

$(\mu$ -2,6-Bis[[(2-hydroxyphenyl)(2-pyridylmethyl)amino]methyl]-4-methylphenolato)bis[*diaquanickel(II)*] acetate dimethylformamide 0.75-hydrate

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Received 24 December 1999

Accepted 28 June 2000

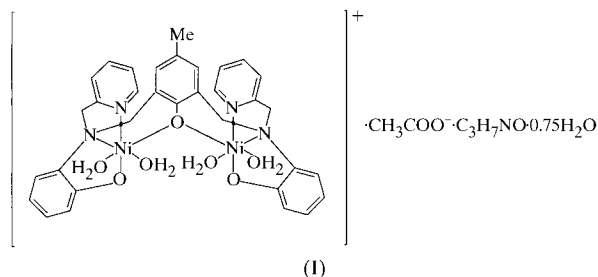
The binuclear cation of the title compound, $[\text{Ni}_2(\text{C}_{33}\text{H}_{29}\text{N}_4\text{O}_3)(\text{H}_2\text{O})_4]\text{C}_2\text{H}_3\text{O}_2 \cdot \text{C}_3\text{H}_7\text{NO} \cdot 0.75\text{H}_2\text{O}$, was synthesized as a model for the active site of urease. Two tridentate halves of the symmetrical 2,6-bis[[(2-hydroxyphenyl)(2-pyridylmethyl)amino]methyl]-4-methylphenolate (BPPMP³⁻) ligand are arranged in a meridional fashion around the two Ni^{II} ions, with the phenoxo O atom bridging the Ni^{II} ions. The cation has an approximate twofold rotation axis running through the C—O bond of the bridging phenolate group. Four water molecules complete the octahedral environment of each Ni^{II} ion.

Comment

Urease is known to catalyze the hydrolysis of urea at a rate 10^{14} times faster than the spontaneous degradation of the amide in water (Buchanan *et al.*, 1989). The enzyme was first isolated from Japanese jack beans by Summer (1926). Recently, an X-ray crystal structure analysis of a bacterial urease has confirmed the binuclear composition of the active site, with the two Ni^{II} ions being separated by 3.5 Å (Jabri *et al.*, 1995). Many dinickel complexes have been reported previously as models for urease (Halcrow & Christon, 1994). We present here the crystal structure of a new model, (I), for the active site of urease using the binucleating ligand 2,6-bis[[(2-hydroxyphenyl)(2-pyridylmethyl)amino]methyl]-4-methylphenol (H₃BPPMP), which was synthesized according to Campbell *et al.* (1993).

The asymmetric unit of the title compound consists of a discrete binuclear $[\text{Ni}_2(\text{BPPMP})(\text{H}_2\text{O})_4]^+$ cation (Fig. 1), one uncoordinated acetate anion, a dimethylformamide molecule and two partially occupied waters of crystallization. The two Ni^{II} ions are in distorted octahedral environments, bridged by the μ -phenoxo-O atom of the binucleating BPPMP³⁻ ligand.

Although the cation has no crystallographic symmetry, an approximate twofold rotation axis runs along the C—O bond of the bridging phenolate group. The N donors (amine and two pyridyl groups) and the two O donors (two pendant phenoxo groups) of the symmetrical ligand, and the four water molecules complete the coordination spheres of the binuclear complex. The two tridentate halves of the BPPMP³⁻ anion adopt a meridional coordination mode, and pertinent



features include an Ni^{II}···Ni^{II} distance of 3.775 (1) Å and a bridging Ni1—O—Ni2 angle of 131.8 (1)°. In the title complex, since there is no other bridging atom, the Ni···Ni distance and Ni—O—Ni angle are significantly greater than those observed in similar binuclear Ni complexes, such as the μ -acetato-bridged (3.422 Å and 116.7°; Buchanan *et al.*, 1989) and isothiocyanate-bridged complexes (2.993 Å and 94.7°; Koga *et al.*, 1998). In the $[\text{Ni}_2(\text{BPPMP})(\text{H}_2\text{O})_4]^+$ cation, one water molecule is coordinated *trans* to the phenoxo bridge and the other is *trans* to the tertiary amine. The final pendant arms (phenolate and pyridyl) were constrained to *trans* positions with respect to each other because the phenolate moiety is linked directly to the tertiary amine. This arrangement is in contrast to other complexes containing the H₃BBPMP ligand, such as $[\text{Fe}_2(\text{BBPMP})(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (Neves *et al.*, 1993), $\text{NH}_4[\text{Fe}_2(\text{BBPMP})(\text{SO}_4)_2]$ (de Brito *et al.*, 1997) and $[\text{In}_2(\text{BBPMP})(\text{OAc})_2](\text{NO}_3)$ (Bortoluzzi *et al.*, 1999), in which the terminal phenolate arm always lies in a *trans* position with respect to the phenoxo bridge.

