

*Acta Cryst.* (1998). **C54**, 349–351

## Hexakis(*N,N*-dimethylformamide-*O*)-nickel(II) Bis(tetrafluoroborate)

WAN-SHEUNG LI,<sup>a</sup> ALEXANDER J. BLAKE,<sup>a</sup> NEIL R. CHAMPNESS,<sup>a</sup> MARTIN SCHRÖDER<sup>a</sup> AND DUNCAN W. BRUCE<sup>b</sup>

<sup>a</sup>Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England, and <sup>b</sup>Department of Chemistry, University of Exeter, Exeter EX4 4QD, England. E-mail: a.j.blake@nottingham.ac.uk

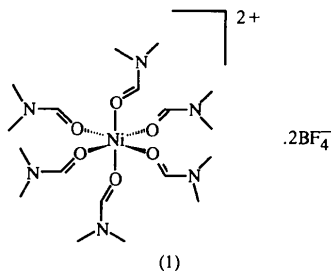
(Received 21 May 1997; accepted 20 October 1997)

### Abstract

In the title compound,  $[\text{Ni}(\text{C}_3\text{H}_7\text{NO})_6](\text{BF}_4)_2$ , there are two independent  $[\text{Ni}(\text{dmf})_6]^{2+}$  cations (dmf is *N,N*-dimethylformamide), each with a crystallographically imposed centre of symmetry. Hydrogen-bonding interactions between the cations and  $\text{BF}_4^-$  anions allow the formation of polymeric chains.

### Comment

The title compound, (1), exists as an air-stable green solid and is a potentially useful starting reagent for the synthesis of  $\text{Ni}^{\text{II}}$  complexes. Fig. 1 shows the two independent  $[\text{Ni}(\text{dmf})_6]^{2+}$  cations (dmf is *N,N*-dimethylformamide), which have the expected octahedral geometry, with each dmf molecule acting as a monodentate ligand via its O-atom donor. Ni—O distances range from 2.033 (3) to 2.066 (3) Å and the Ni—O—C angles are in the range 118.0 (3)–131.3 (3)°. Compound (1) is isostructural with the analogous perchlorate salts  $[\text{Ni}(\text{dmf})_6](\text{ClO}_4)_2$  (McKee *et al.*, 1996) and  $[\text{Fe}(\text{dmf})_6](\text{ClO}_4)_2$  (Baumgartner, 1986).



The relative orientations of the dmf molecules in the two independent cations differ; a similar situation was reported by McKee *et al.* (1996). In cation A, the mean plane of the axial dmf ligands (atoms O3, C7, N3, C8 and C9) approximately bisects the  $\text{O1}_{\text{dmf}}\text{—Ni1—O2}_{\text{dmf}}$  angle of the equatorial dmf ligands, the torsion angles  $\text{O1}^1\text{—Ni1—O3—C7}$  and  $\text{O2}^1\text{—Ni1—}$

