

Bis(μ -acetato)(μ -2,6-bis{[(2-hydroxyethyl)(2-pyridylmethyl)amino]methyl}-4-methylphenolato)dinickel(II) hexafluorophosphate hemihydrate

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Received 31 October 2006

Accepted 11 December 2006

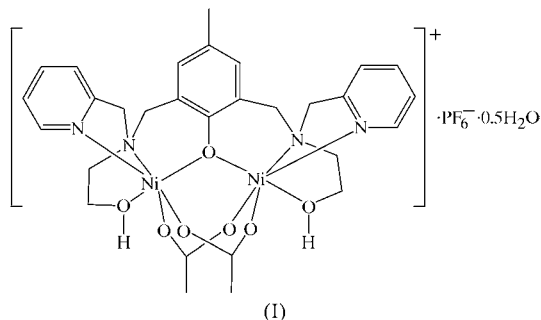
Online 13 January 2007

The asymmetric unit of the title compound, $[\text{Ni}_2(\text{C}_{25}\text{H}_{31}\text{N}_4\text{O}_3)(\text{C}_2\text{H}_3\text{O}_2)_2]\text{PF}_6 \cdot 0.5\text{H}_2\text{O}$, consists of two dinuclear nickel cations, two hexafluorophosphate anions and one water molecule of crystallization. Within each cation, the Ni atoms are bridged by two exogenous acetate groups and an endogenous cresol O atom of a phenolate-based 'end-off' compartmental ligand that possesses two pendant chelating arms attached to the *ortho* positions of the phenol ring. Each Ni atom is six-coordinate with a slightly distorted octahedral geometry. The two symmetry-independent cations are linked into a dimeric unit through O—H...O hydrogen bonds. Additional O—H...O, C—H...F and C—H...O intermolecular interactions link all of the units in the structure into a three-dimensional framework.

Comment

The hydrolysis of biomolecules by dinuclear metallohydrolases has been a hot subject for bioinorganic chemists for many years (Wilcox, 1996). Dinuclear nickel complexes have long been of great interest because the Ni atom was found to act as the active centre of urease (Lippard, 1995), which is an enzyme isolated from various bacteria and plants that can hydrolyse urea to form carbamate and ammonia. To gain an insight into the relationship of the structure and catalytic activity of urease, as well as its hydrolytic mechanism, a number of synthetic functional models containing dinuclear nickel of relevance to the active site of urease have been reported (Barrios & Lippard, 2000; Carlsson *et al.*, 2004; Beddie *et al.*, 2005). We have synthesized previously a symmetrical ligand, namely 2,6-bis{[(2-hydroxyethyl)(2-pyridylmethyl)amino]methyl}-4-methylphenol, (*L*), and showed

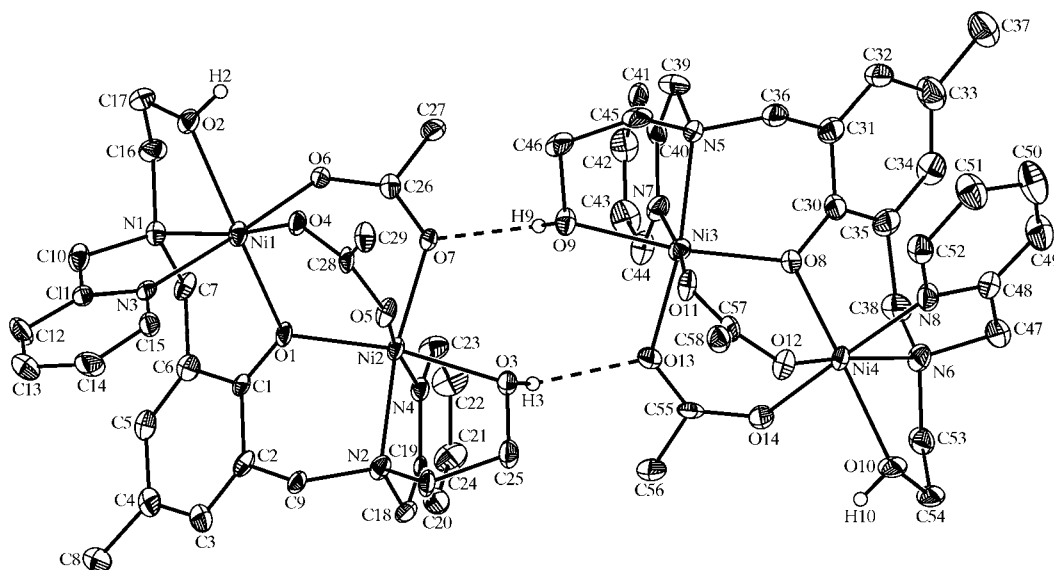
that it can form a dinuclear zinc complex with phenolate and acetate bridges (Chen *et al.*, 2005). We report here the crystal structure of the title compound, (I), whose structure is different from that of the previously reported dinuclear zinc complex.