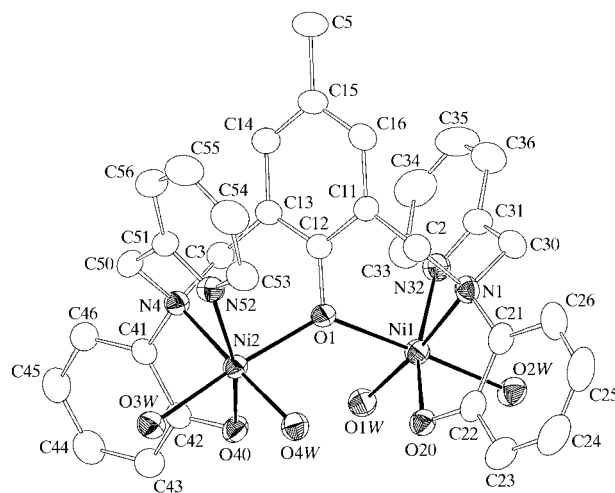


Figure 1

A view of the structure of the $[\text{Ni}_2(\text{BPPMP})(\text{H}_2\text{O})_4]^+$ cation with displacement ellipsoids shown at the 40% probability level. The labeling scheme is presented and H atoms have been omitted for clarity.

The average Ni–N (2.091 Å) and Ni–O (2.067 Å) distances agree with the values expected for octahedral Ni^{II} complexes (Buchanan *et al.*, 1989), but the Ni1–O2W [2.131 (2) Å] and Ni2–O3W [2.140 (2) Å] distances are greater than usual values due to a *trans* effect of the bridging phenoxo group.

Cohesion in the three-dimensional structure results from the extensive hydrogen-bond network. The H atoms of the coordinated water molecules take part in both intra- and intermolecular interactions with some neighboring acceptors (Table 2). It should be noted that the acetate counter-ion is strongly hydrogen bonded to the coordinated water molecules of the binuclear cation. One acetate O atom (O1C) takes part in two strong and one weak hydrogen-bond interaction, while the other (O2C) takes part in only two hydrogen-bond interactions. This results in different bond lengths in the uncoordinated acetate group (Table 1).

Experimental

The reaction of Ni(CH₃COO)₂·3H₂O with H₃BPPMP and ammonium acetate (molar ratio 2:1:2) in methanol afforded a green precipitate which was filtered off and washed with cold 2-propanol and ether. Single crystals suitable for X-ray analysis were obtained by recrystallization from a methanol–dimethylformamide (2:1) solution. Analysis, calculated for C₃₈H_{48.5}N₅Ni₂O_{10.75}: C 52.8, H 5.7, N 8.1%; found: C 52.3, H 5.6, N 8.0%.

Crystal data

[Ni ₂ (C ₃₃ H ₂₉ N ₄ O ₃)(H ₂ O) ₄]C ₂ H ₃ O ₂ · C ₃ H ₇ NO·0.75H ₂ O	Z = 2
<i>M_r</i> = 864.74	<i>D_x</i> = 1.435 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 12.170 (2) Å	Cell parameters from 25 reflections
<i>b</i> = 12.934 (3) Å	<i>θ</i> = 9.87–15.29°
<i>c</i> = 14.112 (3) Å	<i>μ</i> = 1.004 mm ⁻¹
<i>α</i> = 66.46 (3)°	<i>T</i> = 293 (2) K
<i>β</i> = 85.71 (3)°	Irregular, blue
<i>γ</i> = 79.46 (3)°	0.36 × 0.36 × 0.30 mm
<i>V</i> = 2001.9 (7) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.021
<i>ω</i> –2 <i>θ</i> scans	<i>θ</i> _{max} = 25.17°
Absorption correction: <i>ψ</i> scan (PLATON; Spek, 1990)	<i>h</i> = –14 → 14
<i>T</i> _{min} = 0.699, <i>T</i> _{max} = 0.740	<i>k</i> = –14 → 15
7501 measured reflections	<i>l</i> = 0 → 16
7184 independent reflections	3 standard reflections
5348 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 120 min
	intensity decay: 2.0%

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0550 <i>P</i>) ² + 1.4276 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.107	(Δ/ <i>σ</i>) _{max} = 0.001
<i>S</i> = 1.013	Δ <i>ρ</i> _{max} = 0.75 e Å ⁻³
7184 reflections	Δ <i>ρ</i> _{min} = –0.47 e Å ⁻³
523 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0034 (6)

Table 1

Selected geometric parameters (Å, °).