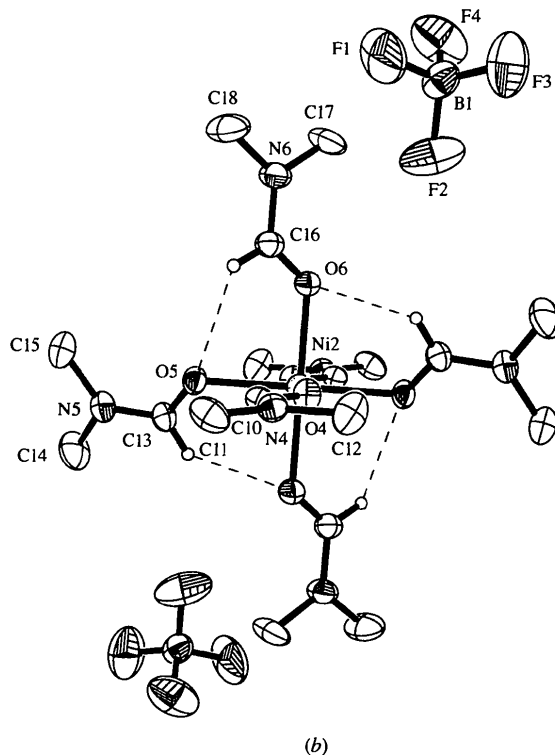
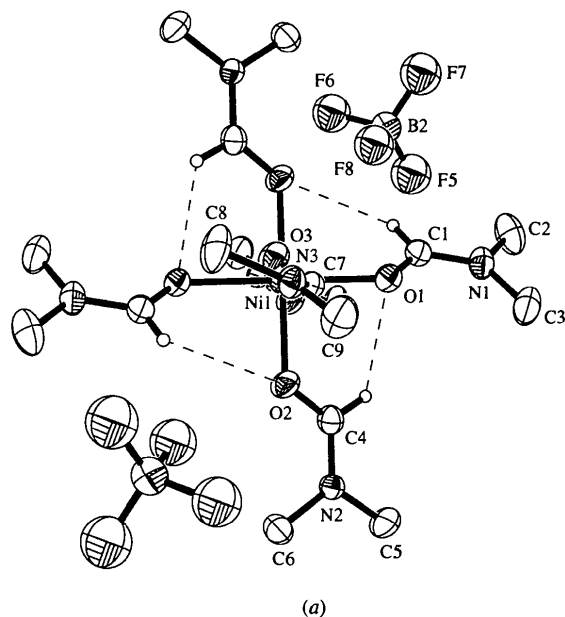


Fig. 1. (a) A view of the  $[\text{Ni}(\text{dmf})_6]^{2+}$  cation A and the associated anions, projected onto the plane of the equatorial dmf ligands; only the major component of the disorder in the anions is shown. (b) A corresponding view of cation B and its associated anions. Displacement ellipsoids enclose 50% probability surfaces. Methyl H atoms have been omitted for clarity and others are shown as small spheres of arbitrary radii. Dashed lines indicate interactions between adjacent coordinated dmf ligands.

O3—C7 being 43.2(4) and -46.5(4)°, respectively [symmetry code: (i) -x, 1-y, -z]. In cation B, the axial dmf ligands (atoms O4, C10, N4, C11 and C12) almost coincide with the Ni2—O5 vector of a dmf ligand in the equatorial plane; the torsion angles O6—Ni2—O4—C10 and O5<sup>ii</sup>—Ni2—O4—C10 are 84.4(4) and -4.8(4)°, respectively [symmetry code: (ii) 1-x, 1-y, -z].

There are interactions between the equatorial dmf ligands within the molecules, with each O atom interacting weakly with the amide C—H of a neighbouring ligand at O...H distances of 2.42–2.69 Å. Significant hydrogen-bonding interactions are observed between the BF<sub>4</sub><sup>-</sup> anions and the cations in compound (1), forming columns of cations along the a axis in the crystal lattice via F...H(C) contacts of 2.12–2.60 Å. In the analogous perchlorate salts, [Ni(dmf)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Fe(dmf)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>, hydrogen-bonding interactions via O...H(C) contacts of 2.31–2.70 Å were observed between the cations and the perchlorate anions.

## Experimental

Green crystals of [Ni(dmf)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> were prepared by the diffusion of diethyl ether into dimethylformamide solutions of Ni(BF<sub>4</sub>)<sub>2</sub>.

### Crystal data

[Ni(C<sub>3</sub>H<sub>7</sub>NO)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>

*M<sub>r</sub>* = 670.91

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 14.612(3) Å

*b* = 10.715(3) Å

*c* = 20.636(4) Å

β = 92.88(2)°

*V* = 3226.9(13) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.381 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

### Data collection

Stoe Stadi-4 four-circle diffractometer with an Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)

ω-2θ scans

Absorption correction: ψ scans (North *et al.*, 1968)

