

## The Crystal Structure of Bis- $[\mu$ -(tri-1,2,4-triazolo- $N^1, N^2$ )-triaquonickel]nickel Hexanitrate Dihydrate, $[(H_2O)_3(C_2H_3N_3)_3Ni]_2Ni(NO_3)_6(H_2O)_2$

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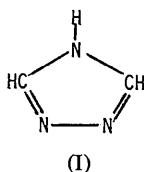
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The crystal structure of bis- $[\mu$ -(tri-1,2,4-triazolo- $N^1, N^2$ )-triaquonickel]nickel hexanitrate dihydrate,  $[(H_2O)_3(C_2H_3N_3)_3Ni]_2Ni(NO_3)_6(H_2O)_2$ , has been solved by the Patterson method. This compound crystallizes in the monoclinic system with  $a = 14.261$  (8),  $b = 11.745$  (6),  $c = 14.948$  (8) Å,  $\beta = 127.13$  (4)°, space group  $P2_1/c$ ,  $\rho_c = 1.84$  g.cm<sup>-3</sup>, and  $Z = 2$ . The structure consists of discrete centrosymmetric trinuclear cations,  $[(H_2O)_3(C_2H_3N_3)_3Ni]_2Ni^{6+}$ , in which the central nickel ion is joined to each terminal nickel ion by three planar triazole molecule bridges. The nickel-nickel distance is 3.737 Å. Three molecules of water complete the octahedral coordination of the terminal nickel ions. The N-H groups in the triazole rings and the coordinated water molecules participate in hydrogen bonding with the nitrate groups and non-coordinating water molecules. All hydrogen atoms in this structure were located in a difference map. Final refinement by three-dimensional anisotropic least-squares analysis resulted in an  $R$  value of 0.045 based upon 5201 observed reflections.

### Introduction

The spectroscopic and magnetic properties of paramagnetic polynuclear inorganic complexes have been studied extensively recently in an effort to determine the nature of the metal-metal exchange interactions which result in reduced magnetic moments (Kokoszka & Gordon, 1969). To undertake a thorough analysis of the magnetic properties of clusters of interacting paramagnetic ions, however, the structure of the polynuclear species and its orientation in the unit cell must be known.

The ligand 1,2,4-triazole (I) contains two nitrogen atoms which coordinate to metal ions



and, as these donor atoms are adjacent, triazole may act as a metal-metal bridge in the formation of polymeric species. Cupric chloride, for example, forms a 1:1 complex with triazole in which a single ligand molecule bridges between pairs of cupric ions along infinite chains (Jarvis, 1962). A 1:2 complex of  $Ni(NO_3)_2$  and triazole has been shown to contain linear clusters of three nickel ions bridged by six triazole molecules (Reimann & Zocchi, 1968). In this report the detailed geometry of the trinuclear cation is presented and the hydrogen bonding network which involves the N-H groups, water molecules, and nitrate groups is described.

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### Experimental

The compound bis- $[\mu$ -(tri-1,2,4-triazolo- $N^1, N^2$ )-triaquonickel]nickel hexanitrate dihydrate,



separates as purple-blue plates from an aqueous solution (1:2) of  $Ni(NO_3)_2$  and 1,2,4-triazole. Cell data were obtained from zero and upper level precession photographs taken with Mo  $K\alpha$  ( $\lambda = 0.7107$  Å) radiation. Systematic extinctions ( $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ) are consistent with the monoclinic space group  $P2_1/c$ .

To determine more precise unit-cell dimensions, a single crystal was mounted on a diffractometer and the  $2\theta$  angles of 26 strong reflections were measured with Mo radiation ( $\lambda = 0.710688$  Å) (weighted average for  $K\alpha_1$  and  $K\alpha_2$ ). The approximate cell parameters determined from the precession photographs were then refined by least-squares analysis to obtain the optimum agreement between the observed and calculated  $2\theta$  angles. The X-ray density, calculated from the refined cell parameters and assuming  $Z = 2$ , is 1.84 g.cm<sup>-3</sup>. This compares with the observed density of 1.85 g.cm<sup>-3</sup> which was measured by flotation. A summary of the crystal data is given in Table 1.

Table 1. Crystal data for bis- $[\mu$ -(tri-1,2,4-triazolo- $N^1, N^2$ -triaquonickel)]nickel hexanitrate dihydrate,  $[(H_2O)_3(C_2H_3N_3)_3Ni]_2Ni(NO_3)_6(H_2O)_2$

$a = 14.261$ (8) Å	Space group $P2_1/c$
$b = 11.745$ (6)	$Z = 2$
$c = 14.948$ (8)	$\rho_c = 1.85$ g.cm <sup>-3</sup>
$\beta = 127.13$ (4)°	$\rho_c = 1.84$ g.cm <sup>-3</sup>
Systematic extinctions	
$h0l$	$l = 2n + 1$
$0k0$	$k = 2n + 1$

For the structure determination, a crystal ( $\sim 0.2 \times 0.2 \times 0.2$  mm) was oriented with the  $a$  axis along the  $\phi$  axis of the diffractometer. Angular settings were computed from the refined cell parameters and the known orientation of the crystal. The  $2\theta$  settings for measuring peak intensities were calculated using a wavelength of  $0.710688 \text{ \AA}$  (weighted average of  $K\alpha_1$  and  $K\alpha_2$ ) for all reflections with  $2\theta \leq 65^\circ$ . Background settings for each calculated  $2\theta$  were determined from the expression  $2\theta \pm \Delta 2\theta$  where  $\Delta 2\theta = 1.80 + 1.0 \tan \theta$  is the scan range recommended by Alexander & Smith (1962).

