The Structure of Hexakis(imidazole)nickel(II) Diperchlorate

By Gun J. M. Ivarsson and Willis Forsling

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Abstract. $[Ni(C_3H_4N_2)_6](ClO_4)_2$, $(C_{18}H_{24}N_{12}-Ni)^{2+}.2ClO_4^-$, monoclinic, $P2_1/n$, $a = 16.229$ (1), $b = 7.217$ (2), $c = 11.469$ (1) Å, $\beta = 90.00$ (1)°, $Z = 2$, $V = 1343.3$ Å^3, $D_x = 1.640$, $D_m = 1.64$ (1) Mg m^{-3}, μ(Mo $K\alpha$) = 0.99 mm^{-1}. Final $R = 0.060$ for 1936 counter reflexions. The Ni is octahedrally coordinated to six imidazole N atoms (2.125, 2.131, 2.134 Å) and the $Ni(C_3H_4N_2)_6^{2+}$ complex cations thus formed are linked together through perchlorate anions by hydrogen bonds.

Introduction. Crystals were prepared by adding 2 g imidazole to 10 ml 0.755 M Ni(ClO$_4$)$_2$ solution. The precipitate of Ni(C$_3$H$_4$N$_2$)$_6$(ClO$_4$)$_2$ was filtered and the filtrate left to evaporate. Well defined light blue-violet needles formed within a few days. Weissenberg photographs showed monoclinic symmetry and systematic extinctions were found for $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$. The cell dimensions were refined from a Guinier–Hägg powder photograph taken with Cu $K\alpha$ radiation ($\lambda = 1.54051$ Å) with Si ($a = 5.43059$ Å) as internal standard. The density was determined by flotation in bromoform/xylol. A crystal (0.10 × 0.17 × 0.12 mm) was mounted and rotated around b parallel to the 0.17 mm edge. Intensities for 2982 reflexions (sin $\theta_{max} = 0.46$) were measured on a linear diffractometer (Philips Pailred) with graphite-monochromatized Mo $K\alpha$ radiation. Reflexions with $I < \sigma(I)$ were omitted, leaving a data set of 1936 unique reflexions. Besides corrections for Lorentz and polarization effects, an absorption correction was applied. The transmission factor varied from 0.890 to 0.913. The Ni and Cl atoms were located from a Patterson map, and the remaining non-hydrogen atoms by Fourier methods. Full-matrix least-squares refinement with anisotropic temperature factors gave $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.068$. The function minimized was $\sum w(\Delta F^2)^2$, where $w = 1/\sigma^2$ with $\sigma^2 = [0.85\sigma(F_o)]^2 + (0.08F_o)^2$.

The H atoms were located from a difference synthesis. When the positional parameters and an overall isotropic temperature factor of 3.5 Å^2 for these H atoms were included in the refinement, R decreased to 0.060. Scattering factors for Ni^{2+}, Cl$^-$, O, N, C and H were used (*International Tables for X-ray Crystallography*, 1974).

Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *with e.s.d.'s in parentheses*

	x	y	z
Ni	0	0	0
Cl	1295 (1)	2563 (2)	5119 (1)
O(1)	1856 (4)	2415 (9)	6051 (5)
O(2)	474 (4)	2408 (14)	5487 (5)
O(3)	1494 (4)	1363 (15)	4224 (7)
O(4)	1347 (6)	4397 (12)	4681 (7)
N(1)	−375 (3)	1591 (6)	1469 (4)
N(2)	−526 (4)	2728 (9)	3221 (5)
N(3)	1051 (3)	1738 (7)	−218 (4)
N(4)	2041 (3)	3733 (8)	142 (6)
N(5)	−705 (3)	1690 (6)	−1156 (4)
N(6)	−1005 (4)	3444 (8)	−2646 (4)
C(1)	−127 (4)	1516 (9)	2563 (6)
C(2)	−1057 (4)	3647 (9)	2556 (6)
C(3)	−974 (4)	2944 (9)	1469 (6)
C(4)	1331 (4)	2989 (9)	503 (6)
C(5)	2216 (4)	2916 (11)	−902 (7)
C(6)	1613 (4)	1728 (10)	−1113 (6)
C(7)	−402 (4)	2770 (9)	−1960 (5)
C(8)	−1730 (5)	2750 (10)	−2262 (6)
C(9)	−1549 (4)	1631 (9)	−1336 (6)
H(1)	957 (5)	282 (12)	381 (6)
H(2)	24 (5)	73 (11)	283 (6)
H(3)	861 (5)	438 (11)	271 (6)
H(4)	881 (5)	322 (11)	89 (7)
H(5)	246 (5)	457 (11)	48 (6)
H(6)	106 (5)	334 (11)	122 (7)
H(7)	766 (5)	163 (11)	390 (6)
H(8)	658 (5)	404 (11)	328 (7)
H(9)	405 (5)	85 (11)	171 (6)
H(10)	519 (5)	209 (11)	294 (6)
H(11)	273 (5)	189 (11)	246 (6)
H(12)	306 (5)	396 (11)	423 (6)

The computer programs were those of Antti (1976). The final positional parameters are given in Table 1.*

Discussion. The formation of complexes between Ni^{II} and imidazole (ImH) has been studied in the ionic media 3 M NaClO$_4$ and 3 M NaCl as well as in

