1091. *The Crystal Structure of Dipotassium Bis(trimethylenedinitramine)nickelate(II) Tetrahydrate*

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The crystal structure of the neutral potassium salt of the nickel(II) complex of trimethylenedinitramine has been determined from three-dimensional *X*-ray data at room temperature. The salt crystallises as a red tetrahydrate but the water molecule takes no part in the co-ordination of the nickel. The complex ion is formed by the co-ordination of two trimethylenedinitramine molecules to one nickel atom and has the nickel in square-planar co-ordination, with the octahedral position unfilled. The ligand molecules are bonded to the nickel atom through the amino-nitrogen atoms. The nitro-groups, although near to the nickel, are not bonded to it; instead, they block the approach to the octahedral position, in consequence of the planarity of the $O_2N{-}N(N{:})C$ system. The length of the N–N bond is 1·29 Å, showing considerable double-bond character. The fact that the red crystal dissolves to give a green solution is believed to be due to the breakdown of the steric hindrance to the nitro-groups, permitting two solvent molecules to fill the octahedral positions.

Nickel forms complexes or complex salts with three homologous polymethylenedinitramines ($O_2N{\cdot}NH{\cdot}[CH_2]_n{\cdot}NH{\cdot}NO_2$) as follows (where L^n represents the corresponding ligand molecule): $Ni[L^2],4H_2O$, bluish, microcrystalline, paramagnetic; $Ni[L^3]_2,4H_2O$, red, very well crystalline, diamagnetic; $Ni[L^4],2H_2O$, green, well crystalline, paramagnetic. It is clear that the nickel atom is quite differently co-ordinated in these complexes, despite the similarity of the ligands. The magnetic properties and the colours indicate that there is octahedral co-ordination in the first and third compound listed, but planar co-ordination in the second. It was thought that an *X*-ray diffraction study might reveal steric reasons for the differences, besides giving the exact configuration of the molecules. The complex formed by trimethylenedinitramine is especially interesting because, whilst it is deep red in the solid state its aqueous solution is dark green. *X*-Ray structural work on this compound is described below. The structure of the complex formed by tetramethylenedinitramine (it is polymeric, with distorted octahedral co-ordination at the nickel atoms) will be reported in a subsequent Paper.

Experimental

Preparation and Properties of $K_2Ni(O_2N{\cdot}N{\cdot}[CH_2]_3{\cdot}N{\cdot}NO_2)_2,4H_2O$.—Trimethylenedinitramine was heated gently with nickel sulphate and potassium hydroxide in aqueous solution. The dark green solution deposited red crystals of the required salt tetrahydrate which were then recrystallised from water. The salt was readily soluble in water, giving a green solution, but insoluble in most organic solvents; it dissolved readily in pyridine, giving a bright green solution from which green crystals were deposited. The formula of the salt established by Hawkins [1] is confirmed by the *X*-ray analysis. The salt melts at 234—236°, with decomposition, turning green; it is diamagnetic.[1] The crystals were obtained usually as (001) plates showing the {110} faces. Viewed with polarised light, the material was pleochroic, the colour varying from dark red to orange; the relative degree of absorption when the electric vector lay in the three axial directions was $c > a > b$.

Absorption Spectra.—The spectrum of the crystalline salt was obtained by Dr. B. J. Hathaway; a Beckman D.K. 2 double-beam spectrometer, fitted with a reflection attachment, was used. For the aqueous solution a Unicam S.P. 500 spectrophotometer was employed. In Figure 1 these spectra are compared. In the case of the crystalline solid the large absorption peak at 475 mμ is indicative of planar co-ordination around the nickel atom. In the case of the solution, the spectrum obtained, showing absorption at 400, 700, and probably 1100—1200 mμ,

[1] S. W. Hawkins, personal communication.

is similar to that given by the hexahydrated ion and other known octahedrally co-ordinated nickel complexes.

Crystal Data.—$C_6H_{14}N_8O_{12}K_2Ni$, $M = 533{\cdot}1$, Orthorhombic, $a = 8{\cdot}91$, $b = 10{\cdot}86$, $c = 10{\cdot}22 \pm 0{\cdot}01$ Å, $U = 998$ Å, $D_m = 1{\cdot}808$ (by flotation), $Z = 2$, $D_c = 1{\cdot}818$, $F(000) = 540$. Space group, *Pbam* (D_{2h}^9, No. 55). Absorption coefficient for X-rays ($\lambda = 1{\cdot}542$ Å) $\mu = 58{\cdot}5$ cm.$^{-1}$.