Intensities of reflections with  $2\theta \leq 65^\circ$  were measured automatically by the stationary-crystal stationary-counter method. Molybdenum radiation was used with a  $\beta$  filter of  $0.025$  mm niobium. The detector was a scintillation counter equipped with a pulse-height analyzer. Attenuation filters (niobium) were used in the measurement of intensities for which the counting rate exceeded 20,000 counts per second. Coincidence losses were thus kept below two per cent. The counting time was 10 seconds for a peak and each background. During data collection the intensities of standard reflections were measured periodically to monitor possible changes in source intensity and crystal decomposition. The crystal orientation was checked every few hours. Approximately 150 reflections measured at the beginning of the data collection process were repeated after all other data were taken. These measurements agreed to within about 3%.

The observed peak height intensities,  $I_o$ , were converted into integrated intensities,  $I_i$ , by utilizing a curve of  $I_i/I_o$  versus  $2\theta$ . This curve was determined by manually measuring both the integrated and peak height intensities of reflections covering the  $2\theta$  range of measurement. These reflections, as well as reflections from which the cell parameters were determined, were traced on a strip-chart recorder. The tracings show no significant variation in either peak width or peak shape as a function of  $\psi$  or  $\phi$ . The  $I_i/I_o$  curve varies between 1.0 at the lowest values of  $2\theta$  and 1.29 at the  $2\theta$  maximum of  $65^\circ$ . Reflections for which the net counts observed did not exceed zero by at least twice the standard deviation involved in making the measurements were labeled unobserved and assigned a net number of counts equal to one standard deviation. Of the 6860 reflections measured, 5201 were observed and 1659 were unobserved. These data were corrected for Lorentz and polarization factors but no corrections were applied for anomalous scattering or absorption. The linear absorption coefficient for



is  $15.2 \text{ cm}^{-1}$ . The average error in the intensities due to neglect of the absorption correction is estimated to be approximately 5–6%.

### Determination of the structure

A three-dimensional Patterson map was calculated using the complete set of data. The number, size, and

location of the largest peaks in this map indicated that the structure contains two sets of crystallographically inequivalent nickel atoms. One set of peaks corresponds to nickel atoms in general positions and the other set to nickel atoms in  $\bar{1}$  special positions at  $(0,0,0)$  and  $(\frac{1}{2}, \frac{1}{2}, 0)$ . The distance between the general position and special position nickel atoms ( $\sim 3.7 \text{ \AA}$ ) suggested that triazole molecules bridge between these atoms. Three sets of triazole peaks were located in the Patterson map between the general and special position nickel atoms. Three water molecules were also located approximately  $2 \text{ \AA}$  from the general position nickel atoms. In all, six coordination sites for each nickel atom were assigned on the basis of Patterson peaks. These atoms define a complex trinuclear cation consisting of a linear array of three nickel atoms with the central nickel atom bridged to the two terminal nickel atoms by triazole rings. The coordination of the terminal nickel atoms is completed by three molecules of water.

An electron density Fourier synthesis, with phases determined by the trial model, was then calculated. Three nitrate groups and one water molecule were located in this synthesis. Full-matrix isotropic least-squares analysis (*ORFLS*) was carried out on this model. Scattering factors for neutral nickel, nitrogen, hydrogen, carbon and singly negative oxygen were taken from *International Tables for X-ray Crystallography* (1962). Anomalous scattering contributions were not included. The quantity minimized in this refinement was  $\sum W(|F_o| - |F_c|)^2$  with the following weighting scheme:  $W=1$  for  $|F_o| < 50$  and  $W=50/|F_o|$  for  $|F_o| > 50$ . The unobserved reflections were given zero weight in the refinement unless  $|F_c|$  exceeded  $|F_o|$ . When this occurred unit weight was assigned. As a result of the refinement, the agreement index,  $R$ , where

$$R = \sum (|F_o| - |F_c|) / \sum |F_o|,$$

based upon 5201 observed reflections was 0.099. A difference electron density ( $F_o - F_c$ ) map was then calculated and no peaks comparable with those in the electron density map were observed. This indicated that, except for hydrogen atoms, the model was complete.

The structure was next refined by block-diagonal anisotropic least-squares analysis (*BLOKLS*). After two cycles the  $R$  value diminished to 0.053. A final difference electron density ( $F_o - F_c$ ) map was then computed and the positions of all seventeen hydrogen atoms were easily located. To complete the refinement of the structure the hydrogen atom contribution to the structure factors were included but their coordinates and temperature factors (isotropic  $B=3.5$ ) were held constant. Three cycles of block-diagonal anisotropic least-squares refinement on the complete model resulted in an  $R$  value of 0.045. The final weighted  $R$  value was 0.056 and the average shift divided by error was 0.148. In Table 2 final positional parameters are given. In Table 3 anisotropic thermal parameters and

root-mean-square amplitudes are presented. Structure factors are listed in Table 4.

