

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ni1—N34	2.126 (4)	Ni1—S1	2.561 (2)
Ni1—N1	2.131 (4)	S1—C33	1.846 (5)
Ni1—N23	2.153 (4)	S1—C44	1.849 (5)
Ni1—N12	2.159 (4)	S2—C11	1.836 (5)
Ni1—S2	2.547 (2)	S2—C22	1.837 (6)
N34—Ni1—N1	90.8 (1)	N1—Ni1—S1	96.5 (1)
N34—Ni1—N23	87.0 (1)	N23—Ni1—S1	86.8 (1)
N1—Ni1—N23	176.0 (1)	N12—Ni1—S1	89.1 (1)
N34—Ni1—N12	176.1 (1)	S2—Ni1—S1	174.0 (1)
N1—Ni1—N12	87.1 (1)	C33—S1—C44	101.8 (2)
N23—Ni1—N12	95.2 (1)	C33—S1—Ni1	107.2 (2)
N34—Ni1—S2	96.2 (1)	C44—S1—Ni1	107.8 (2)
N1—Ni1—S2	88.0 (1)	C11—S2—C22	102.0 (3)
N23—Ni1—S2	88.9 (1)	C11—S2—Ni1	108.3 (2)
N12—Ni1—S2	87.1 (1)	C22—S2—Ni1	107.2 (2)
N34—Ni1—S1	87.8 (1)		

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
N3—H3...O48	0.85 (5)	2.04 (5)	2.883 (4)	172 (5)
N14—H14...O48 <sup>i</sup>	0.69 (5)	2.48 (5)	3.066 (4)	144 (5)
N25—H25...O50 <sup>ii</sup>	0.86 (4)	2.02 (4)	2.862 (4)	163 (4)
N36—H36...O50 <sup>iii</sup>	0.82 (4)	2.08 (4)	2.894 (5)	176 (4)
C8—H8...O52	1.05 (5)	2.64 (5)	3.360 (5)	126 (3)
C11—H11...O47 <sup>iv</sup>	1.07 (4)	2.46 (4)	3.355 (6)	141 (3)
C16—H16...O46 <sup>v</sup>	0.95 (4)	2.42 (4)	3.243 (6)	147 (4)
C21—H21...O47	1.13 (5)	2.29 (5)	3.395 (5)	168 (4)
C21—H21...O48 <sup>i</sup>	1.13 (5)	2.60 (5)	3.399 (5)	127 (3)
C27—H27...O51 <sup>v</sup>	0.96 (5)	2.56 (5)	3.435 (5)	151 (4)
C32—H32...O52 <sup>i</sup>	1.04 (4)	2.38 (4)	3.386 (5)	162 (4)
C44—H44...O52	0.98 (5)	2.70 (5)	3.483 (7)	138 (4)

Symmetry codes: (i)  $1-x, -y, 1-z$ ; (ii)  $1+x, y, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $-x, -y, 1-z$ ; (v)  $1-x, -y, -z$ .

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus (Sheldrick, 1991). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Hexakis(*N,N*-dimethylformamide)nickel(II) Diperchlorate

VICKIE MCKEE,<sup>a</sup> TED METCALFE<sup>a</sup> AND JAN WIKAIRA<sup>b</sup>

<sup>a</sup>School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland, and <sup>b</sup>Department of Chemistry, University of Canterbury, Christchurch, New Zealand. E-mail: v.mckee@qub.ac.uk

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## Abstract

The asymmetric unit of  $[\text{Ni}(\text{C}_3\text{H}_7\text{NO})_6](\text{ClO}_4)_2$  contains two independent  $\text{ClO}_4^-$  anions along with two independent halves of the  $[\text{Ni}(\text{dmf})_6]^{2+}$  cation, each  $\text{Ni}^{2+}$  ion being located on a centre of symmetry. The two cations differ in the orientation of the dmf ligands.

## Comment

Hexakis(*N,N*-dimethylformamide)nickel(II) diperchlorate,  $[\text{Ni}(\text{dmf})_6](\text{ClO}_4)_2$ , (I), is a potentially useful source of anhydrous  $\text{Ni}^{2+}$  for syntheses. It can be readily prepared and is surprisingly air-stable.