*T<sub>min</sub>* = 0.792, *T<sub>max</sub>* = 0.828

7347 measured reflections

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 29 reflections

θ = 12.5–14.0°

μ = 0.687 mm<sup>-1</sup>

*T* = 150(2) K

Irregular block

0.50 × 0.31 × 0.30 mm

Green

5691 independent reflections

4045 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.089

θ<sub>max</sub> = 25.02°

*h* = -17 → 17

*k* = 0 → 12

*l* = -24 → 24

3 standard reflections

frequency: 60 min

intensity variation: ±4%

### Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.061

w*R*(*F*<sup>2</sup>) = 0.139

(Δ/σ)<sub>max</sub> = 0.018

Δρ<sub>max</sub> = 0.94 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.72 e Å<sup>-3</sup>

*S* = 1.139

5691 reflections

381 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.019*P*)<sup>2</sup> + 12.5*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

Table 1. Selected geometric and hydrogen-bonding parameters (Å, °)

Ni1—O1	2.056 (3)	Ni2—O4	2.066 (3)
Ni1—O2	2.038 (3)	Ni2—O5	2.049 (3)
Ni1—O3	2.041 (3)	Ni2—O6	2.033 (3)
O1—Ni1—O2	89.65 (13)	Ni1—O1—C1	119.9 (3)
O1—Ni1—O3	87.65 (13)	Ni1—O2—C4	120.0 (3)
O2—Ni1—O3	89.24 (14)	Ni1—O3—C7	127.2 (3)
O4—Ni2—O5	86.48 (13)	Ni2—O4—C10	131.3 (3)
O4—Ni2—O6	90.48 (13)	Ni2—O5—C13	118.0 (3)
O5—Ni2—O6	90.84 (13)	Ni2—O6—C16	124.0 (3)
O1 <sup>i</sup> —Ni1—O3—C7	43.2 (4)	O6—Ni2—O4—C10	84.4 (4)
O2 <sup>i</sup> —Ni1—O3—C7	-46.5 (4)	O5 <sup>ii</sup> —Ni2—O4—C10	-4.8 (4)
D—H...A	H...A	D...A	D—H...A
C4—H4...O1	2.46	2.989 (6)	114.9
C1—H1...O2 <sup>i</sup>	2.68	3.142 (6)	110.4
C16—H16...O5	2.69	3.110 (6)	107.3
C13—H13...O6 <sup>ii</sup>	2.42	2.975 (6)	117.2

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

One of the BF<sub>4</sub><sup>-</sup> anions was found to be disordered, with each F atom split over two sites of occupancies 0.60 and 0.40. Methyl H atoms were located from a circular difference Fourier synthesis and thereafter refined as a rigid group allowed to rotate about its local C—N axis with a C—H distance of 0.98 Å and with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C). Other H atoms were included at geometrically calculated positions; each was constrained to ride at a distance of 0.95 Å from its parent C atom with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

Data collection: *STADIA* (Stoe & Cie, 1995a). Cell refinement: *STADIA*. Data reduction: *X-RED* (Stoe & Cie, 1995b). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL97*.

We thank EPSRC for provision of a four-circle diffractometer and for a postdoctoral fellowship (to W-SL).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1501). Services for accessing these data are described at the back of the journal.

## References

- Baumgartner, O. (1986). *Z. Kristallogr.* **174**, 253–263.  
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.  
 McKee, M., Metcalfe, T. & Wikaira, J. (1996). *Acta Cryst.* **C52**, 1139–1141.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Stoe & Cie (1995a). *STAD14. Diffractometer Control Program for Windows*. Stoe & Cie, Darmstadt, Germany.  
 Stoe & Cie (1995b). *X-RED. Data Reduction Program for Windows*. Stoe & Cie, Darmstadt, Germany.

*Acta Cryst.* (1998). **C54**, 351–352

## Sodium Hydrogen Hexacetatodirrhodate(II)

XINYI WEI, MICHAEL H. DICKMAN AND MICHAEL T. POPE

*Department of Chemistry, Georgetown University, Washington, DC 20057, USA. E-mail: pope@guvax.georgetown.edu*

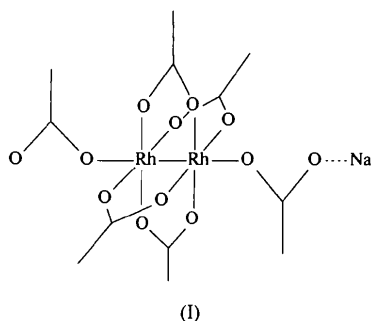
(Received 18 July 1997; accepted 27 October 1997)