Table 2. Atomic coordinates

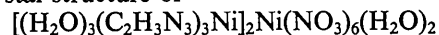
	x	y	z
Ni(1)	0	0	0
Ni(2)	0.26488 (3)	0.16793 (3)	0.08559 (3)
N(1)	0.14665 (18)	0.02973 (19)	0.16607 (17)
N(2)	0.24636 (18)	0.08680 (19)	0.19572 (18)
N(3)	0.27394 (21)	0.02862 (21)	0.34812 (18)
N(4)	-0.00201 (17)	0.17307 (19)	0.96143 (18)
N(5)	0.09669 (18)	0.23273 (19)	-0.00734 (19)
N(6)	0.94511 (22)	0.34612 (21)	0.89752 (22)
N(7)	0.11180 (18)	0.95968 (19)	0.95612 (18)
N(8)	0.20875 (18)	0.02349 (20)	0.98793 (18)
N(9)	0.20564 (22)	0.87249 (23)	0.90269 (21)
N(10)	0.11396 (26)	0.10830 (25)	0.71879 (23)
N(11)	0.69199 (24)	0.10740 (26)	0.43465 (23)
N(12)	0.57811 (24)	0.23228 (28)	0.57360 (25)
C(1)	0.32115 (22)	0.08438 (26)	0.30536 (21)
C(2)	0.16584 (23)	-0.00463 (24)	0.25948 (21)
C(3)	0.06269 (25)	0.33663 (25)	0.95316 (26)
C(4)	0.90812 (23)	0.24307 (25)	0.90461 (24)
C(5)	0.26335 (23)	0.96888 (25)	0.95509 (23)
C(6)	0.11213 (25)	0.86937 (25)	0.90464 (25)
O(1)	0.43536 (16)	0.10498 (19)	0.16843 (18)
O(2)	0.32885 (20)	0.30871 (21)	0.18699 (23)
O(3)	0.28699 (19)	0.25344 (21)	-0.02154 (18)
O(4)	0.17544 (26)	0.05152 (25)	0.69990 (29)

Table 2 (cont.)

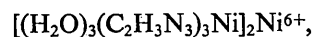
	x	y	z
O(5)	0.03318 (29)	0.05984 (34)	0.70997 (34)
O(6)	0.13794 (32)	0.20927 (25)	0.74789 (26)
O(7)	0.61664 (25)	0.04936 (31)	0.43155 (23)
O(8)	0.79565 (25)	0.10165 (37)	0.51686 (27)
O(9)	0.66238 (25)	0.17041 (28)	0.35390 (23)
O(10)	0.68487 (20)	0.23232 (24)	0.65645 (20)
O(11)	0.50926 (21)	0.16468 (25)	0.57271 (24)
O(12)	0.54112 (30)	0.29539 (40)	0.49409 (32)
O(13)	0.55355 (24)	0.11817 (24)	0.77644 (25)

## Description of the structure

The crystal structure of



consists of discrete trinuclear cations,



linked to one another by N-H...O and O-H...O hydrogen bonds. One such cation is shown in Fig. 1. All unique coordination bond distances and angles are given in Table 5. The packing of the cations in the monoclinic unit-cell is shown in Fig. 2. Fig. 3 shows the immediate environment about a single cation. Hydrogen bonding data are summarized in Table 6.

Table 3. Anisotropic thermal parameters and root-mean-square displacements

	Anisotropic thermal parameters*						R.m.s. displacements (Å)		
	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{23}$	$10^5\beta_{31}$	$\mu(1)$	$\mu(2)$	$\mu(3)$
Ni(1)	154 (2)	248 (3)	216 (2)	-15 (2)	85 (2)	2(2)	0.100	0.130	0.140
Ni(2)	188 (2)	285 (2)	265 (2)	-31 (2)	105 (2)	9 (2)	0.109	0.138	0.157
N(1)	251 (12)	369 (14)	269 (12)	-42 (11)	128 (10)	-2 (11)	0.125	0.149	0.166
N(2)	251 (13)	336 (14)	281 (12)	-46 (11)	121 (11)	-14 (11)	0.122	0.153	0.164
C(1)	292 (16)	478 (19)	275 (14)	-61 (14)	105 (13)	5 (14)	0.128	0.165	0.194
N(3)	406 (16)	428 (16)	245 (12)	-12 (13)	129 (12)	8 (12)	0.132	0.172	0.189
C(2)	360 (17)	417 (18)	295 (14)	-6 (14)	176 (13)	19 (13)	0.145	0.160	0.173
N(4)	204 (12)	318 (14)	325 (13)	-20 (11)	117 (10)	22 (11)	0.115	0.146	0.174
N(5)	242 (13)	288 (13)	377 (14)	-25 (11)	150 (11)	38 (11)	0.122	0.140	0.184
C(3)	399 (18)	316 (17)	536 (20)	1 (15)	236 (16)	57 (16)	0.145	0.162	0.214
N(6)	404 (16)	342 (16)	524 (17)	125 (13)	215 (14)	102 (14)	0.128	0.184	0.216
C(4)	301 (16)	397 (18)	393 (17)	46 (14)	145 (14)	63 (14)	0.134	0.168	0.195
N(7)	277 (13)	334 (14)	322 (13)	-38 (11)	174 (11)	-41 (11)	0.130	0.149	0.162
N(8)	270 (13)	373 (15)	331 (13)	-27 (11)	168 (11)	-10 (11)	0.131	0.161	0.163
C(5)	333 (17)	459 (19)	393 (17)	35 (14)	226 (14)	-10 (15)	0.140	0.168	0.183
N(9)	444 (17)	463 (17)	450 (16)	56 (14)	290 (15)	-52 (14)	0.144	0.178	0.197
C(6)	400 (12)	1381 (18)	441 (18)	-21 (15)	249 (16)	-62 (15)	0.155	0.161	0.188
O(1)	244 (12)	485 (15)	432 (14)	7 (11)	111 (11)	52 (12)	0.125	0.180	0.213
O(2)	443 (16)	529 (17)	775 (20)	200 (13)	359 (16)	302 (15)	0.136	0.182	0.268
O(3)	424 (15)	634 (18)	444 (14)	125 (13)	244 (13)	-90 (13)	0.142	0.173	0.237
N(10)	601 (21)	480 (20)	450 (18)	-18 (17)	253 (17)	33 (15)	0.175	0.184	0.221
O(4)	817 (24)	588 (21)	1174 (30)	-172 (18)	729 (24)	-166 (20)	0.179	0.209	0.296
O(5)	768 (26)	1121 (35)	1379 (38)	-211 (25)	757 (28)	-162 (30)	0.182	0.278	0.324
O(6)	1293 (35)	489 (20)	710 (23)	-60 (22)	481 (24)	-64 (18)	0.182	0.228	0.316
N(11)	468 (19)	615 (22)	435 (17)	-48 (16)	203 (15)	85 (16)	0.167	0.181	0.231
O(7)	645 (22)	1243 (34)	526 (19)	-317 (22)	227 (17)	182 (21)	0.183	0.186	0.339
O(8)	489 (20)	1600 (44)	681 (23)	-144 (25)	71 (18)	405 (27)	0.162	0.238	0.384
O(9)	651 (21)	930 (27)	593 (19)	-85 (20)	257 (17)	329 (19)	0.163	0.203	0.312
N(12)	427 (18)	665 (23)	582 (20)	-20 (17)	282 (17)	107 (18)	0.163	0.191	0.238
O(10)	413 (16)	778 (22)	517 (17)	-108 (15)	195 (14)	122 (16)	0.159	0.188	0.264
O(11)	449 (17)	756 (22)	802 (22)	-72 (16)	383 (17)	112 (18)	0.151	0.218	0.264
O(12)	706 (27)	1609 (48)	955 (31)	-128 (29)	191 (24)	670 (32)	0.192	0.227	0.424
O(13)	688 (21)	597 (21)	758 (22)	136 (17)	385 (18)	145 (17)	0.182	0.228	0.251