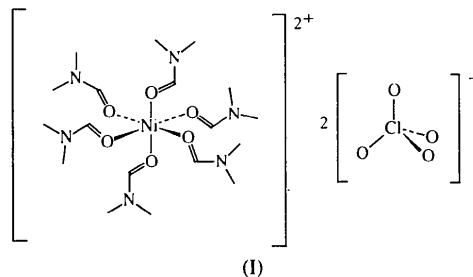


Fig. 1 shows the two independent  $[\text{Ni}(\text{dmf})_6]^{2+}$  cations. The cations can be distinguished by examining the conformation of the dmf ligands about the metal

ions. In the cation centred on Ni2, the planes containing each dmf molecule approximately bisect the (dmf)O—Ni—O(dm) angle involving the other two independent dmf ligands (e.g. the mean plane of O61, C61, N61, C62 and C63 approximately bisects the O41—Ni2—O51 angle). In the cation containing Ni1, one dmf molecule (and its symmetry equivalent) has a different geometry; the mean plane of O21, C21, N21, C22 and C23 almost includes the Ni1—O11 bond. This geometry can be described in terms of the dihedral angles between the carbonyl bond of the dmf ligand in question and the Ni—O bonds to the remaining ligands. These values lie in the range 37–50°, except for those of C21—O21—Ni1—O11 and C21—O21—Ni1—O31a which are 9.55 and 79.5°, respectively. There are no significant interactions apparent between cations or between cations and the perchlorate anions.

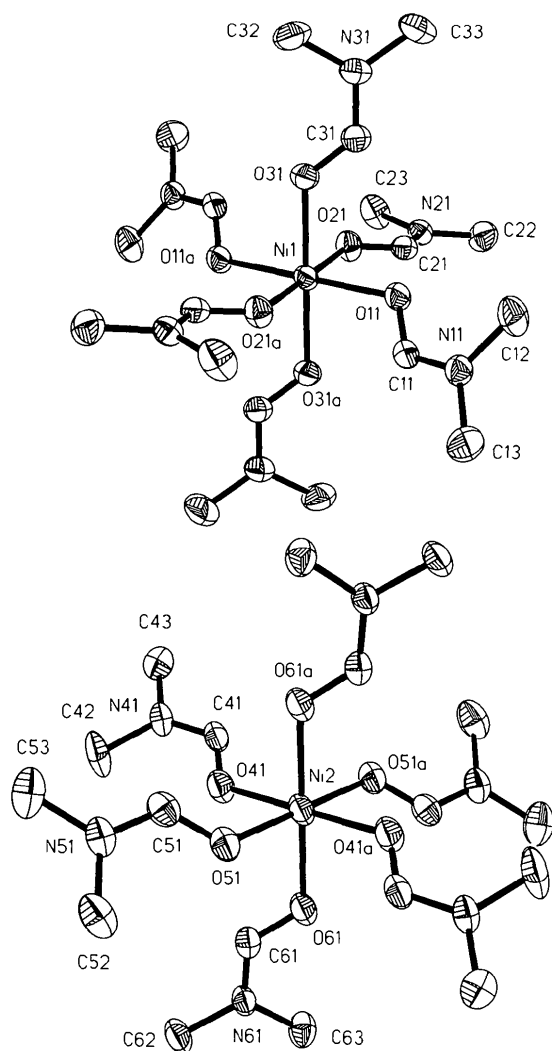


Fig. 1. Perspective views of the two [Ni(dmf)<sub>6</sub>]<sup>2+</sup> cations showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

A search of the April 1995 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed no previous determinations of the [Ni(dmf)<sub>6</sub>]<sup>2+</sup> ion, although a number of related iron complexes have been reported. [Fe(dmf)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> is isomorphous with the present complex (Baumgartner, 1986). The iron(III) analogue [Fe(dmf)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> has also been structurally characterized (Holt, Alcock, Sumner & Asplund, 1979); this cation is centrosymmetric and has the same conformation as that at Ni1, with one pair of dmf ligands 'eclipsed' with respect to one of the other Ni—O bonds.

## Experimental

During our syntheses of macrocyclic nickel complexes, excess Ni<sup>2+</sup> in the preparations was isolated as [Ni(dmf)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> crystals by ether diffusion into dmf solutions. We have obtained identical crystals as by-products of several different macrocyclic syntheses.