Collection of Reflexion Intensities.—The specimens used for X-ray work were about $0{\cdot}5 \times 0{\cdot}4 \times 0{\cdot}1$ mm. in size. Absorption was neglected. Copper radiation was used with a nickel filter. With a Leeds Weissenberg goniometer, seven layer-lines were photographed in the *a*-axis setting, *viz.*, 0*kl* to 6*kl*, and eight layer-lines in the *b*-axis setting, *viz.*, *h*0*l* to *h*7*l*. Accurate unit-cell parameters were obtained from high-order spectra on the zero-layer-line photographs, which were calibrated with power-lines from aluminium. The reflexion intensities were estimated visually by means of a calibrated strip. Lorentz and polarisation corrections were applied, and the observations correlated by the use of computer programmes written by J. Smith. The approximate absolute scale was obtained by Wilson's method [2] in the usual way. Out of 1005 possible independent reflexions, 771 were measured.

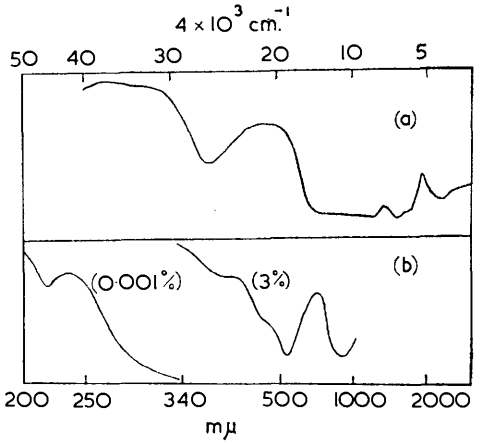

FIGURE 1. Absorption spectra of dipotassium bis(trimethylenedinitramine)nickelate(II) tetrahydrate. (a) Solid by reflectance; (b) aqueous solution by transmission

Structure Determination and Refinement.—Systematic absences gave two alternatives for the space group, *Pba*2 and *Pbam*. The latter was assumed to be correct (and was confirmed by the structure analysis) but the possibility of the former had to be borne in mind continuously during the early stages. The space group *Pbam* has a multiplicity of 8, but the unit-cell size and the crystal density showed that the number of molecules in the cell was 2. Both Ni and K atoms had to be on special positions. The Ni atom was clearly at the origin. The K atom was located first from Patterson projections and later from the three dimensional Patterson function on the mirror plane at $z = c/2$, with $x \sim 0$ and $y \sim b/5$. The location of the light atoms, C, N, and O, was attempted unsuccessfully by calculation of the three-dimensional electron density with the phases of Fourier terms determined by the two heavy atoms; their location was found by study of the heavy-atom to light-atom vectors in the three-dimensional Patterson function. The ligand lay across the mirror plane at $z = 0$; the water molecules were also in special positions, two on the mirror plane at $z = c/2$, the other two on the two-fold axis. The approximate structural parameters thus obtained were refined by successive cycles, with the SFLS programme of Cruickshank *et al.*[3] When the value of R, the conventional discrepancy factor, reached 0·18, anisotropic thermal vibration parameters were introduced, and refinement continued until atomic shifts became less than their standard deviations. The value of R was then 0·125. The calculated structure factors are listed with the observed structure amplitudes in Table 1. The final atomic parameters are set out in Tables 2—5. The numbering of the atoms of the ligand is shown in Figure 3.

[2] A. J. C. Wilson, *Nature*, 1942, **150**, 152.
[3] D. W. J. Cruickshank *et al.*, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon, London, 1960, p. 32.

