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Bis(iminodiacetamide)nickel(II) Perchlorate

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Abstract. $Ni\{HN(CH_2CONH_2)_2\}_2(ClO_4)_2$, orthorhombic, *Pbca*, $a=15{\cdot}627$ (4), $b=21{\cdot}565$ (4), $c=11{\cdot}120$ (3) Å ($\lambda=0{\cdot}70926$ Å); $M=519{\cdot}88$, $Z=8$, $D_x=1{\cdot}843$, $D_m=1{\cdot}846$ g cm^{-3}. The structure was solved by the symbolic addition method and refined by block-diagonal least-squares methods to give $R=0{\cdot}054$ for the 2817 non-zero reflexions. The two ligand molecules coordinate to the central Ni atom through two imino nitrogen and four amide oxygen atoms in *u-fac* positions, exhibiting a distorted octahedral coordination.

Introduction. The molecular structure of the title complex has been discussed by comparison of the IR and visible spectra with those of the elongated octahedral complex, *s-fac* $Cu\{HN(CH_2CONH_2)_2\}_2(ClO_4)_2$ (Sekizaki, Yamada & Takahashi, 1974), the crystal structure of which has already been reported (Sekizaki, 1974). It has been suggested that the nickel complex is distorted octahedral with the coordination of the ligand through amide oxygen and imino nitrogen atoms, but it is not clear whether it is *u-* or *s-fac*. To find the details of the structure the complex was subjected to an X-ray crystal analysis.

The greenish-blue crystals prepared by the reported method are elongated along the *a* axis. A crystal with a diameter of about 0·3 mm was sealed in a glass capillary. The intensities were collected on a Rigaku automatic four-circle diffractometer (Mo $K\alpha$ radiation, ω–2θ scans). Of a total of 4311 independent reflexions collected in the range of $2\theta<55°$, 2718 greater than $3\sigma(F)$ were used in the analysis. Absorption and extinction corrections were not made because of the small size of the crystal ($\mu r=0{\cdot}4$). The space group *Pbca* was deduced from systematic absences $0kl$, $h0l$ and $hk0$ with k, l and h odd, respectively.

The analysis was carried out by means of a symbolic addition method. The probabilities were calculated using the formula:

$$P=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\sigma_3\,.\,\sigma_2^{-3/2}|E(h)E(h')E(h-h')|\right].$$

After several cycles of $\sum_2$-interaction lists with $P\geq 0{\cdot}90$, 302 reflexions with $|E|\geq 1{\cdot}5$ were phased. Because almost all the reflexions phased at this stage had even h's, the next cycle of interactions was listed with $|E|\geq 0{\cdot}8$* and $P\geq 0{\cdot}75$. As a result, 103 reflexions with odd h's were phased. An E map calculated from these phases yielded 20 atoms. Subsequent three-dimensional electron density maps gave all the remaining non-hydrogen atoms. Of seven peaks around Cl(1), the strongest was assigned to O(101), and the other six broad and weak peaks to O(102)···O(107). The block-diagonal least-squares refinement was carried out for the 2718 non-zero reflexions with the weights 0·5 for $|F_o|<15$ and 1·0 for the others. Each of the weights of the above perchlorate oxygens was included in the refinement. After several cycles of refinements with isotropic, and successively with anisotropic temperature factors, R became 0·059. All the hydrogen atoms were determined by the subsequent difference Fourier synthesis. A structure factor calculation including the hydrogen atoms reduced R to 0·054.*

The Fourier syntheses calculations were carried out with the program written by the author. The *HBLS*-4 program (Ashida, 1967) was used for refinements, *SIGMA* (Ashida, 1967) for $\sum_2$-interaction lists and *ORTEP* (Johnson, 1965) for drawing the thermal ellipsoids. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). All the calculations were carried out on a FACOM 230-35 computer at the Data Processing Centre of this University and on a FACOM 230-60 computer at the Computation Centre of Nagoya University. The final atomic coordinates are listed in Table 1.

