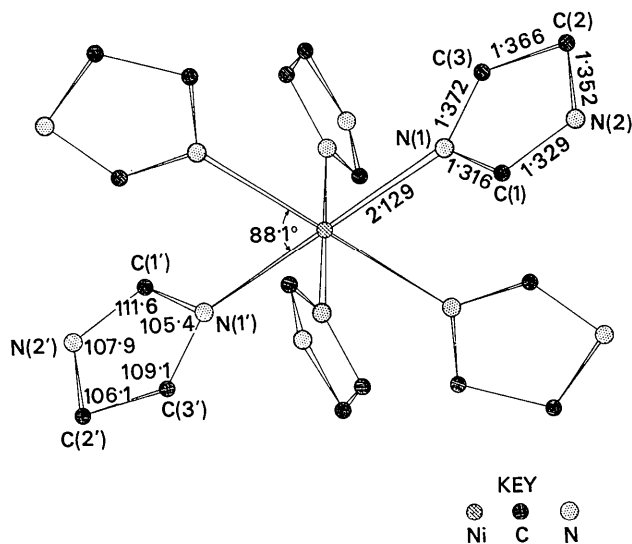

Fig. 2. The complex cation. The unique bond distances and angles are indicated. The average of the standard deviations on the bond lengths and angles in the unique imidazole ring are 0·007 Å and 0·41°, respectively.
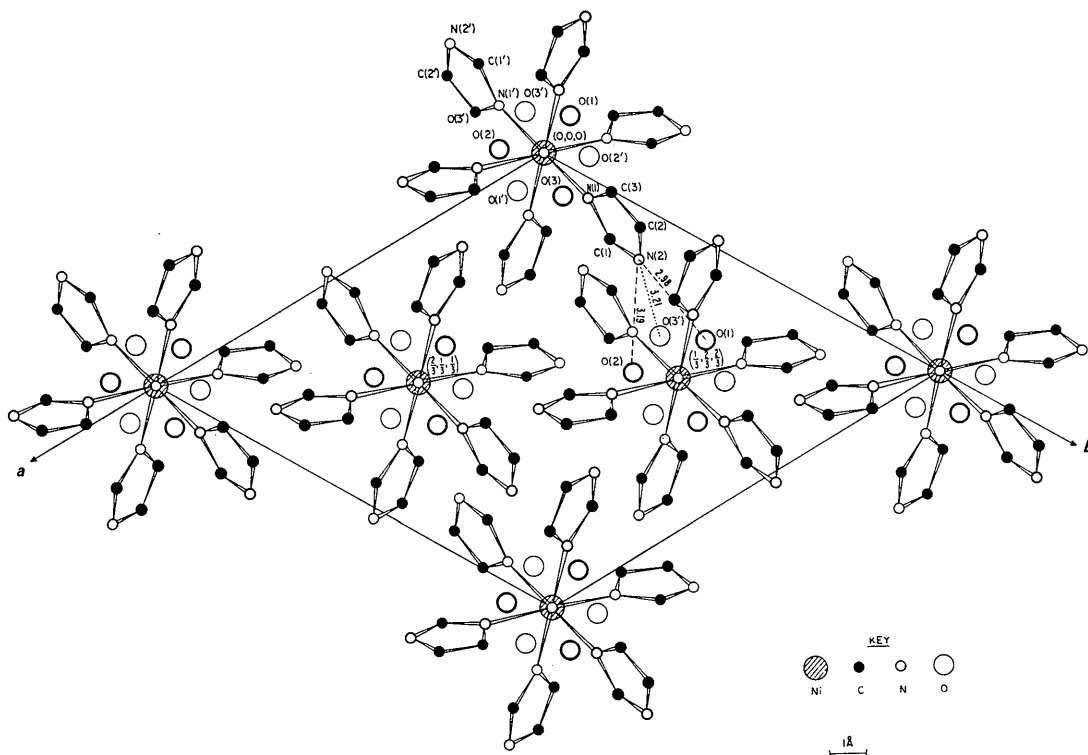

Fig. 1. Crystal structure of $(C_3H_4N_2)_6Ni(NO_3)_2$ projected on the (001) plane of the hexagonal unit cell. The shortest cation–anion distances are between the N(2) and O(3′) (dotted line) and between N(2) and the oxygen atoms O(2) and O(3) translated down one unit cell from those labeled (dashed lines).

Mauer, in the press). The bond distances observed in coordinated imidazole are in substantial agreement with those found for corresponding bonds in coordinated biimidazole. Related pairs agree to within two standard deviations of the imidazole bond distances. The observed distances in the imidazole ring, moreover, are in close agreement with the values calculated by Dewar & Gleicher (1966) and with those found by Lundberg (1966) in diimidazolezinc(II) dichloride. The shortest observed and calculated distances in the imidazole ring is between atoms involved in the classical C–N double bond.

Table 5. *Distances from the ring atoms to the least-squares planes of the imidazole ring*

The equation of the plane in direct space is given by $PX + QY + RZ = S$ ($P = 11\cdot385$, $Q = -5\cdot0896$, $R = 5\cdot6823$ and $S = 0\cdot16597$).

N(1)	0·00574 Å
N(2)	0·00593
C(1)	−0·00742
C(2)	−0·00221
C(3)	−0·00204

A number of computer programs were written at the NBS specifically for this problem. We would like to acknowledge the use of the X-ray 63 system developed at the Universities of Maryland and Washington. The authors wish to thank Professor J.Stewart for assistance in using the system. Thanks are also due to Mrs Marlene Morris for determining the lattice parameters with the powder method.

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The Crystal Structure of NaNbO2F2

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$NaNbO_2F_2$, a new niobium oxide fluoride, is monoclinic, with $a = 8\cdot063$, $b = 5\cdot405$, $c = 7\cdot626$ Å, $\beta = 101\cdot70°$, space group $P2_1/c$. The structure, refined by the least-squares method, contains layers of corner-sharing NbO_4F_2 octahedra. The structure of the layers with the composition $(NbO_2F_2)_n^{n-}$ is related to the PdF_3 structure type. The structure of $NaNbO_2F_2$ is also related to the $\alpha\text{-}PbO_2$ structure type. The anion arrangement is probably ordered.

Introduction

The substitution of F^- for O^{2-} in niobium oxides has been useful in making compounds of simple and predictable structures, which can serve as model substances for the study of the principles of synthesis, nonstoichiometry, and possible mechanisms of reaction (Andersson, 1967). Preparative and structural studies have been made on the $NaNbO_3$–Nb_2O_5, $NaNbO_3$–Nb_2O_5–H_2O and NaF–Nb_2O_5 systems. The present paper reports the crystal structure of $NaNbO_2F_2$, a new compound which has been prepared in the NaF–NbO_2F system.

Experimental

Heating a mixture of NaF and NbO_2F in the mole ratio 1:1 in a sealed platinum capsule for one day at 600 °C resulted in a product consisting of colourless plate-shaped crystals. Single-crystal X-ray studies showed the crystals to be of monoclinic symmetry and the crystallographic constants are given in Table 1. The Hägg–Guinier powder pattern is given in Table 2. The $h0l$, $h1l$, $h2l$ and $h3l$ reflexions were registered on multiple films by the integrating Weissenberg method using Cu $K\alpha$ radiation and were measured by means of a calibrated film strip. Because of the small crystal