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

Table 4. Observed and calculated structure factors ( $\times 10$ )

The columns are  $h, l, F_o$  and  $F_c$  respectively. Reflections for which the net number of counts did not exceed zero by at least twice the standard deviation are marked by an L. The value assigned to the observed intensities for these reflections is equal to one standard deviation.

$h$	$l$	$F_o$	$F_c$	$h$	$l$	$F_o$	$F_c$	$h$	$l$	$F_o$	$F_c$	$h$	$l$	$F_o$	$F_c$
0	0	150	156	16	-1	218	220	16	-15	80	81	2	0	446	451
0	1	348	358	16	1	272	272	16	15	226	228	2	1	688	688
0	2	534	546	16	2	326	326	16	30	390	390	2	2	1030	1030
0	3	720	732	16	3	380	380	16	45	510	510	2	3	1372	1372
0	4	906	918	16	4	434	434	16	60	570	570	2	4	1714	1714
0	5	1092	1104	16	5	488	488	16	75	630	630	2	5	2056	2056
0	6	1278	1290	16	6	542	542	16	90	690	690	2	6	2398	2398
0	7	1464	1476	16	7	596	596	16	105	750	750	2	7	2740	2740
0	8	1650	1662	16	8	650	650	16	120	810	810	2	8	3082	3082
0	9	1836	1848	16	9	704	704	16	135	870	870	2	9	3424	3424
0	10	2022	2034	16	10	758	758	16	150	930	930	2	10	3766	3766
0	11	2208	2220	16	11	812	812	16	165	990	990	2	11	4108	4108
0	12	2394	2406	16	12	866	866	16	180	1050	1050	2	12	4450	4450
0	13	2580	2592	16	13	920	920	16	195	1110	1110	2	13	4792	4792
0	14	2766	2778	16	14	974	974	16	210	1170	1170	2	14	5134	5134
0	15	2952	2964	16	15	1028	1028	16	225	1230	1230	2	15	5476	5476
0	16	3138	3150	16	16	1082	1082	16	240	1290	1290	2	16	5818	5818
0	17	3324	3336	16	17	1136	1136	16	255	1350	1350	2	17	6160	6160
0	18	3510	3522	16	18	1190	1190	16	270	1410	1410	2	18	6502	6502
0	19	3696	3708	16	19	1244	1244	16	285	1470	1470	2	19	6844	6844
0	20	3882	3894	16	20	1298	1298	16	300	1530	1530	2	20	7186	7186
0	21	4068	4080	16	21	1352	1352	16	315	1590	1590	2	21	7528	7528
0	22	4254	4266	16	22	1406	1406	16	330	1650	1650	2	22	7870	7870
0	23	4440	4452	16	23	1460	1460	16	345	1710	1710	2	23	8212	8212
0	24	4626	4638	16	24	1514	1514	16	360	1770	1770	2	24	8554	8554
0	25	4812	4824	16	25	1568	1568	16	375	1830	1830	2	25	8896	8896
0	26	5000	5012	16	26	1622	1622	16	390	1890	1890	2	26	9238	9238
0	27	5186	5198	16	27	1676	1676	16	405	1950	1950	2	27	9580	9580
0	28	5374	5386	16	28	1730	1730	16	420	2010	2010	2	28	9922	9922
0	29	5560	5572	16	29	1784	1784	16	435	2070	2070	2	29	10264	10264
0	30	5748	5760	16	30	1838	1838	16	450	2130	2130	2	30	10606	10606
0	31	5934	5946	16	31	1892	1892	16	465	2190	2190	2	31	10948	10948
0	32	6122	6134	16	32	1946	1946	16	480	2250	2250	2	32	11290	11290
0	33	6308	6320	16	33	2000	2000	16	495	2310	2310	2	33	11632	11632
0	34	6496	6508	16	34	2054	2054	16	510	2370	2370	2	34	11974	11974
0	35	6682	6694	16	35	2108	2108	16	525	2430	2430	2	35	12316	12316
0	36	6870	6882	16	36	2162	2162	16	540	2490	2490	2	36	12658	12658
0	37	7056	7068	16	37	2216	2216	16	555	2550	2550	2	37	13000	13000
0	38	7244	7256	16	38	2270	2270	16	570	2610	2610	2	38	13342	13342
0	39	7430	7442	16	39	2324	2324	16	585	2670	2670	2	39	13684	13684
0	40	7618	7630	16	40	2378	2378	16	600	2730	2730	2	40	14026	14026
0	41	7804	7816	16	41	2432	2432	16	615	2790	2790	2	41	14368	14368
0	42	7992	8004	16	42	2486	2486	16	630	2850	2850	2	42	14710	14710
0	43	8178	8190	16	43	2540	2540	16	645	2910	2910	2	43	15052	15052
0	44	8366	8378	16	44	2594	2594	16	660	2970	2970	2	44	15394	15394
0	45	8552	8564	16	45	2648	2648	16	675	3030	3030	2	45	15736	15736