TABLE 1

Observed and calculated structure amplitudes

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
0	0	1	172	277	0	10	2	238	212	1	5	4	60	51
0	0	2	115	104	0	10	3	219	-190	1	5	5	525	649
0	0	3	483	-524	0	10	4	484	544	1	5	6	170	-126
0	0	4	844	1103	0	10	5	59	29	1	5	7	493	573
0	0	5	441	-428	0	10	6	314	278	1	5	8	191	-186
0	0	6	935	1030	0	10	7	280	-271	1	5	9	250	233
0	0	7	230	-197	0	10	8	260	287	1	5	11	352	386
0	0	8	741	779	0	12	0	190	230	1	6	0	211	-159
0	0	9	533	524	0	12	1	278	273	1	6	1	215	-197
0	0	10	515	606	0	12	2	176	-156	1	6	2	229	247
0	0	11	401	-502	0	12	3	333	375	1	6	3	122	108
0	0	12	165	134	0	12	4	66	87	1	6	4	101	70
0	2	0	172	208	0	12	5	257	280	1	6	5	156	-154
0	2	1	447	597	1	1	0	829	975	1	6	6	102	104
0	2	2	672	-685	1	1	1	920	1049	1	6	9	165	-157
0	2	3	565	555	1	1	2	93	72	1	7	0	445	520
0	2	4	384	379	1	1	3	50	45	1	7	1	99	97
0	2	5	950	1122	1	1	4	289	352	1	7	2	581	616
0	2	6	268	-155	1	1	5	414	449	1	7	3	114	-74
0	2	7	57	-41	1	1	6	97	59	1	7	4	469	486
0	2	8	81	-23	1	1	7	372	412	1	7	6	293	381
0	2	9	550	519	1	1	8	302	309	1	7	7	74	85
0	2	10	68	-96	1	1	9	363	374	1	7	8	348	372
0	2	11	319	246	1	1	10	209	189	1	7	10	275	309
0	2	12	48	43	1	2	0	569	627	1	8	0	71	-80
0	4	0	832	671	1	2	1	293	244	1	8	1	189	-193
0	4	1	443	480	1	2	2	605	-705	1	8	2	204	199
0	4	2	341	410	1	2	3	318	306	1	8	3	160	149
0	4	3	477	494	1	2	4	138	-122	1	8	4	104	-107
0	4	4	586	513	1	2	5	64	-49	1	8	5	248	-283
0	4	5	539	510	1	2	7	88	102	1	8	6	149	191
0	4	6	331	347	1	2	8	160	-130	1	8	7	101	106
0	4	7	148	107	1	2	9	251	214	1	8	8	81	-76
0	4	8	335	295	1	2	11	161	-145	1	8	9	98	-125
0	4	9	253	228	1	2	12	95	-92	1	9	0	237	226
0	4	10	211	196	1	3	0	225	206	1	9	1	434	467
0	4	11	262	219	1	3	1	83	54	1	9	2	117	112
0	4	12	247	225	1	3	2	895	1062	1	9	5	228	242
0	6	0	513	442	1	3	3	266	-183	1	9	7	252	271
0	6	1	150	-135	1	3	4	829	1029	1	9	8	225	255
0	6	2	93	-62	1	3	5	343	334	1	9	9	179	213
0	6	3	717	699	1	3	6	321	324	1	10	0	159	-187
0	6	4	428	366	1	3	7	98	-51	1	10	1	53	63
0	6	5	97	105	1	3	8	502	451	1	10	2	167	183
0	6	6	365	419	1	3	9	165	-114	1	10	4	135	-130
0	6	7	64	55	1	3	10	387	348	1	10	7	70	77
0	6	8	126	-140	1	3	11	146	131	1	10	8	81	82
0	6	9	132	99	1	3	12	272	290	1	11	0	101	112
0	6	10	210	184	1	4	0	376	-368	1	11	1	196	191
0	6	11	78	72	1	4	1	347	254	1	11	2	100	74
0	8	0	554	570	1	4	3	247	-211	1	11	3	182	199
0	8	1	785	744	1	4	4	95	-89	1	11	4	241	278
0	8	2	84	24	1	4	5	310	289	1	11	5	211	254
0	8	3	265	182	1	4	6	218	-213	1	11	7	70	87
0	8	4	165	-155	1	4	7	88	-63	1	13	0	143	134
0	8	5	445	403	1	4	8	118	117	1	13	2	165	204
0	8	6	64	58	1	4	9	74	48	1	13	4	205	274
0	8	7	295	322	1	4	10	129	-118	2	0	0	929	1013
0	8	8	289	301	1	5	0	638	-577	2	0	1	395	502
0	8	9	503	524	1	5	1	697	740	2	0	2	1593	1530
0	10	0	574	636	1	5	2	64	-65	2	0	3	95	-46
0	10	1	201	-166	1	5	3	712	842	2	0	4	232	-175

TABLE 1 (*Continued*)

