

**Discussion.** The cytosine ring atoms are coplanar to within 0.026 Å. Bond lengths in the ring are similar to those reported for other protonated cytosines (Viswamitra, Reddy, Lin & Sundaralingam, 1971). The sugar ring is puckered with C(3') *endo*, i.e. lying 0.53 Å out of the mean plane through the other ring atoms, on the same side as C(5'). In terms of the mean plane through all five ring atoms, C(2') is *exo* and C(3') is *endo*, the sugar pucker can therefore be described as  ${}^3T_2$  (Young & Wilson, 1975). The mean plane of the sugar ring makes an angle of 107.3° with that of the cytosine ring. The conformation about C(4')–C(5') is *gauche-gauche* with torsion angles O(5')–C(5')–C(4')–

C(3') 54.0 and O(5')–C(5')–C(4')–O(1') –64.6°, in line with other structures of this type. The glycosidic torsion angle C(2)–N(1)–C(1')–O(1') is –163.6, similar to the –162.8° observed in cytidine (Furberg, Petersen & Rømming, 1965), and consistent with other structures containing the *endo* C(3') atom (Young & Wilson, 1975).

The non-bonded distances involved in possible hydrogen bonds are analysed in Table 5. Since the coordinates of the hydrogen atoms involved, except H(5), were allowed to refine freely, the O–H and N–H distances are shorter than the true internuclear separations, as normally found in X-ray diffraction studies. The hydrogen bonds link the ions into layers perpendicular to **a**.

Table 5. Possible hydrogen bonds (Å)

O(2')–H(8)	0.94	N(3)····O(11)	2.725
O(3')–H(10)	0.80	N(4) <sup>iv</sup> ····O(12)	3.033
O(5')–H(14)	0.77	N(4)····O(10)	2.955
N(3)–H(1)	0.79	C(6)····O(5')	3.205
N(4)–H(2)	0.87	H(8) <sup>i</sup> ····O(10)	2.11
N(4)–H(3)	0.82	H(10) <sup>ii</sup> ····O(5')	1.98
C(6)–H(5)	1.01	H(14)····O(2) <sup>iii</sup>	2.29
		H(1)····O(11)	1.94
O(2') <sup>i</sup> ····O(10)	2.986	H(2) <sup>iv</sup> ····O(12)	2.16
O(3') <sup>ii</sup> ····O(5')	2.775	H(3)····O(10)	2.14
O(5')····O(2) <sup>iii</sup>	2.968	H(5)····O(5')	2.27

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z)

(i)	x,	y, 1.0+z	(iii)	x, 1.0+y,	z		
(ii)	1.0–x,	0.5+y,	–z	(iv)	x,	y–1.0,	z

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## Hexakis(imidazole)nickel(II) Chloride Tetrahydrate

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**Abstract.** Ni(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>6</sub>(Cl)<sub>2</sub>·4H<sub>2</sub>O, *M* = 610.1; triclinic, *P* $\bar{1}$ ; *a* = 9.084 (2), *b* = 8.808 (2), *c* = 10.566 (2) Å,  $\alpha$  = 83.16 (2),  $\beta$  = 104.89 (2),  $\gamma$  = 118.28 (2)°, *V* = 719.5 Å<sup>3</sup>; *Z* = 1, *D<sub>m</sub>* = 1.41 (2), *D<sub>c</sub>* = 1.408 g cm<sup>–3</sup>. Final *R* = 0.043. The crystal structure consists of six planar imidazole rings coordinated to Ni with an extensive network of hydrogen bonding.

**Introduction.** Crystals of the title compound were prepared by slow evaporation of an aqueous solution of NiCl<sub>2</sub> and imidazole (Im) in a molecular ratio of approximately 1:6. Analysis calculated from the empirical formula: C, 35.4; H, 5.3; N, 27.6; found: C, 34.2; H, 5.0; N, 27.0. Precession photographs of several

crystals did not reveal symmetry greater than anorthic and the reduced cell matrix (No. 31, *International Tables for X-ray Crystallography*, 1969) confirmed that the metric and crystal symmetry are triclinic. The structure was successfully refined in the space group *P* $\bar{1}$ .