0	46	8740	8752	16	46	2702	2702	16	690	3090	3090	2	46	16078	16078
0	47	8926	8938	16	47	2756	2756	16	705	3150	3150	2	47	16420	16420
0	48	9114	9126	16	48	2810	2810	16	720	3210	3210	2	48	16762	16762
0	49	9300	9312	16	49	2864	2864	16	735	3270	3270	2	49	17104	17104
0	50	9488	9500	16	50	2918	2918	16	750	3330	3330	2	50	17446	17446
0	51	9674	9686	16	51	2972	2972	16	765	3390	3390	2	51	17788	17788
0	52	9862	9874	16	52	3026	3026	16	780	3450	3450	2	52	18130	18130
0	53	10048	10060	16	53	3080	3080	16	795	3510	3510	2	53	18472	18472
0	54	10236	10248	16	54	3134	3134	16	810	3570	3570	2	54	18814	18814
0	55	10422	10434	16	55	3188	3188	16	825	3630	3630	2	55	19156	19156
0	56	10610	10622	16	56	3242	3242	16	840	3690	3690	2	56	19498	19498
0	57	10796	10808	16	57	3296	3296	16	855	3750	3750	2	57	19840	19840
0	58	10984	10996	16	58	3350	3350	16	870	3810	3810	2	58	20182	20182
0	59	11170	11182	16	59	3404	3404	16	885	3870	3870	2	59	20524	20524
0	60	11358	11370	16	60	3458	3458	16	900	3930	3930	2	60	20866	20866
0	61	11544	11556	16	61	3512	3512	16	915	3990	3990	2	61	21208	21208
0	62	11732	11744	16	62	3566	3566	16	930	4050	4050	2	62	21550	21550
0	63	11918	11930	16	63	3620	3620	16	945	4110	4110	2	63	21892	21892
0	64	12106	12118	16	64	3674	3674	16	960	4170	4170	2	64	22234	22234
0	65	12292	12304	16	65	3728	3728	16	975	4230	4230	2	65	22576	22576
0	66	12480	12492	16	66	3782	3782	16	990	4290	4290	2	66	22918	22918
0	67	12666	12678	16	67	3836	3836	16	1005	4350	4350	2	67	23260	23260
0	68	12854	12866	16	68	3890	3890	16	1020	4410	4410	2	68	23602	23602
0	69	13040	13052	16	69	3944	3944	16	1035	4470	4470	2	69	23944	23944
0	70	13228	13240	16	70	3998	3998	16	1050	4530	4530	2	70	24286	24286
0	71	13414	13426	16	71	4052	4052	16	1065	4590	4590	2	71	24628	24628
0	72	13602	13614	16	72	4106	4106	16	1080	4650	4650	2	72	24970	24970
0	73	13788	13800	16	73	4160	4160	16	1095	4710	4710	2	73	25312	25312
0	74	13976	13988	16	74	4214	4214	16	1110	4770	4770	2	74	25654	25654
0	75	14162	14174	16	75	4268	4268	16	1125	4830	4830	2	75	25996	25996
0	76	14350	14362	16	76	4322	4322	16	1140	4890	4890	2	76	26338	26338
0	77	14536	14548	16	77	4376	4376	16	1155	4950	4950	2	77	26680	26680
0	78	14724	14736	16	78	4430	4430	16	1170	5010	5010	2	78	27022	27022

Table 4 (cont.)

10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000
----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	--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Table 4 (cont.)

A large table with multiple columns of numerical data, organized into several sections. The table contains various numbers, some with superscripts, and is divided into sections labeled 'n = 11', 'n = 9', and 'n = 7'. The data is presented in a grid-like format with rows and columns of values.

Table 4 (cont.)

Distance		Angle	
Ni(1)-N(1)	2.095 (2)* Å	O(1)-Ni(2)-O(3)	87.94 (0.11)
Ni(1)-N(4)	2.108 (3)	O(2)-Ni(2)-O(3)	88.45 (0.13)
Ni(1)-N(7)	2.112 (3)	N(2)-Ni(2)-N(5)	92.94 (0.11)
Ni(2)-O(1)	2.087 (2)	N(2)-Ni(2)-O(1)	91.57 (0.11)
Ni(2)-O(2)	2.048 (3)	N(2)-Ni(2)-N(8)	90.17 (0.11)
Ni(2)-O(3)	2.069 (3)	N(2)-Ni(2)-O(2)	89.81 (0.13)
Ni(2)-N(2)	2.052 (3)	N(2)-Ni(2)-O(3)	178.19 (0.08)
Ni(2)-N(5)	2.059 (2)	N(5)-Ni(2)-O(1)	175.26 (0.13)
Ni(2)-N(8)	2.059 (2)	N(5)-Ni(2)-N(8)	91.73 (0.10)
		N(5)-Ni(2)-O(2)	91.03 (0.10)
		N(5)-Ni(2)-O(3)	87.60 (0.11)
		O(1)-Ni(2)-N(8)	86.78 (0.10)
		N(8)-Ni(2)-O(2)	177.24 (0.09)
		N(8)-Ni(2)-O(3)	91.54 (0.12)