Discussion. A projection of the crystal structure along the *b* axis is given in Fig. 1. The anisotropic thermal ellipsoids of the atoms are shown in Fig. 2. Selected bond distances and angles are listed in Table 2. The complex molecule is non-centrosymmetric, with two terdentate ligand molecules coordinating in *u-fac* positions through amide oxygen and imino nitrogen atoms. The coordination-bond distances and angles fall in the ranges 2·01–2·13 Å and 81–108°, respectively. Thus the octahedron is less elongated than observed in the copper(II) complex, but is considerably distorted. This distortion must be due to short C=O bonds in the fused chelate rings. The observed large angle (108°) of N(4)–Ni–N(14) is correlated with this

* Although it is empirically known that the phases determined with respect to $|E|<1{\cdot}5$ are doubtful (Karle & Karle, 1966), the signs of these weak reflexions agreed with those of the F_c values at the final stage of refinement. The details will be discussed elsewhere with some other examples.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31422 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

distortion, rather than due to the repulsion of the two hydrogens bonded to N(4) and N(14), respectively.

The complex ions are connected by hydrogen bonds through N(9^{i})–O(17^{ii}) and O(7^{i})–N(19^{ii}) with the respective distances of 2·93 and 3·00 Å, forming chains parallel to the *a* axis. These chains are con-

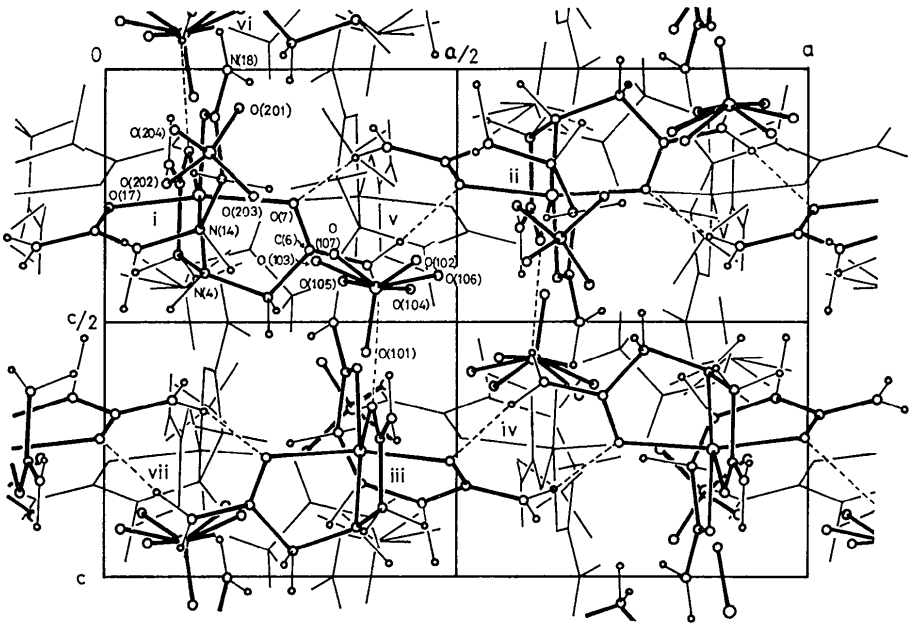

Fig. 1. Projection of the crystal structure along the *b* axis. Broken lines indicate hydrogen bonds among the complex cations. (i) x,y,z; (ii) $\frac{1}{2}+x,y,\frac{1}{2}-z$; (iii) $\frac{1}{2}-x,-y,\frac{1}{2}+z$.