### Crystal data

[Ni(C<sub>3</sub>H<sub>7</sub>NO)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>  
*M<sub>r</sub>* = 696.19  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 14.8190 (10) Å  
*b* = 10.7650 (10) Å  
*c* = 20.673 (2) Å  
 $\beta$  = 92.28°  
*V* = 3295.3 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.403 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 27 reflections  
 $\theta$  = 4–13°  
 $\mu$  = 0.817 mm<sup>-1</sup>  
*T* = 158 (2) K  
 Block  
 0.80 × 0.45 × 0.45 mm  
 Green

### Data collection

Siemens P4 four-circle diffractometer  
 1.2°  $\omega$  scans  
 Absorption correction:  $\psi$  scans (SHELXTL/PC; Sheldrick, 1990)  
*T<sub>min</sub>* = 0.695, *T<sub>max</sub>* = 0.769  
 6740 measured reflections  
 5803 independent reflections

4526 observed reflections  
 $[I > 2\sigma(I)]$   
*R<sub>int</sub>* = 0.015  
 $\theta_{\text{max}}$  = 25°  
*h* = 0 → 17  
*k* = -1 → 12  
*l* = -24 → 24  
 3 standard reflections monitored every 97 reflections  
 intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.0407$   
 $wR(F^2) = 0.1109$   
*S* = 1.035  
 5797 reflections  
 386 parameters  
 H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 4.5888P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = -0.001$

$\Delta\rho_{\text{max}} = 0.718 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.506 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL93 (Sheldrick, 1993)  
 Extinction coefficient: 0.0033 (2)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}$
Ni1	0	0	0	0.02512 (13)
O11	0.04507 (13)	0.0422 (2)	0.09247 (9)	0.0315 (4)
C11	0.0581 (2)	-0.0457 (3)	0.13121 (13)	0.0305 (6)
N11	0.0666 (2)	-0.0341 (2)	0.19439 (11)	0.0324 (6)
C12	0.0589 (2)	0.0859 (3)	0.22588 (15)	0.0447 (8)
C13	0.0807 (2)	-0.1424 (3)	0.2359 (2)	0.0495 (9)
O21	0.09164 (13)	0.1163 (2)	-0.04194 (9)	0.0333 (5)
C21	0.1573 (2)	0.1733 (3)	-0.01803 (13)	0.0291 (6)
N21	0.2150 (2)	0.2363 (2)	-0.05226 (11)	0.0305 (5)
C22	0.2920 (2)	0.3007 (3)	-0.0216 (2)	0.0446 (8)
C23	0.2043 (3)	0.2424 (3)	-0.12270 (14)	0.0473 (8)
O31	-0.09083 (13)	0.1420 (2)	0.00085 (9)	0.0318 (5)
C31	-0.0727 (2)	0.2471 (3)	0.02308 (14)	0.0328 (6)
N31	-0.1309 (2)	0.3389 (2)	0.02278 (13)	0.0398 (6)
C32	-0.2218 (2)	0.3243 (3)	-0.0053 (2)	0.0509 (9)
C33	-0.1067 (3)	0.4602 (3)	0.0495 (2)	0.0634 (11)
Ni2	1/2	0	1	0.03266 (15)
O41	0.41499 (14)	-0.0026 (2)	0.91995 (9)	0.0386 (5)
C41	0.3352 (2)	-0.0365 (3)	0.91658 (13)	0.0328 (7)
N41	0.2902 (2)	-0.0593 (2)	0.86211 (11)	0.0345 (6)
C42	0.3361 (3)	-0.0556 (4)	0.80101 (14)	0.0589 (10)
C43	0.1972 (2)	-0.1020 (3)	0.8593 (2)	0.0471 (8)
O51	0.60020 (13)	-0.0629 (2)	0.94236 (9)	0.0364 (5)
C51	0.5822 (2)	-0.1395 (3)	0.89842 (14)	0.0354 (7)
N51	0.6354 (2)	-0.1633 (3)	0.85043 (11)	0.0387 (6)
C52	0.7206 (2)	-0.0983 (4)	0.8447 (2)	0.0516 (9)
C53	0.6094 (3)	-0.2521 (4)	0.7998 (2)	0.0556 (10)
O61	0.53464 (14)	0.1782 (2)	0.97846 (9)	0.0383 (5)
C61	0.5549 (2)	0.2054 (3)	0.92221 (13)	0.0345 (7)
N61	0.5710 (2)	0.3183 (2)	0.90245 (11)	0.0311 (5)
C62	0.5936 (2)	0.3435 (3)	0.83554 (14)	0.0443 (8)
C63	0.5627 (2)	0.4248 (3)	0.94498 (14)	0.0399 (7)
C11	-0.14659 (5)	0.55618 (8)	-0.15182 (4)	0.0444 (2)
O1	-0.1503 (2)	0.5919 (4)	-0.21838 (13)	0.0922 (11)
O2	-0.2362 (2)	0.5515 (3)	-0.1297 (2)	0.0883 (10)
O3	-0.0988 (2)	0.6486 (3)	-0.1171 (2)	0.0951 (11)
O4	-0.1032 (3)	0.4405 (3)	-0.1415 (2)	0.0999 (12)
C12	0.35796 (6)	0.56771 (8)	0.82856 (4)	0.0503 (2)
O5	0.3970 (4)	0.5887 (4)	0.7700 (2)	0.154 (2)
O6	0.3973 (2)	0.6480 (3)	0.87646 (14)	0.0788 (9)
O7	0.3767 (2)	0.4421 (3)	0.8446 (2)	0.0872 (10)
O8	0.2650 (3)	0.5763 (5)	0.8258 (3)	0.179 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ni1—O31	2.037 (2)	Ni2—O41	2.040 (2)
Ni1—O11	2.051 (2)	Ni2—O61	2.040 (2)
Ni1—O21	2.063 (2)	Ni2—O51	2.055 (2)
O31—Ni1—O11'	89.05 (8)	O41''—Ni2—O61	90.67 (8)
O31—Ni1—O11	90.95 (8)	O41—Ni2—O61	89.33 (8)
O31—Ni1—O21	89.69 (8)	O41''—Ni2—O51	92.16 (8)
O31'—Ni1—O21	90.31 (8)	O41—Ni2—O51	87.84 (8)
O11'—Ni1—O21	86.45 (8)	O61—Ni2—O51	89.40 (8)
O11—Ni1—O21	93.55 (8)	O61''—Ni2—O51	90.60 (8)
C11'—O11'—Ni1—O21	-46.1 (2)	C41''—O41''—Ni2—O51	40.5 (2)
C11'—O11'—Ni1—O31	43.7 (2)	C41''—O41''—Ni2—O61	-49.0 (2)
C21—O21—Ni1—O11	9.6 (2)	C51—O51—Ni2—O41	-37.3 (2)
C21'—O21'—Ni1—O31	79.5 (2)	C51''—O51''—Ni2—O61	-53.4 (2)
C31—O31—Ni1—O11	42.9 (2)	C61—O61—Ni2—O41	-47.8 (2)
C31—O31—Ni1—O21	-50.7 (2)	C61—O61—Ni2—O51	40.1 (2)