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
2	0	5	422	-361	2	5	11	65	69	3	1	6	98	82
2	0	6	747	749	2	6	0	69	45	3	1	7	695	689
2	0	7	375	352	2	6	1	177	-104	3	1	8	256	214
2	0	8	735	772	2	6	2	635	614	3	1	9	82	57
2	0	9	57	59	2	6	3	346	310	3	1	11	415	380
2	0	10	230	210	2	6	4	393	404	3	2	0	593	574
2	0	12	195	245	2	6	5	181	194	3	2	1	189	149
2	1	0	415	466	2	6	6	334	372	3	2	2	75	28
2	1	1	55	-29	2	6	8	201	191	3	2	3	375	-404
2	1	2	664	-709	2	6	10	138	93	3	2	4	77	-49
2	1	3	45	68	2	6	11	123	176	3	2	5	116	-89
2	1	4	287	-188	2	7	0	72	-46	3	2	8	254	214
2	1	5	289	-194	2	7	1	185	-150	3	2	9	138	98
2	1	6	93	-58	2	7	2	211	176	3	2	11	136	-126
2	1	8	167	-150	2	7	3	334	301	3	2	12	71	-73
2	1	9	181	138	2	7	4	77	60	3	3	0	734	701
2	1	11	190	-161	2	7	5	165	-152	3	3	1	243	-180
2	1	12	113	-112	2	7	6	162	203	3	3	2	691	739
2	2	0	674	-535	2	7	7	129	130	3	3	3	268	229
2	2	1	445	419	2	7	8	115	-124	3	3	4	733	723
2	2	2	103	94	2	7	9	116	-110	3	3	5	242	-207
2	2	3	1174	1495	2	7	10	76	78	3	3	6	638	602
2	2	4	232	-215	2	7	11	51	69	3	3	7	172	140
2	2	5	383	374	2	8	0	276	277	3	3	8	240	206
2	2	6	255	237	2	8	1	552	582	3	3	9	104	-76
2	2	7	624	583	2	8	3	463	501	3	3	10	540	463
2	2	8	276	-219	2	8	4	309	-325	3	3	12	192	239
2	2	9	339	265	2	8	5	148	103	3	4	0	321	254
2	2	11	477	382	2	8	6	126	122	3	4	1	41	22
2	2	12	119	120	2	8	7	486	543	3	4	2	222	-187
2	3	0	580	547	2	8	8	85	108	3	4	3	155	-92
2	3	1	563	473	2	8	9	349	363	3	4	9	114	64
2	3	2	295	-230	2	9	0	178	-159	3	5	0	345	-252
2	3	3	73	-89	2	9	1	98	-84	3	5	1	784	673
2	3	5	301	211	2	9	2	170	145	3	5	2	208	175
2	3	6	70	-64	2	9	3	57	-58	3	5	3	326	279
2	3	8	141	138	2	9	4	151	-159	3	5	4	170	182
2	3	9	286	239	2	9	5	148	-147	3	5	5	695	700
2	3	11	98	-95	2	9	7	121	28	3	5	6	161	-126
2	3	12	67	-78	2	9	9	80	-102	3	5	7	328	300
2	4	0	780	726	2	10	0	261	256	3	5	8	90	85
2	4	1	89	-50	2	10	1	114	-120	3	5	9	322	288
2	4	2	752	768	2	10	2	420	396	3	5	11	241	281
2	4	3	518	505	2	10	3	125	148	3	6	0	249	-154
2	4	4	335	328	2	10	4	267	243	3	6	1	152	-101
2	4	5	134	-128	2	10	5	127	-88	3	6	2	48	-43
2	4	6	591	633	2	10	6	369	387	3	6	3	201	147
2	4	7	156	160	2	10	8	173	169	3	6	4	225	202
2	4	8	319	276	2	11	0	54	31	3	6	5	174	167
2	4	9	112	111	2	11	1	142	142	3	6	7	130	-121
2	4	10	291	239	2	11	7	76	93	3	6	8	126	-121
2	4	11	104	84	2	12	0	82	-71	3	7	0	441	341
2	4	12	242	276	2	12	1	304	275	3	7	1	85	68
2	5	0	519	-426	2	12	3	327	315	3	7	2	721	586
2	5	1	134	-119	2	12	4	97	-86	3	7	3	205	-162
2	5	2	80	56	2	12	5	191	212	3	7	4	550	511
2	5	3	177	-177	3	1	0	665	-753	3	7	5	57	55
2	5	4	47	48	3	1	1	783	923	3	7	6	253	262
2	5	5	101	107	3	1	2	700	832	3	7	8	326	372
2	5	6	152	-157	3	1	3	400	411	3	7	10	227	287
2	5	7	126	-140	3	1	4	246	-200	3	8	0	110	-84
2	5	9	134	-113	3	1	5	376	379	3	9	0	82	79

TABLE 1 (*Continued*)