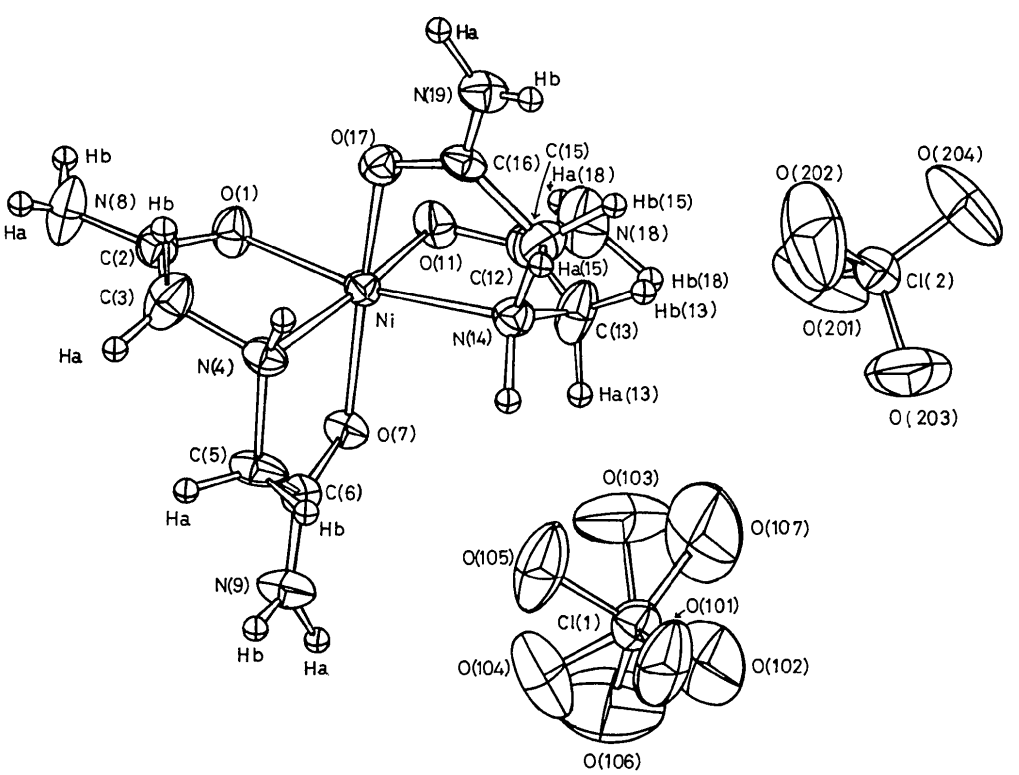

Fig. 2. Thermal ellipsoids of the atoms at 50% probability level. Hydrogen atoms are drawn as spheres with a diameter of 0·1 Å.

Table 1. *Final positional parameters and their e.s.d.'s in parentheses*

Values are given $\times 10^3$ (hydrogen) and $\times 10^4$ (others). The parameters are expressed as fractions of the lattice parameters. The weights are 0·639(*), 0·361(†), and 1·0 (others).

	x	*y*	*z*
Ni	1368 (1)	583 (1)	2512 (1)
Cl(1)	3865 (2)	2292 (1)	4311 (2)
Cl(2)	1469 (2)	3731 (1)	1668 (2)
O(1)	1207 (4)	−223 (3)	1630 (5)
C(2)	1085 (5)	−682 (4)	2286 (7)
C(3)	1060 (6)	−610 (4)	3657 (7)
N(4)	1428 (4)	−10 (3)	4026 (5)
C(5)	2331 (5)	−43 (5)	4474 (7)
C(6)	2934 (5)	223 (4)	3567 (6)
O(7)	2690 (3)	499 (3)	2639 (5)
N(8)	921 (6)	−1240 (3)	1861 (7)
N(9)	3762 (4)	147 (4)	3845 (6)
O(11)	1395 (4)	1024 (3)	896 (5)
C(12)	1572 (5)	1591 (4)	962 (7)
C(13)	1703 (7)	1898 (4)	2163 (7)
N(14)	1360 (4)	1508 (3)	3147 (5)
C(15)	472 (5)	1681 (4)	3535 (8)
C(16)	−158 (5)	1190 (4)	3207 (6)
O(17)	62 (3)	690 (3)	2733 (5)
N(18)	1715 (7)	1930 (4)	−7 (7)
N(19)	−963 (4)	1305 (3)	3482 (6)
O(101)	3730 (6)	2469 (4)	5547 (7)
O(102)*	4451 (10)	2736 (7)	3762 (13)
O(103)*	3045 (8)	2199 (8)	3788 (12)
O(104)*	4358 (10)	1723 (6)	4324 (10)
O(105)†	3382 (19)	1702 (9)	4143 (18)
O(106)†	4761 (16)	2139 (19)	4050 (44)
O(107)†	3241 (31)	2698 (15)	3599 (30)
O(201)	1913 (6)	3386 (5)	760 (7)
O(202)	873 (7)	3341 (4)	2313 (12)
O(203)	2110 (5)	3933 (5)	2499 (10)
O(204)	1007 (5)	4257 (4)	1216 (7)
H*a*C(3)	130	−90	410
H*b*C(3)	45	−65	400
H N(4)	95	15	470
H*a*C(5)	245	−47	470
H*b*C(5)	235	27	520
H*a*N(8)	85	−155	230
H*b*N(8)	95	−132	100
H*a*N(9)	420	30	340
H*b*N(9)	390	−10	440
H*a*C(13)	235	190	235
H*b*C(13)	130	228	205
H N(14)	180	150	395
H*a*C(15)	30	170	470
H*b*C(15)	30	210	340
H*a*N(18)	165	178	−80
H*b*N(18)	205	235	25
H*a*N(19)	−138	102	330
H*b*N(19)	−115	168	385