A spherical crystal of 0.1 mm radius was mounted on a diffractometer. With Mo *K* $\alpha$  radiation ( $\lambda$  = 0.71069 Å) and  $\theta_{\max}$  = 30°, a total of 3940 reflections were measured with the stationary-crystal stationary-counter technique. 508 of these reflections with *I* < 2 $\sigma$ (*I*) { $\sigma$ (*I*) = [peak + background + (0.005 peak)<sup>1/2</sup>] } were included in the refinement only if *F<sub>c</sub>* > *F<sub>o</sub>*. All reflections were included in the calculation of both *R* and *R<sub>w</sub>*. A graph giving peak/integrated ratio as a function of 2 $\theta$  was determined. The data were then converted to integrated intensities and corrected for Lorentz and polarization factors. No absorption correction was re-

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quired ( $\mu=9.0 \text{ cm}^{-1}$ ). The atomic positions of all heavy atoms and that of one H atom of a water molecule were determined by a combination of Patterson and Fourier methods. In the refinement of this model, the ring H atoms were assigned calculated positional parameters. The thermal parameters were assigned values related to the thermal motion of the atoms to which they are bonded. These parameters were not allowed to shift. The scattering factors used for  $\text{Ni}^{2+}$ , N, C,  $\text{Cl}^-$  and the anomalous dispersion correction parameters for Ni and Cl were those reported in *International Tables for X-ray Crystallography* (1968). The scattering factor adopted for the O atoms was that

given by Hanson, Herman, Lea & Skillman (1964). All the parameters of the initial model, including isotropic extinction correction, were refined by full-matrix least-squares analysis to a conventional  $R$  value of 0.045 and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.051$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = [\sigma(F_o)]^{-2}$ . The final extinction parameter was  $21.2 (4) \times 10^{-3}$ .

The average and maximum shift/error for atomic parameters were 0.04 and 1.04 respectively. In a final difference map no peak exceeded  $0.30 \text{ e } \text{Å}^{-3}$ . No attempt was made to refine the structure in the non-centrosymmetric space group  $P1$ . Final atomic parameters are listed in Tables 1 and 2, while selected inter-

Table 1. Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{Å}^2 \times 10^4$ )

The temperature factor is in the form:  $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
<b>Ring 1</b>									
N(11)	356 (3)	1981 (3)	1198 (2)	350 (13)	353 (13)	270 (11)	164 (11)	51 (9)	-21 (9)
C(11)	-301 (4)	1745 (4)	2239 (3)	489 (19)	520 (19)	366 (16)	247 (16)	94 (13)	-45 (13)
N(21)	211 (4)	3267 (4)	2788 (2)	726 (21)	580 (18)	398 (15)	377 (16)	172 (14)	-72 (13)
C(21)	1241 (5)	4543 (4)	2081 (3)	887 (29)	459 (20)	595 (22)	299 (20)	213 (20)	-88 (17)
C(31)	1314 (4)	3743 (4)	1102 (3)	629 (22)	389 (17)	476 (18)	199 (16)	193 (16)	-17 (14)
<b>Ring 2</b>									
N(12)	1433 (3)	1929 (3)	-1241 (2)	341 (13)	329 (12)	265 (11)	151 (10)	63 (9)	10 (9)
C(12)	772 (4)	2592 (4)	-2290 (3)	503 (19)	460 (17)	349 (15)	239 (15)	119 (13)	68 (13)
N(22)	2019 (4)	3851 (3)	-2812 (2)	585 (19)	458 (15)	428 (15)	246 (14)	203 (13)	185 (12)
C(22)	3557 (5)	4006 (4)	-2072 (3)	516 (22)	550 (21)	611 (22)	149 (17)	239 (17)	152 (17)
C(32)	3189 (4)	2826 (4)	-1113 (3)	366 (17)	518 (19)	453 (17)	164 (15)	114 (13)	80 (14)
<b>Ring 3</b>									
N(13)	2305 (3)	36 (3)	1153 (2)	308 (13)	354 (12)	280 (11)	136 (10)	35 (9)	9 (9)
C(13)	3304 (4)	1015 (4)	2193 (3)	383 (17)	487 (18)	372 (16)	176 (14)	-10 (12)	-24 (13)
N(23)	4674 (3)	738 (4)	2679 (2)	341 (15)	568 (17)	436 (15)	192 (13)	-82 (11)	-65 (13)
C(23)	4564 (5)	-474 (5)	1925 (3)	518 (22)	840 (27)	624 (23)	445 (21)	-18 (17)	-96 (19)
C(33)	3099 (4)	-900 (4)	983 (3)	423 (19)	587 (20)	508 (19)	281 (16)	12 (14)	-102 (15)
Ni	0	0	0	287 (3)	309 (3)	230 (3)	128 (2)	40 (2)	-4 (2)
O(1)	5419 (4)	6665 (4)	5120 (3)	775 (21)	776 (19)	1499 (29)	328 (16)	367 (19)	-155 (19)
O(2)	1734 (4)	10404 (3)	5250 (3)	877 (21)	657 (16)	974 (20)	392 (15)	388 (16)	99 (14)
Cl	2065 (1)	6972 (1)	5047 (1)	402 (5)	474 (5)	387 (4)	184 (4)	33 (3)	-2 (3)