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
3	9	1	356	360	4	4	2	40	−38	5	1	5	435	388
3	9	2	153	125	4	4	3	54	42	5	1	6	111	101
3	9	3	332	327	4	4	4	340	282	5	1	7	241	174
3	9	4	99	−83	4	4	5	200	176	5	1	8	171	145
3	9	5	78	71	4	4	6	310	266	5	1	9	287	211
3	9	6	139	135	4	4	7	99	−63	5	1	10	218	194
3	9	7	413	435	4	4	8	314	258	5	2	0	152	−119
3	9	9	132	142	4	4	9	391	342	5	2	1	154	131
3	10	0	171	180	4	4	10	220	191	5	2	2	391	350
3	10	1	114	89	4	4	11	68	−77	5	2	3	263	−201
3	11	0	220	−210	4	5	1	310	−224	5	2	4	310	−286
3	11	1	242	200	4	5	2	222	−198	5	2	5	222	−181
3	11	2	275	263	4	5	3	206	177	5	2	7	215	183
3	11	3	245	201	4	5	4	108	113	5	2	8	236	203
3	11	5	182	187	4	5	5	94	−66	5	2	9	97	−94
3	11	7	173	190	4	5	7	90	−98	5	3	0	474	436
3	12	0	121	158	4	5	8	189	−203	5	3	1	256	266
3	12	2	115	−61	4	6	0	648	560	5	3	2	475	455
3	13	0	152	133	4	6	1	186	163	5	3	3	337	−292
3	13	2	214	267	4	6	2	143	108	5	3	4	618	590
4	0	0	795	1100	4	6	3	254	236	5	3	5	367	321
4	0	1	74	−52	4	6	4	579	571	5	3	6	164	132
4	0	2	575	706	4	6	5	466	451	5	3	7	84	−59
4	0	3	274	−253	4	6	6	245	242	5	3	8	481	449
4	0	4	278	332	4	6	7	136	−102	5	3	10	270	224
4	0	5	217	−197	4	6	8	175	166	5	4	1	61	−27
4	0	6	551	596	4	6	9	210	221	5	4	3	220	182
4	0	7	108	−41	4	6	10	163	171	5	4	4	220	−196
4	0	8	477	506	4	7	0	228	−213	5	4	5	275	−216
4	0	10	292	286	4	7	1	172	120	5	4	6	117	94
4	0	12	169	200	4	7	2	104	−89	5	4	7	196	176
4	1	0	187	−238	4	7	4	175	140	5	4	8	111	−80
4	1	1	123	76	4	7	5	365	373	5	5	0	222	135
4	1	2	314	251	4	7	6	173	−165	5	5	1	813	726
4	1	3	423	−411	4	7	7	124	−121	5	5	2	312	−255
4	1	4	237	−194	4	8	0	332	304	5	5	3	452	429
4	1	6	113	−112	4	8	1	421	381	5	5	4	67	59
4	1	8	243	181	4	8	2	150	−134	5	5	5	537	525
4	1	10	129	−100	4	8	3	292	283	5	5	6	160	−155
4	2	0	327	292	4	8	4	99	−104	5	5	7	436	433
4	2	1	585	540	4	8	5	226	214	5	5	9	413	385
4	2	2	171	−125	4	8	7	229	234	5	6	0	177	−158
4	2	3	902	917	4	8	9	302	336	5	6	1	160	−153
4	2	4	245	239	4	9	0	115	142	5	6	2	55	27
4	2	5	657	684	4	9	2	172	−164	5	6	3	117	96
4	2	6	229	200	4	9	3	98	−102	5	6	4	220	195
4	2	7	318	276	4	9	4	78	44	5	6	5	152	110
4	2	8	137	−104	4	10	0	304	336	5	6	7	158	−161
4	2	9	477	403	4	10	1	96	−97	5	6	8	74	−84
4	2	11	327	286	4	10	2	370	373	5	7	0	462	388
4	2	12	71	98	4	10	3	107	111	5	7	2	329	264
4	3	0	482	416	4	10	4	349	358	5	7	4	513	473
4	3	1	78	78	4	10	6	312	384	5	7	5	106	99
4	3	2	283	254	4	11	0	261	241	5	7	6	206	209
4	3	3	216	−202	4	12	1	237	251	5	7	7	53	−56
4	3	4	92	−86	4	12	3	187	192	5	7	8	240	212
4	3	5	266	−250	4	12	4	110	−128	5	8	2	103	−76
4	3	6	166	155	5	1	0	424	479	5	8	3	59	−72
4	3	7	170	146	5	1	1	335	368	5	8	4	102	70
4	3	8	206	203	5	1	2	93	90	5	8	5	114	105
4	4	0	1032	1001	5	1	3	183	177	5	8	6	92	−100
4	4	1	278	234	5	1	4	547	529	5	8	7	96	−77

TABLE 1 (*Continued*)