### Abstract

The centrosymmetric title compound,  $\text{Na}(\text{H})[\text{Rh}_2(\text{C}_2\text{H}_3\text{O}_2)_6]$ , consists of dirrhodium(II) tetraacetate with two additional axial acetate ligands. Charges are balanced by a sodium ion and a disordered proton. The sodium coordination sphere includes O atoms bound equatorially to the rhodium, as well as O atoms from the axial acetates. The Rh—Rh distance is 2.3827 (5) Å, Rh—O(axial) is 2.279 (2) Å, and the average Rh—O(equatorial) distance is 2.040 (4) Å.

### Comment

Dirrhodium tetraacetate complexes with a metal–metal bond and various axial ligands are well known (Cotton & Walton, 1993). The present compound, (I), was iso-



lated during an attempt to extend the preparation of bis(acetato)dirrhodium-11-tungstophosphate (Wei *et al.*, 1997) to the  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$  system. X-ray structure analysis revealed a centrosymmetric dirrhodium tetra-

acetate dimer with axial acetate ligands (Fig. 1). A similar arrangement of acetate ions has been observed in the compound  $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{CCH}_3)_2][\text{Rh}(\text{tmtaa})\text{-(PhCCPh)}]_2$  (Cotton & Czuchajowska-Wiesinger, 1992), where tmtaa is 5,7,12,14-tetramethyldibenzo[*b,i*]-[1,4,8,11]tetraazacyclotetradecine. In that compound, the axial acetate ligands linked Rh atoms in the cation and anion. Here, the axial acetate connects to a sodium counterion. The sodium lies on a twofold axis and has a distorted octahedral coordination sphere containing O atoms from one of the acetates bound equatorially to a rhodium (O4), as well as from the axial acetate (O5 and O6). Asymmetric C—O distances for the axial acetate show a greater degree of single-bond character for the C5—O6 bond compared with the C5—O5 bond. A disordered proton is involved in an apparent hydrogen bond between O6 and O6<sup>iii</sup>.

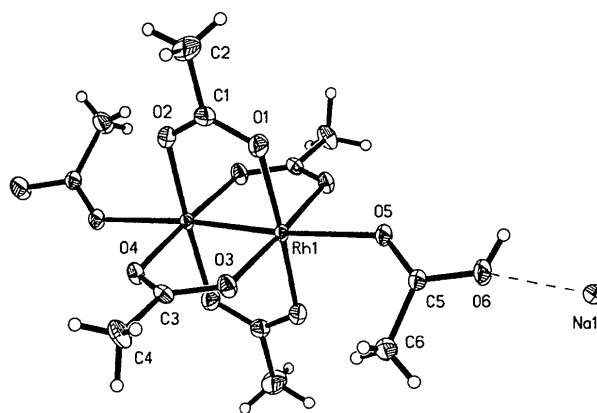


Fig. 1. View of the title compound. Anisotropic displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

### Experimental

$\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$  (Contant, 1990) was converted to the lithium salt by ion exchange. 10 ml of an aqueous solution which had been adjusted to pH 3.0 with 1.0 M HCl and containing 0.5 g of the lithium salt and 0.04 g  $\text{Rh}_2(\text{OAc})_4$  (Aldrich Chemical Company, Milwaukee, Wisconsin, USA) was heated in a Parr Acid Digestion bomb at 393 K for 17 h. The resulting mixture was loaded onto a Sephadex G-50 column and eluted with an aqueous solution of 0.1 M sodium acetate and 0.1 M acetic acid. The first dark-brown band was collected and 0.2 g solid CsCl was dissolved in it. After a dark-brown precipitate was removed by vacuum filtration, the blue filtrate was allowed to stand. After two days, blue plate-like crystals of the title compound formed. These displayed blue–green dichroism when observed under a polarizing microscope.

### Crystal data

$\text{Na}(\text{H})[\text{Rh}_2(\text{C}_2\text{H}_3\text{O}_2)_6]$   
 $M_r = 584.08$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$