Table 5. Coordination bond distances and angles

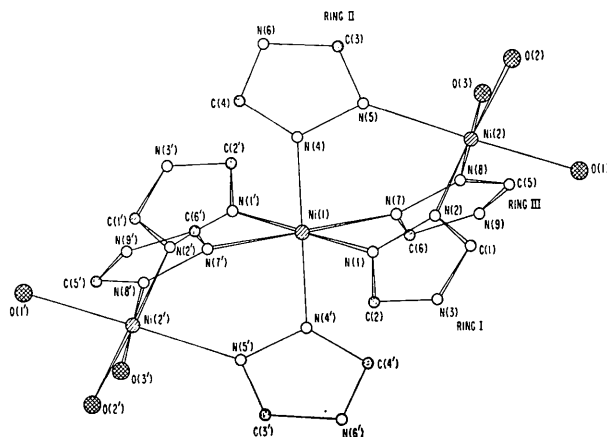
Table 5 (cont.)

Distance	Angle
N(1)-Ni(1)-N(4)	90.14 (0.08)°
N(1)-Ni(1)-N(7)	90.26 (0.11)
N(7)-Ni(1)-N(4)	91.11 (0.11)
O(1)-Ni(2)-O(2)	90.45 (0.10)

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

Table 6. *Hydrogen bonding distances*

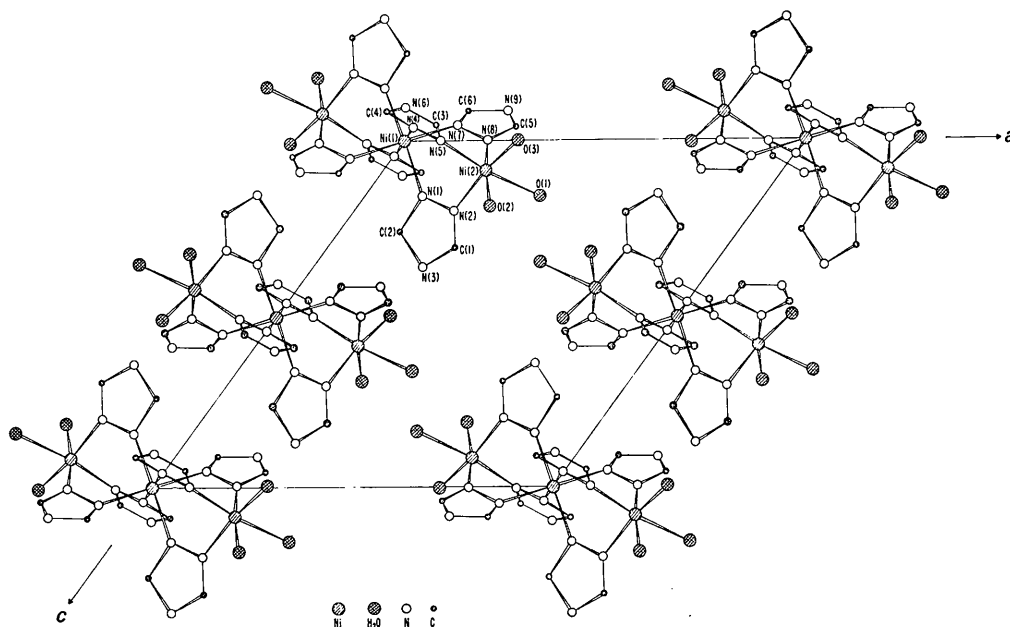
Hydrogen-bonded system	Distance between terminal atoms
N(3)—H···O(7)	2.813 Å
N(6)—H···O(4)	2.806
N(9)—H···O(10)	2.756
O(1)—H···O(9)	2.815
O(1)—H···O(13)	2.723
O(2)—H···O(4)	2.833
O(2)—H···O(13)	2.761
O(3)—H···O(6)	2.797
O(3)—H···O(11)	2.751
O(13)—H···O(9)	2.783
O(13)—H···O(11)	2.766

Fig. 1. The structure of the trinuclear  $[(\text{H}_2\text{O})_3(\text{C}_2\text{H}_3\text{N}_2)_3\text{Ni}]_2\text{Ni}_6^+$  cation.*The complex cation*

The data of Table 5 show that the coordination polyhedra about the central and terminal nickel atoms are slightly distorted octahedra. As these octahedra are linked by relatively rigid triazole molecules, the line defined by Ni(2)—Ni(1)—Ni(2') is, approximately, a threefold axis of the cation. In depicting the cation, it is convenient to consider its structure in relation to the highest possible point symmetry for the isolated cation, namely,  $D_{3d}$ . In  $D_{3d}$  symmetry, centrosymmetrically related pairs of triazole rings and oxygen atoms would be coplanar. Moreover, the line of intersection of the three planes so defined would be the threefold axis of the cation. Accordingly, the normal to each ring would make an angle of  $90^\circ$  with the reference line [Ni(2)—Ni(1)—Ni(2')], the extended plane of each ring would contain all three nickel atoms, and the angles between the planes of the triazole rings would be  $120^\circ$ .