Ni1–O20	2.029 (2)	Ni2–O4W	2.041 (2)
Ni1–O1W	2.039 (2)	Ni2–O40	2.052 (2)
Ni1–O1	2.069 (2)	Ni2–O1	2.067 (2)
Ni1–N32	2.071 (3)	Ni2–N52	2.079 (3)
Ni1–N1	2.111 (3)	Ni2–N4	2.103 (3)
Ni1–O2W	2.131 (2)	Ni2–O3W	2.140 (2)
O20–Ni1–O1W	102.97 (9)	O4W–Ni2–O1	86.94 (9)
O20–Ni1–O1	92.12 (8)	O40–Ni2–O1	94.09 (8)
O1W–Ni1–O1	84.55 (9)	O4W–Ni2–N52	98.00 (10)
O20–Ni1–N32	162.24 (10)	O40–Ni2–N52	162.10 (10)
O1W–Ni1–N32	94.04 (10)	O1–Ni2–N52	91.33 (9)
O1–Ni1–N32	94.59 (9)	O4W–Ni2–N4	178.12 (9)
O20–Ni1–N1	81.82 (10)	O40–Ni2–N4	81.38 (10)
O1W–Ni1–N1	173.43 (9)	O1–Ni2–N4	91.28 (9)
O1–Ni1–N1	90.83 (9)	N52–Ni2–N4	81.45 (11)
N32–Ni1–N1	81.66 (11)	O4W–Ni2–O3W	86.77 (9)
O20–Ni1–O2W	88.20 (9)	O40–Ni2–O3W	88.37 (9)
O1W–Ni1–O2W	93.28 (9)	O1–Ni2–O3W	173.54 (8)
O1–Ni1–O2W	177.83 (9)	N52–Ni2–O3W	88.10 (10)
N32–Ni1–O2W	85.71 (10)	N4–Ni2–O3W	95.00 (9)
N1–Ni1–O2W	91.35 (10)	Ni2–O1–Ni1	131.77 (10)
O4W–Ni2–O40	99.32 (9)		

Table 2

Hydrogen-bonding 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>
O1W–H1WB···O20 ⁱ	1.01	1.66	2.658 (3)	171
O1W–H1WA···O40	0.86	1.87	2.720 (3)	166
O2W–H2WA···O1C	0.96	1.77	2.699 (4)	163
O2W–H2WB···O40 ⁱ	0.96	1.88	2.750 (3)	149
O3W–H3WA···O2C ⁱⁱ	0.85	2.03	2.805 (4)	152
O3W–H3WB···O2C ⁱ	1.09	1.77	2.823 (4)	160
O3W–H3WB···O1C ⁱ	1.09	2.56	3.446 (4)	138
O4W–H4WA···O20	0.94	1.74	2.666 (3)	170
O4W–H4WB···O1C ⁱ	0.93	1.75	2.680 (4)	175

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

After all the atoms of the structure had been placed in the refinement list, two isolated peaks were observed in the difference Fourier map with electron densities greater than 1.6 e Å⁻³. These peaks were attributed to partially occupied solvate water. The disordered water molecules are situated in cavities large enough to accommodate them (radii ≈ 3 Å). H atoms surround these cavities so that the disordered water molecules could be linked by hydrogen bonding, such as O–H···O or C–H···O. The occupancy factors for O5W [0.247 (6)] and O6W [0.494 (5)] were fixed at 0.25 and 0.50, respectively, based on their refinement. H atoms attached to C atoms were placed in the model at their idealized positions, with C–H distances and *U*_{eq} taken as the default of the refinement program. The H atoms of the coordinated water molecules were located in difference Fourier maps, were treated as riding and were refined with free isotropic displacement parameters [0.054 (11)–0.15 (2) Å²]. Although O5W and O6W were refined with anisotropic displacement parameters, their H atoms could not be found. The major peak is located near O1C (1.06 Å), which belongs to the acetate group, while the deepest hole is situated 0.79 Å from Ni1.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: SET4 in CAD-4 EXPRESS; data reduction: HELENA (Spek, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97

(Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai *et al.*, 1996); software used to prepare material for publication: *SHELXL97*.

This work was supported by grants from PADCT III and CAPES, Brazil.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1519). Services for accessing these data are described at the back of the journal.

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