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Table 2. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ni–N(1)	2·128 (4)	N(1)–C(1)	1·320 (8)	N(3)–C(4)	1·307 (8)	N(5)–C(7)	1·304 (8)
Ni–N(3)	2·131 (5)	C(1)–N(2)	1·325 (9)	C(4)–N(4)	1·336 (9)	C(7)–N(6)	1·348 (9)
Ni–N(5)	2·134 (5)	N(2)–C(2)	1·328 (9)	N(4)–C(5)	1·365 (10)	N(6)–C(8)	1·352 (10)
		C(2)–C(3)	1·353 (9)	C(5)–C(6)	1·323 (10)	C(8)–C(9)	1·366 (9)
		C(3)–N(1)	1·378 (8)	C(6)–N(3)	1·373 (9)	C(9)–N(5)	1·387 (8)
Cl–O(1)	1·409 (6)	N(2)–H(1)	0·70 (7)	N(4)–H(5)	0·98 (8)	N(6)–H(9)	0·90 (8)
Cl–O(2)	1·402 (7)	C(1)–H(2)	0·88 (8)	C(4)–H(6)	0·96 (8)	C(7)–H(10)	0·98 (8)
Cl–O(3)	1·381 (9)	C(2)–H(3)	0·77 (8)	C(5)–H(7)	0·83 (8)	C(8)–H(11)	0·96 (8)
Cl–O(4)	1·418 (9)	C(3)–H(4)	0·77 (8)	C(6)–H(8)	0·89 (8)	C(9)–H(12)	1·00 (8)

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N(1)–Ni–N(3)	90·3 (2)	N(1)–C(1)–N(2)	111·4 (6)	N(3)–C(4)–N(4)	112·4 (6)
N(1)–Ni–N(5)	91·7 (2)	C(1)–N(2)–C(2)	108·7 (6)	C(4)–N(4)–C(5)	106·2 (6)
N(3)–Ni–N(5)	91·1 (2)	N(2)–C(2)–C(3)	106·1 (6)	N(4)–C(5)–C(6)	106·6 (6)
Ni–N(1)–C(1)	130·0 (4)	C(2)–C(3)–N(1)	109·6 (6)	C(5)–C(6)–N(3)	110·6 (6)
Ni–N(1)–C(3)	125·8 (4)	C(3)–N(1)–C(1)	104·2 (5)	C(6)–N(3)–C(4)	104·2 (5)
Ni–N(3)–C(4)	127·7 (4)				
Ni–N(3)–C(6)	128·1 (4)	O(1)–Cl–O(2)	112·3 (4)	N(2)···O(2)	3·074 (9)
Ni–N(5)–C(7)	125·4 (4)	O(1)–Cl–O(3)	111·4 (4)	N(4)···O(3)	3·128 (0)
Ni–N(5)–C(9)	127·2 (4)	O(1)–Cl–O(4)	107·5 (5)	N(6)···O(4)	2·860 (9)
		O(2)–Cl–O(3)	113·3 (5)		
N(5)–C(7)–N(6)	110·8 (6)	O(2)–Cl–O(4)	103·8 (6)	N(2)–H(1)···O(2)	152 (8)
C(7)–N(6)–C(8)	108·0 (6)	O(3)–Cl–O(4)	108·0 (5)	N(4)–H(5)···O(3)	165 (6)
N(6)–C(8)–C(9)	106·6 (6)			N(6)–H(9)···O(4)	156 (7)
C(8)–C(9)–N(5)	108·1 (6)				
C(9)–N(5)–C(7)	106·6 (5)				
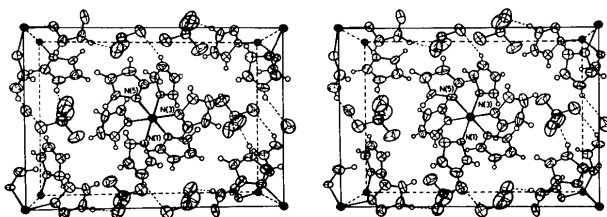
Fig. 1. A stereoscopic representation of the molecular packing in the unit cell. The nickel atoms are illustrated by filled circles. The hydrogen bonds are indicated by dashed lines. Thermal ellipsoids are scaled to include 50% probability.

mixtures of these two with $0 \leq [Cl^-] \leq 3\cdot0\,M$ (Forsling & Sjöberg, 1975; Forsling, 1978). The results obtained in $3\cdot0\,M$ NaClO$_4$ could be explained by the formation of a series of Ni(ImH)$_n^{2+}$ species ($n = 1$–4) and the ternary complex NiOH(ImH)$^+$. As an essential part of these investigations the solid phases obtained from the equilibrium solutions were characterized by X-ray diffraction methods. In the 3 M perchlorate medium, a microcrystalline nickel–hydroxy precipitate was always formed at low ratios of ImH/Ni.

With ImH/Ni > 4 the only crystalline precipitate obtained is the title compound. This compound was found to be built up of discrete Ni(C$_3$H$_4$N$_2$)$_6^{2+}$ cations and perchlorate anions as shown in Fig. 1. The closest cation–anion approach involves the pyrrole (>N–H) N and perchlorate O atoms which are linked by means of hydrogen bonds. The Ni atom, which lies on a center of symmetry, is surrounded by six imidazole N atoms in a slightly distorted octahedral arrangement with an average Ni–N distance of 2·131 Å (range 2·128–

2·134 Å). These distances are in good agreement with those found in similar compounds (Kronopelski, Reimann, Hubbard, Mighell & Santoro, 1976; van Ingen Schenau, 1975; Santoro, Mighell, Zocchi & Reimann, 1969). This is also true for distances and angles within the imidazole rings. The rings are all planar; maximum distances to the least-squares planes through respective ring atoms are 0·009 (9) for the non-hydrogen and 0·15 (9) Å for the H atoms. The distances to the planes from the Ni atom are 0·030 (7), 0·143 (6) and 0·263 (6) Å.

The ClO$_4$ tetrahedron is slightly distorted. Three of the four O atoms in the group are in hydrogen-bond contact with surrounding cations (Fig. 1).

Interatomic distances and angles are given in Table 2.

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