nected to one another by hydrogen bonds through N(9^{i})–O(1^{iii}) (3·10 Å), two-dimensional sheets thus being formed along the *xz* plane. Perchlorate ions join these sheets together with hydrogen bonds (2·90–3·04 Å). The crystal thus consists of three-dimensional networks of hydrogen bonds connecting the complex and perchlorate ions.

Table 2. *Selected bond distances and angles*

Ni—O(1)	2·012 (5) Å	O(1)—Ni—N(4)	82·6 (2)°
Ni—N(4)	2·116 (5)	O(1)—Ni—O(7)	94·7 (2)
Ni—O(7)	2·078 (4)	N(4)—Ni—O(7)	81·3 (2)
Ni—O(11)	2·034 (5)	O(11)–Ni—N(14)	81·6 (3)
Ni—N(14)	2·118 (5)	O(11)–Ni—O(17)	94·2 (2)
Ni—O(17)	2·069 (4)	N(14)–Ni—O(17)	81·3 (2)
O(1)—C(2)	1·244 (8)	O(1)—Ni—O(11)	88·6 (2)
O(7)—C(6)	1·251 (8)	N(4)—Ni—N(14)	107·7 (3)
O(11)–C(12)	1·256 (9)	Ni—O(1)—C(2)	114·9 (5)
O(17)–C(16)	1·248 (8)	Ni—O(7)—C(6)	113·6 (4)
C(2)—N(8)	1·317 (10)	Ni—O(11)–C(12)	114·1 (5)
C(6)—N(9)	1·340 (9)	Ni—O(17)–C(16)	114·7 (5)
C(12)–N(18)	1·321 (12)	Ni—N(4)—C(3)	106·9 (5)
C(16)–N(19)	1·318 (9)	Ni—N(4)—C(5)	109·6 (5)
		C(3)—N(4)—C(5)	114·8 (6)
C—C	1·490–1·533	Ni—N(14)–C(13)	106·7 (5)
C—N(imino)	1·474–1·500	Ni—N(14)–C(15)	109·5 (5)
Cl—O	1·42 –1·49	C(13)–N(14)–C(15)	114·0 (6)
C—H or			
N—H	0·8 –1·1		

The perchlorate ions are regular tetrahedra and the thermal motions of the oxygen atoms are larger than those of the atoms in the complex ion. In one of the two anions including Cl(1), there are two arrangements of the oxygen atoms: O(101), O(102), O(103), O(104) and O(101), O(105), O(106), O(107), which are roughly related to each other by rotation of the tetrahedral anion by about 60° around the Cl(1)–O(101) bond.

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