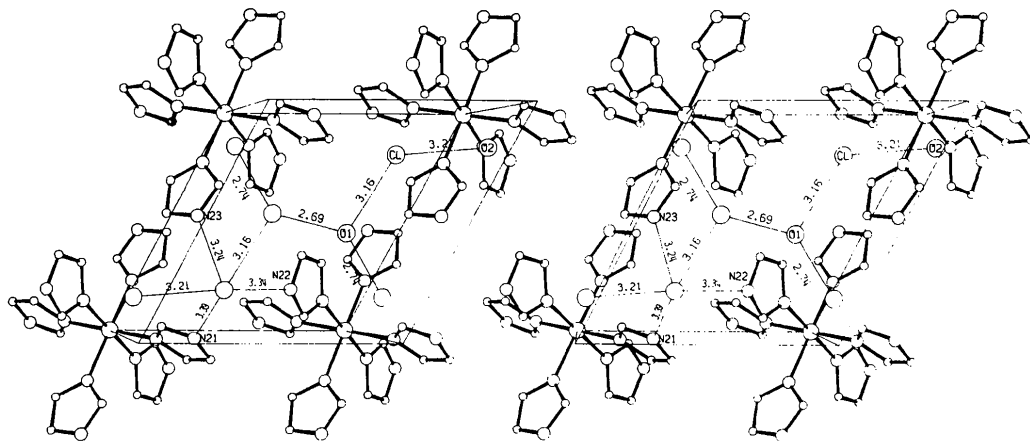


Fig. 1. Stereoscopic view of four  $\text{Ni}(\text{Im})^{2+}$  ions and the proposed hydrogen-bonding network. Within the Im rings the larger circles represent N. The view is down  $z$  with  $y$  across the page.

atomic distances and angles are given in Table 3.\* Because there are three crystallographically independent Im rings, the ring atoms are labeled with a two-number designation. The second number is the ring number and the first is the atom number within the ring. Computer programs used for the determination and refinement were those of X-RAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31866 (28 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Hydrogen-atom coordinates* ( $\times 10^3$ )

The H atoms H(1*x*), H(2*x*), and H(3*x*) (*x*=ring number) are labeled with the same numbers as the C atoms to which they are bonded. The atom H(4*x*) is bonded to the N atom N(2*x*), and the H atom H(O2) is bonded to the oxygen atom O(2).