The normals to rings I, II, and III make angles of  $86.9$ ,  $89.1$ , and  $89.8^\circ$  respectively, with the line defined by Ni(2)—Ni(1)—Ni(2'). The deviations from  $90^\circ$  represent small twists of the rings about axes perpendicular to the reference axis. Neither of the nickel atoms is coplanar with the extended planes of the triazole rings. Ni(1) lies  $0.087$  Å and Ni(2) lies  $0.113$  Å in opposite senses from the extended plane of ring I; Ni(1) lies  $0.033$  Å and Ni(2) lies  $0.023$  Å in opposite senses from the extended plane of ring II; Ni(1) lies  $0.584$  Å and Ni(2) lies  $0.570$  Å in the same sense from the extended plane of ring III.

None of the coordinated oxygen atoms deviates greatly from coplanarity with a triazole ring. O(3) lies

Fig. 2. Projection of the structure down the  $b$  axis showing the locations of the  $[(\text{H}_2\text{O})_3(\text{C}_2\text{H}_3\text{N}_2)_3\text{Ni}]_2\text{Ni}_6^+$  cations.



0.26 Å from the extended plane of ring I and O(1) lies 0.11 Å and O(2) lies 0.32 Å from the extended planes of ring II and ring III, respectively.

The angle between rings I and II ( $120.5^\circ$ ) is close to the trigonal angle but ring III is displaced toward ring I ( $112.2^\circ$ ) and away from ring II ( $126.2^\circ$ ). In view of the octahedral coordination about the nickel ions, the angular displacement of ring III from its idealized location and the fact that the nickel atoms lie furthest from the extended plane of that ring are consistent.

Although the triazole rings bridge between identical atoms the Ni-N distances involving the central nickel atom are longer than those involving the terminal nickel atoms. The central nickel atom, however, is coordinated by six triazole rings while the terminal nickel atoms are coordinated by three rings and three oxygen atoms. The repulsion between the rings and average coordinate bond distances increase with the number of rings coordinated to a metal ion which would account for the difference in the Ni-N distances noted above. However, the longer Ni-N distances involving the central nickel ion may also receive a contribution arising from a greater repulsion between bonding electrons. In the case of  $\text{Ni}^{2+}$  in an octahedral field, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are singly occupied. The central nickel ion is coordinated by six relatively strong electron donor nitrogen atoms while the terminal nickel atoms are coordinated by three nitrogen atoms and three relatively weaker electron donor water molecules. The reduction in repulsion between electrons occupying shared orbitals belonging to the terminal nickel atoms compared with those belonging to the central nickel atoms would also act to permit closer approach of the triazole molecules to the terminal nickel atoms.

### The triazole rings

All three triazole rings were found by least-squares analysis to be planar to within experimental error. The equations for these planes and the individual atom deviations from them are given in Table 7.

Table 7. Distances from the ring atoms to the least-squares planes of the triazole rings

The equation of the plane in direct space is given by  $PX + QY + RZ = S$ . For ring I,  $P = -7.3031$ ,  $Q = 10.073$ ,  $R = 0.1769$ ,  $S = 0.08749$ ; for ring II,  $P = -6.4416$ ,  $Q = 3.2712$ ,  $R = 14.177$ ,  $S = 14.210$ ; for ring III,  $P = 0.41525$ ,  $Q = -5.7577$ ,  $R = 10.130$ ,  $S = 0.58370$ .

Ring I		Ring II		Ring III	
	Distance		Distance		Distance
N(1)	-0.001	N(4)	0.001	N(7)	0.002
N(2)	-0.001	N(5)	-0.001	N(8)	-0.002
C(1)	0.002	C(3)	0.000	C(5)	0.001
C(2)	0.002	C(4)	-0.001	C(6)	-0.001
N(3)	-0.003	N(6)	0.001	N(9)	0.000

Although the triazole rings are crystallographically independent, corresponding bond distances and angles

agree closely. Observed bond distances and angles in the three rings are given in Fig. 4. The composite triazole ring (average of the corresponding parameters for the three rings) has a twofold axis within the standard deviations of these parameters. In the triazole-cupric chloride complex (Jarvis, 1962), the triazole rings actually occupy crystallographic twofold axes. The only significant difference in the triazole molecule reported here is in the N-C single-bond distance which is 0.038 Å longer than in the cupric chloride complex.

The structure of crystalline 1,2,4-triazole has been determined at room temperature by Deuschl (1965) and

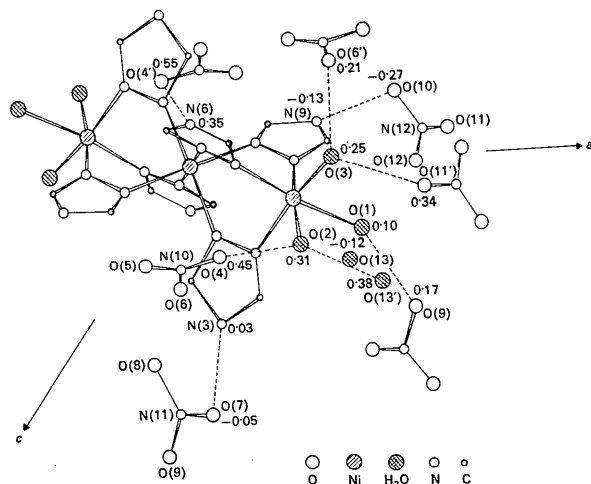


Fig. 3. Unique hydrogen bonds involving one trinuclear cation. The decimal numbers give the heights of the atoms in units of  $b$ .