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
5	8	8	118	29	6	5	4	122	79	8	0	3	55	83
5	9	0	144	90	6	6	0	306	256	8	0	4	256	321
5	9	1	282	270	6	6	2	336	286	8	0	5	205	218
5	9	2	130	161	6	6	3	518	518	8	0	6	264	262
5	9	3	57	58	6	6	4	229	195	8	0	8	182	199
5	9	4	200	216	6	6	6	342	383	8	1	0	171	153
5	9	5	295	308	6	6	7	220	217	8	1	1	70	46
5	9	7	138	124	6	7	1	142	-113	8	1	2	70	-76
5	9	8	164	162	6	7	4	113	68	8	1	3	69	104
5	10	0	110	121	6	8	1	249	241	8	1	4	119	105
5	10	7	76	78	6	8	2	62	58	8	2	0	73	80
5	11	0	118	115	6	8	3	280	265	8	2	1	208	210
5	11	1	142	127	6	8	5	217	214	8	2	2	73	-39
5	11	3	86	89	6	8	7	184	158	8	2	3	450	460
5	11	4	166	159	6	10	0	294	282	8	2	4	102	88
5	11	5	123	114	6	10	2	274	251	8	2	5	317	298
6	0	0	745	932	6	10	4	342	402	8	2	6	150	137
6	0	1	197	-236	7	1	0	115	-118	8	2	7	174	173
6	0	2	243	243	7	1	1	314	296	8	2	8	127	-121
6	0	3	166	175	7	1	2	225	219	8	2	9	171	188
6	0	4	432	463	7	1	3	308	341	8	3	0	169	180
6	0	5	220	-228	7	1	4	252	229	8	3	2	181	-159
6	0	6	469	489	7	1	5	289	336	8	3	3	190	-214
6	0	7	108	-90	7	1	7	235	228	8	3	5	167	42
6	0	8	274	235	7	1	9	119	101	8	4	0	569	555
6	0	9	161	101	7	2	0	223	225	8	4	1	253	208
6	0	10	252	271	7	2	2	203	-155	8	4	2	307	259
6	0	11	99	-165	7	2	3	73	48	8	4	3	66	52
6	1	0	76	-18	7	2	4	104	-71	8	4	5	121	-107
6	1	1	145	142	7	2	9	99	75	8	4	6	409	328
6	1	3	155	165	7	3	0	176	168	8	4	7	216	199
6	1	4	172	-142	7	3	1	125	115	8	4	8	245	262
6	1	7	202	186	7	3	2	592	597	8	5	4	117	141
6	1	8	65	-33	7	3	4	248	197	8	5	5	129	124
6	2	1	407	398	7	3	6	289	286	8	6	0	109	104
6	2	2	179	163	7	3	7	269	232	8	6	2	301	268
6	2	3	548	622	7	3	8	343	317	8	6	3	133	103
6	2	4	217	186	7	4	0	150	-108	8	6	4	169	148
6	2	5	550	526	7	4	1	177	142	8	6	5	164	131
6	2	6	105	101	7	4	3	118	-85	8	6	6	191	208
6	2	7	229	241	7	4	5	189	152	9	1	1	213	195
6	2	8	64	64	7	4	6	111	-98	9	1	2	149	126
6	2	9	358	268	7	5	0	128	-135	9	1	3	130	130
6	3	0	104	-94	7	5	1	427	412	9	1	4	263	282
6	3	1	144	107	7	5	2	311	328	9	1	5	300	330
6	3	4	340	-331	7	5	3	316	310	9	1	7	85	62
6	3	5	179	-168	7	5	4	197	-192	9	2	0	70	75
6	3	7	196	187	7	5	5	96	75	9	2	3	116	-115
6	4	0	381	342	7	5	6	127	108	9	2	4	128	138
6	4	1	297	237	7	5	7	505	520	9	2	7	113	-152
6	4	2	437	365	7	5	8	96	95	9	3	0	475	469
6	4	3	148	93	7	6	0	66	-47	9	3	1	170	146
6	4	4	138	-104	7	6	1	147	-135	9	3	2	186	112
6	4	5	149	-120	7	6	4	110	119	9	3	3	99	-31
6	4	6	268	229	7	7	2	468	450	9	3	4	282	258
6	4	7	285	260	7	7	3	89	86	9	3	5	193	55
6	4	8	380	343	7	7	4	285	235	9	4	0	164	129
6	4	9	126	112	7	7	6	280	241	9	4	2	121	-107
6	5	0	214	-194	7	7	7	84	88	9	4	3	101	26
6	5	1	66	-60	8	0	0	214	271	9	5	0	201	185
6	5	2	177	156	8	0	1	55	70	9	5	1	379	393
6	5	3	102	80	8	0	2	283	332	9	5	5	271	304

TABLE 1 (*Continued*)

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
9	7	0	221	198	10	1	4	143	−165	10	4	4	117	80
9	7	1	82	52	10	1	5	105	127	10	6	0	183	203
9	7	2	164	147	10	2	1	102	86	11	1	1	70	78
9	7	4	303	341	10	2	3	250	252	11	1	2	146	207
10	0	0	208	265	10	2	4	86	70	11	1	3	129	208
10	0	2	276	332	10	2	5	154	167	11	2	0	148	−187
10	0	3	147	187	10	4	0	519	477	11	3	0	56	73
10	0	4	211	284	10	4	1	277	259	11	3	1	98	120
10	0	6	205	265	10	4	2	83	59	11	3	2	163	257

TABLE 2

Atomic co-ordinates (Å) and estimated standard deviations (Å × 10^{-3})