Ring		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
Ring 1	H(11)	-106	60	257	50
	H(41)	-9	343	353	57
	H(21)	182	581	225	75
	H(31)	196	434	41	50
Ring 2	H(12)	-48	221	-265	50
	H(42)	186	451	-355	57
	H(22)	472	483	-221	75
	H(32)	406	263	-41	50
Ring 3	H(13)	307	185	257	50
	H(43)	556	129	341	57
	H(23)	539	-95	204	75
	H(33)	266	-177	27	50
	H(O2)	178	944	500	92

Table 3. *Bond lengths* (Å) *and angles* (°)

The second digit (ring designation) of the atom label is omitted as it may be obtained from the appropriate column heading.

	Ring 1	Ring 2	Ring 3
Ni—N(1)	2.130 (3)	2.140 (2)	2.120 (3)
N(1)—C(1)	1.334 (4)	1.328 (4)	1.322 (3)
C(1)—N(2)	1.346 (5)	1.348 (4)	1.340 (5)
N(2)—C(2)	1.369 (4)	1.364 (5)	1.359 (6)
C(2)—C(3)	1.350 (6)	1.349 (5)	1.355 (5)
C(3)—N(1)	1.384 (4)	1.384 (4)	1.376 (6)
C(3)—N(1)—C(1)	105.4 (3)	105.0 (2)	105.4 (3)
N(1)—C(1)—N(2)	110.2 (3)	110.9 (3)	110.8 (3)
C(1)—N(2)—C(2)	108.4 (3)	107.9 (3)	108.1 (3)
N(2)—C(2)—C(3)	105.9 (3)	106.0 (3)	105.9 (4)
C(2)—C(3)—N(1)	110.0 (3)	110.1 (3)	109.7 (3)
Ni—N(1)—C(1)	125.7 (2)	125.3 (2)	126.1 (3)

**Discussion.** The structure consists of Ni(Im)<sub>6</sub><sup>2+</sup> ions, Cl<sup>-</sup> ions and water molecules. The structure and the proposed hydrogen-bonding scheme are shown in Fig. 1. The Im rings are planar within experimental error. Each crystallographically independent ring exhibits the same pattern of ring bond distances and angles (Table 3). In each ring, the shortest bond is N(1)—C(1) (1.32–1.33 Å), and the longest is N(1)—C(3) (1.38 Å). Similar ring parameters are observed in the Im ligand of related complexes (Santoro, Mighell, Zocchi & Reimann, 1969; Prince, Mighell, Reimann & Santoro, 1972). The Im ring contains two distinct types of N atoms – the ‘pyridine’-type (>N) which coordinates to the Ni<sup>2+</sup> ion and the ‘pyrrole’-type (>N—H) which is hydrogen-bonded to the Cl<sup>-</sup> ion.

In the complex cation, six Im rings are coordinated to the Ni<sup>2+</sup> ion *via* the pyridine-type N atom. The approximate point symmetry of the six N(2) atoms about the Ni is *O<sub>h</sub>*. The Ni<sup>2+</sup> is displaced by 0.05, 0.11 and 0.03 Å from the least-squares plane defined by Im rings 1, 2 and 3 respectively. The planes of the three independent rings (Table 1) are nearly orthogonal to each other, with angles between the planes of the rings ranging from 84.9 to 88.6°. Each Cl<sup>-</sup> ion is hydrogen-bonded (*via* a N—H hydrogen atom) to three Im rings in three translationally related molecules of the complex (Fig. 1). The Cl<sup>-</sup> is at the apex of a pyramid, 2.25 Å from the plane defined by the three N atoms. The N—H—Cl angles (156–170°) and the N—Cl distances (3.24–3.39 Å) are in good agreement with published data for such hydrogen bonds (Hamilton & Ibers, 1968). The Cl<sup>-</sup> ion is probably involved in an extensive hydrogen-bonding network with the water molecules because of the appropriate O—O and O—Cl<sup>-</sup> distances (see Fig. 1) and the fact that the O atoms and the Cl<sup>-</sup> ions all lie within 0.3 Å of the plane (*x, y, 0.5*).

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