The asymmetric unit of (I) (Fig. 1) contains two dinuclear nickel cations, two hexafluorophosphate anions and one water molecule of crystallization. The two symmetry-independent dinuclear cations are linked into a dimeric unit through co-operative O—H...O hydrogen bonds (O9—H9...O7 and O3—H3...O13; Table 1). For each cation, one hydroxy O atom links to an acetate O atom of another cation, but the second hydroxy O atom in each cation forms a hydrogen bond with the O atom of a neighbouring water molecule. The water H atoms, in turn, interact with hydroxy O atoms and an acetate O atom in two different but symmetry-related cations. Together, these interactions link the cations into extended chains which run parallel to the [100] direction. Additional weak intermolecular C—H...F and C—H...O interactions (Table 1) link all of the units in the structure into a three-dimensional framework.

Within each cation, the two Ni atoms are bridged by two exogenous acetate groups and an endogenous cresol O atom of *L* in a *syn-syn* mode, providing a μ -phenolato-di- μ -acetato-dinickel(II) core. Both nickel centres have an N_2O_4 coordination environment and the geometry around each Ni atom can be regarded as that of a slightly distorted octahedron. The two octahedra in each dinuclear nickel cation are corner-shared *via* the bridging phenolate O atom. The planes defined by each Ni atom and its coordinated N atoms from the imine pendant arm (represented by atoms N1, N2, N5 and N6) and the pyridine ring include the two coordinated O atoms of the acetate bridges and are almost coplanar with the associated pyridine ring. The structure of (I) is different from that of the analogous dinuclear zinc complex (Chen *et al.*, 2005). In the latter complex, the independent Zn atoms have different coordination numbers and geometry. One Zn atom is six-coordinate with an N_2O_4 donor set having a slightly distorted octahedral geometry, whereas the other Zn atom is five-coordinate with an N_2O_3 donor set having a roughly trigonal-bipyramidal geometry. Moreover, the two zinc-bound terminal alcohol hydroxy groups are also different: one is deprotonated but the other is protonated.

The average separation between the two Ni atoms in (I) is 3.399 (1) Å, which is comparable to that in urease (3.5 Å; Jabri

**Figure 1**

The two symmetry-independent dinuclear nickel cations of the title compound, showing 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms, except for H9 and H3, have been omitted for clarity.

et al., 1995) and also similar to the Ni···Ni distances in most of the reported 'end-off' compartmental ligand-derived dinuclear nickel complexes with additional bridges (Koga *et al.*, 1998; Uozumi *et al.*, 1998; Adams *et al.*, 2003; Carlsson *et al.*, 2004). The average Ni—O_{ethanol} bond length is 2.136 (3) Å, which is longer than those for Ni—O_{cresol} [1.992 (3) Å] and Ni—O_{acetate} [2.048 (2) Å]. The Ni—O distances for the acetate O atom not accepting a hydrogen bond are longer than those where a hydrogen bond is involved. As a result of the two exogenous acetate (OAc) bridges, the Ni···Ni distance and the Ni—O_{cresol}—Ni angle [116.40 (12)°] are somewhat smaller than those observed in similar binuclear nickel complexes without additional bridges, *e.g.* [Ni₂L⁴(OAc)(μ-OAc)-(CH₃OH)(H₂O)]⁺ [Ni···Ni = 3.5419 (12) Å and Ni—O_{cresol}—Ni = 121.40 (19)°; Adams *et al.*, 2003] and [Ni₂(BPPMP)-(H₂O)₄]⁺ [Ni···Ni = 3.775 (1) Å and Ni—O_{cresol}—Ni = 131.8 (1)°; de Brito *et al.*, 2000]. The average Ni—N distance in (I) [2.083 (3) Å] agrees with the values expected for octahedral Ni^{II} complexes (Buchanan *et al.*, 1989).