Atom	*x*	*y*	*z*	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Ni	0·000	0·000	0·000	0	0	0
K	0·036	3·277	5·110	4	3	0
C(1)	0·870	2·800	0·000	14	15	0
C(2)	0·080	2·648	1·273	10	9	9
N(1)	−0·529	1·282	1·295	7	7	8
N(2)	−1·323	1·019	2·272	8	7	7
O(1)	−1·938	−0·135	2·253	7	7	8
O(2)	−1·567	1·855	3·181	8	8	6
O(3)	0·000	5·430	3·447	0	0	10
O(4)	1·742	1·102	5·110	13	12	0

TABLE 3

Thermal vibration tensor components, U_{ij} (Å^2), and estimated standard deviations (Å × 10^{-4}) in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ni	0·0219(11)	0·0257(12)	0·0177(11)	0·0025(26)	0·0000(0)	0·0000(0)
K	0·0450(20)	0·0201(15)	0·0173(14)	0·0107(35)	0·0000(0)	0·0000(0)
C(1)	0·0189(63)	0·0179(66)	0·0323(66)	0·0172(120)	0·0000(0)	0·0000(0)
C(2)	0·0263(45)	0·0154(40)	0·0190(37)	0·0275(85)	0·0168(82)	0·0254(108)
N(1)	0·0063(28)	0·0090(30)	0·0090(29)	0·0013(60)	−0·0052(56)	0·0105(60)
N(2)	0·0113(35)	0·0190(36)	0·0104(32)	−0·0068(68)	0·0054(65)	0·0042(70)
O(1)	0·0192(35)	0·0255(36)	0·0274(33)	−0·0037(61)	−0·0024(66)	−0·0330(60)
O(2)	0·0312(36)	0·0348(40)	0·0123(33)	−0·0085(70)	0·0317(62)	0·0130(65)
O(3)	0·0208(47)	0·0255(50)	0·0206(47)	−0·0154(97)	0·0000(0)	0·0000(0)
O(4)	0·0432(66)	0·0327(64)	0·0309(60)	0·0134(111)	0·00000(0)	0·0000(0)

TABLE 4

Bond lengths and e.s.d. (Å)

Ni–N(1)	1·898 (0·007)
C(1)–C(2)	1·51 (0·01)
C(2)–N(1)	1·50 (0·01)
N(1)–N(2)	1·29 (0·01)
N(2)–O(1)	1·31 (0·01)
N(2)–O(2)	1·26 (0·01)

Bond Angles and e.s.d. (the primes refer to mirror-related atoms)

N(1)–Ni–N(1′)	86° 05′ (35′)
C(2)–C(1)–C(2′)	115° 25′ (38′)
C(1)–C(2)–N(1)	108° 33′ (45′)
C(2)–N(1)–N(2)	116° 42′ (41′)
N(1)–N(2)–O(1)	117° 22′ (43′)
N(1)–N(2)–O(2)	122° 10′ (44′)
O(1)–N(2)–O(2)	120° 21′ (45′)
Ni–N(1)–N(2)	123° 32′ (33′)
Ni–N(1)–C(2)	119° 34′ (33′)

TABLE 5

Closest approaches between non-bonded atoms (Å)

K–O(3)	2·74	Ni–O(1)	2·97	O(2)–O(3)	3·42	O(3)–O(4)	3·35
K–O(4)	2·74	O(1)–O(2)	2·23	O(2)–O(4)	3·38	O(1)–O(4)	3·02
K–O(4)	2·97	O(1)–O(3)	2·79	O(3)–O(3)	3·33		

Discussion

The unit cell contains two anions associated with four potassium ions and eight water molecules. Each anion is formed by the co-ordination of two ligand molecules around one nickel atom. A two-fold axis relates the ligand molecules to one another; at the same time, each ligand molecule has *m* symmetry. The anion as a whole has $2/m$ symmetry; its appearance, when viewed down the two-fold axis direction, is shown in Figure 2. The nickel is square-planar bonded to the amino-group nitrogen atoms. The octahedral positions of the nickel atom are not occupied but are sterically barred by the nearness of the oxygen atoms of the nitro-groups. These oxygen atoms, related by the mirror, are 2·97 Å from the nickel and 4·50 Å apart, with the vacant octahedral position between them. The bonds from nickel to nitrogen, 1·898 Å, with standard deviation 0·007 Å, are of normal length for square-planar nickel complexes; for example, in the compounds formed with salicylaldoxime,[4] dimethylglyoxime,[5] and thiosemicarbazide,[6] the Ni–N distances are,