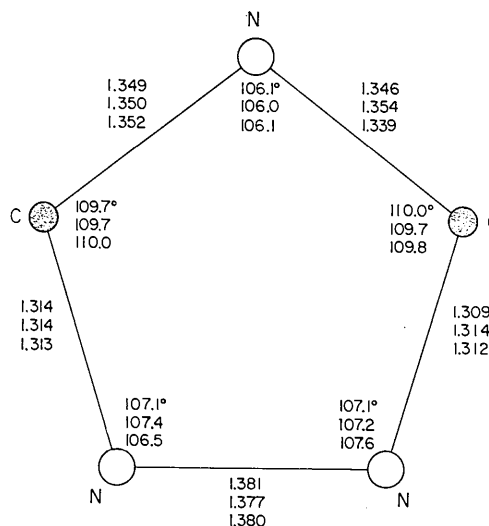


Fig. 4. The triazole molecule. Bond distances and angles for the three independent rings are indicated. The average standard deviations in the bond lengths are as follows: N-N, 0.005; C-N 0.006 Å. The average standard deviation in the bond angles is 0.25°.

at  $-155^{\circ}\text{C}$  by Goldstein, Ladell & Abowitz (1969). In the low temperature study the hydrogen atoms were located and triazole was shown to exist exclusively in tautomeric form (II). However, in coordinated triazole, bridging through adjacent nitrogen atoms and



$\text{N-H}\cdots\text{O}$  hydrogen bonding stabilize tautomer (I). The different relative positions of the double bonds in two tautomers precludes a meaningful comparison between corresponding bonds.

The bond distances for molecular triazole have been calculated by Dewar & Gleicher (1966) assuming tautomeric form (I). The calculated  $\text{N-N}$  (1.362 Å) and  $\text{N=C}$  (1.283 Å) distances are shorter and the calculated  $\text{N-C}$  (1.401 Å) distance is longer than observed in the coordinated molecule. Although the differences are qualitatively consistent with changes expected to occur with coordination, the magnitudes of the differences appear too large to attribute to such interactions. This is particularly true of the calculated  $\text{N-C}$  bond distance which is about 0.05 Å longer than observed in the coordinated molecule. The observed  $\text{N-C}$  distances in tautomer (II), in the complexes and in similar ring sys-

tems are all considerably shorter than the calculated distance of 1.401 Å.

#### Nitrate groups

The configurations of the three unique nitrate anions are shown in Fig. 5. Each nitrate group is planar within the standard deviations of the atoms normal to the calculated planes. The average deviation of the atoms from the least-squares plane of  $\text{N}(10)\text{O}(4)\text{O}(5)\text{O}(6)$  is 0.004 Å and, in the remaining nitrate groups, it is 0.002 Å. Two oxygen atoms in each of the nitrate groups participate in hydrogen bonding with water molecules or with  $\text{N-H}$  groups (see Table 6). These six  $\text{N-O}$  bond distances are longer than those which involve the other three oxygen atoms,  $\text{O}(5)\text{O}(8)\text{O}(12)$ , which do not participate in hydrogen bonding. The average difference in the  $\text{N-O}$  bond distances between the hydrogen bonded and non-hydrogen-bonded oxygen atoms is 0.030 Å. The lengthening of  $\text{N-O}$  bond distances in nitrate groups is also observed when the oxygen atom is coordinated to a metal ion. Distances as long as 1.33 Å have been reported for  $\text{N-O}$  bonds in coordinated nitrate groups (Addison & Sutton, 1967). The thermal parameters of the atoms in the nitrate groups corroborate these conclusions regarding hydrogen bonding and  $\text{N-O}$  bond distances. Table 3 shows that the root-mean-square amplitudes of vibration of the non-hydrogen-bonded oxygen atoms,  $\text{O}(5)$ ,  $\text{O}(8)$  and  $\text{O}(12)$  are larger than those of the hydrogen-bonded oxygen atoms.

All computer calculations on this structure were performed using the *Program System for X-ray Crystallography* 1967, developed at the University of Maryland in collaboration with the National Bureau of Standards and the Geological Survey. The authors would also like to thank Floyd Mauer for his assistance in the use of the diffractometer and Dr Alan Mighell for his aid in adapting programs specifically for our use.

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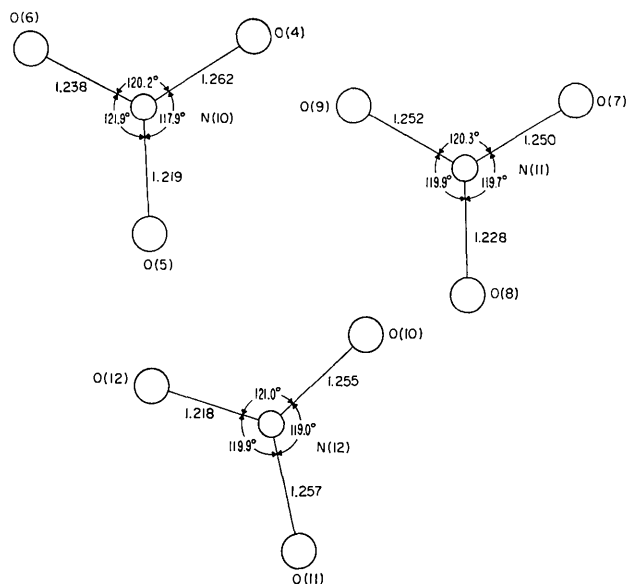


Fig. 5. The nitrate groups. Bond distances and angles are indicated. The average standard deviation in the  $\text{N-O}$  bond lengths is 0.005 Å. The average standard deviation in the  $\text{O-N-O}$  bond angles is  $0.37^{\circ}$ .