Experimental

Nickel acetate trihydrate (230 mg, 1.0 mmol) dissolved in methanol was added dropwise to a stirred solution of 2,6-bis[(2-hydroxyethyl)(2-pyridylmethyl)amino]methyl-4-methylphenol (218.3 mg, 0.5 mmol) in methanol (25 ml) and refluxed for 30 min in air. The mixture was cooled to room temperature and a green precipitate formed on addition of potassium hexafluorophosphate (184.2 mg, 0.5 mmol) in portions. The precipitate was filtered off and washed with cold methanol and diethyl ether. Green needle-shaped single crystals of (I) suitable for a crystal structure determination were obtained after *ca* one week by slow evaporation of the filtrate at room temperature [m.p. 509.6 (5) K].

Crystal data

[Ni₂(C₂₅H₃₁N₄O₃)(C₂H₃O₂)₂]
PF₆·0.5H₂O
M_r = 825.03
Monoclinic, *P*₂₁/*c*
a = 15.7776 (19) Å
b = 17.191 (2) Å
c = 25.513 (3) Å
β = 93.914 (3)°

V = 6904.0 (14) Å³
Z = 8
D_x = 1.587 Mg m^{−3}
Mo Kα radiation
μ = 1.22 mm^{−1}
T = 291 (2) K
Needle, green
0.28 × 0.24 × 0.22 mm

Data collection

Bruker APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2000)
*T*_{min} = 0.72, *T*_{max} = 0.76

36723 measured reflections
13513 independent reflections
9603 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.044
θ_{max} = 26.0°

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···O15	0.76 (4)	2.48 (5)	2.956 (4)	122 (4)
O3—H3···O13	0.84 (4)	2.11 (4)	2.714 (4)	129 (4)
O9—H9···O7	0.80 (4)	2.04 (4)	2.737 (4)	145 (4)
O10—H10···O15 ⁱ	0.81 (5)	2.39 (5)	2.876 (5)	120 (4)
O15—H15A···O10 ⁱⁱ	0.85 (5)	2.48 (5)	2.876 (5)	109 (4)
O15—H15A···O5 ⁱⁱⁱ	0.85 (5)	2.58 (5)	3.079 (4)	118 (4)
O15—H15B···O9 ⁱⁱⁱ	0.82 (5)	2.22 (5)	3.009 (4)	162 (5)
C8—H8C···F1 ^{iv}	0.96	2.69	3.466 (5)	139
C10—H10A···F12	0.97	2.52	3.348 (5)	143
C14—H14···F5	0.93	2.48	3.355 (6)	158
C22—H22···F4 ^v	0.93	2.52	3.377 (5)	154
C29—H29B···O15 ⁱⁱⁱ	0.96	2.54	3.209 (5)	127
C34—H34···F11 ^{vi}	0.93	2.66	3.479 (6)	148
C39—H39A···F2 ⁱⁱⁱ	0.97	2.42	3.370 (6)	166
C46—H46A···O4 ⁱⁱⁱ	0.97	2.61	3.373 (5)	136
C47—H47A···F4 ^{vii}	0.97	2.54	3.267 (6)	132
C54—H54B···F6 ^{vii}	0.97	2.50	3.406 (6)	155
C58—H58A···F7 ⁱⁱⁱ	0.96	2.57	3.491 (5)	162
C58—H58B···O12 ^{vii}	0.96	2.56	3.293 (5)	133

Symmetry codes: (i) *x* − 1, *y*, *z*; (ii) *x* + 1, *y*, *z*; (iii) −*x* + 1, −*y* + 2, −*z* + 1; (iv) −*x* + 1, *y* − ½, −*z* + ½; (v) *x*, −*y* + ½, *z* + ½; (vi) *x* − 1, −*y* + ½, *z* + ½; (vii) −*x*, −*y* + 2, −*z* + 1.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.102$
 $S = 1.10$
 13513 reflections
 916 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 5.0551P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.020$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

The water and hydroxy H atoms were located in a difference Fourier map and their positions were refined [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$]. The methyl H atoms were constrained to an ideal geometry with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C—C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atom at a distance of 0.93 or 0.97 Å for phenyl and methylene groups, respectively, and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors are grateful for financial support from the Natural Science Basic Research Project of Jiangsu Province University (grant No. 06KJB150120).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3026). Services for accessing these data are described at the back of the journal.

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