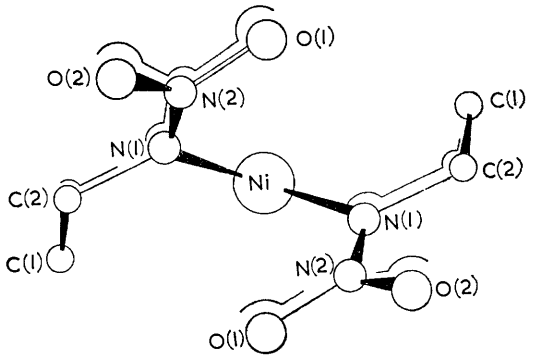

FIGURE 2. Appearance of the complex ion, viewed in the *c*-direction along the two-fold-axis

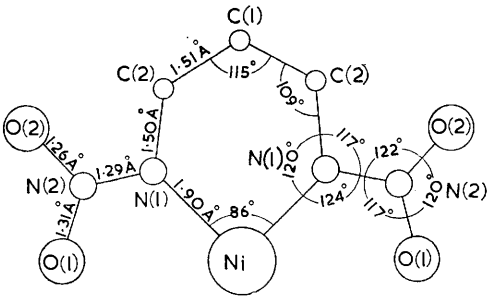

FIGURE 3. Numbering of the atoms, and bond lengths (Å) and angles

respectively, 1·86, 1·85 ± 0·015, and 1·911 ± 0·014 Å. Within the ligand, there are several features of interest. The nitro-group is not symmetrical, one of the N–O bonds being longer than normal and the angles correspondingly altered. The N–N bond is strikingly short (1·29 Å; e.s.d. 0·01 Å) and must have considerable double-bond character; the N–N single bond length is 1·46 Å (*e.g.*, in hydrazine and dimethylhydrazine); the double-bond length is 1·25 Å [N_2F_2, 1·25 Å; $N_2(CH_3)_2$, 1·24 Å].[7] The marked double-bond character of the N–N linkage is characteristic of nitramines. It has been found in ethylenedinitramine [8] (N–N = 1·33 Å) and its sodium salt [9] (N–N = 1·28 Å), and also, less marked, in cyclotrimethylenetrinitramine [10] (N–N = 1·36 and 1·41 Å) and cyclotetramethylenetetranitramine [11] (N–N = 1·35 and 1·37 Å). Consistent with this partial double bond it is also characteristic that there is planarity of the six atoms comprising the O_2N–NHR system; in the nickel complex, the atoms in O_2N–N(Ni)C are found in a plane. It is the planar configuration of this system which holds the nitro-group oxygen atoms in such a position, relative to the nickel, that octahedral co-ordination of the nickel is barred. Only a slight

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rotation of the N–N bond would suffice to carry the oxygen away from the octahedral site sufficiently to allow the approach of, say, a water molecule. It is believed that a distortion of this kind does occur when the salt is dissolved in water, when, because of the thermal motion and buffetting of solvent molecules, the octahedral site is reached with such frequency by solvent molecules that the nickel passes into d^2sp^3 hybridisation. The solution should then be paramagnetic, but we have not yet been able to confirm this.

Turning to the crystal structure as a whole, the anions, each of an overall flat-ellipsoidal shape, are packed in a thick layer on the mirror plane $z = 0$. Above (and below) this, another thick layer, on the mirror planes $z = c/2$, is formed by the potassium ions and their associated water molecules. The layers are held together by electrostatic forces and hydrogen bonding. In the anion layer, the non-planar methylene chains are innermost, and the nitro-groups form its surface. The particular oxygen atoms which most project towards the cation–water layer are those (O_2) having the shorter N–O bonds. These

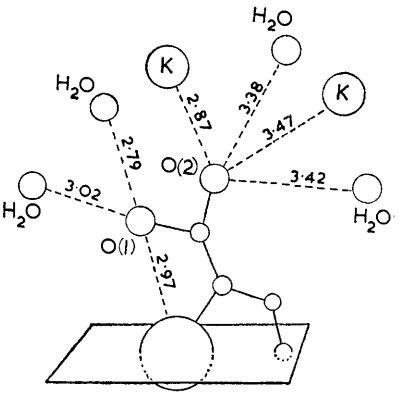

FIGURE 4. Environment of the nitro-group (distances in Å)

oxygen atoms make one direct contact with the potassium ion ($O_2 \cdots K = 2{\cdot}87$ Å). The other nitro-group oxygen atoms (O_1) are those responsible for the steric hindrance of the nickel; these make two contacts of hydrogen-bonding length with water molecules (3·02 and 2·79 Å), besides being fairly close to the nickel. It is presumably the charge on the nickel, together with these hydrogen bonds, which attracts the more negatively charged oxygen atom, O_1, inwards. These oxygen contacts are shown in Figure 4. In the cation–water layer, the potassium atoms have six nearest neighbours; there are three water molecules at 2·7 Å, one water molecule at 2·97 Å, and two nitro-group oxygens at 2·87 Å.

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