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $1-x, -y, 2-z$ .

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Bis[*N*-(4-chlorobenzylidene)-2-mercaptoanilinato]nickel(II)

FILİZ ERCAN,<sup>a</sup> DİNÇER ÜLKÜ,<sup>a</sup> NILGÜN ANCI,<sup>b</sup> S. GÜL OZTAS<sup>b</sup> AND MÜRSEDE TÜZÜN<sup>b</sup>

<sup>a</sup>Hacettepe University, Department of Engineering Physics, 06532 Beytepe, Ankara, Turkey, and <sup>b</sup>Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey. E-mail: filiz@eti.cc.hun.edu.tr

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## Abstract

The title structure consists of discrete  $[\text{Ni}(\text{C}_{13}\text{H}_9\text{CINS})_2]$  molecules with each Ni atom located on a crystallographic twofold axis. The coordination around Ni is approximately square planar and *N*-(4-chlorobenzylidene)-2-mercaptoaniline acts as a monoanionic bidentate ligand [IUPAC name: 2-(4-chlorobenzylidene-amino)benzenethiolato] coordinating to nickel(II) via the mercapto S and the imino N atoms.

## Comment

Several related metal derivatives of Schiff bases have been reported (Soriano-Garcia, Toscano, Valdes-Martinez & Fernandez-G., 1985; Elerman, Fuess & Paulus, 1992). Some transition metal Schiff base complexes containing N and S donor atoms have been