

Urmila Pal Chaudhuri,^a Babu Varghese^b and Narasimha N. Murthy^{a*}

^aDepartment of Chemistry, Indian Institute of Technology–Madras, Chennai 600 036, India, and ^bRegional Sophisticated Instrumentation Centre, Indian Institute of Technology–Madras, Chennai 600 036, India

Correspondence e-mail: nnmurthy@iitm.ac.in

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.053

wR factor = 0.145

Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis[μ -2-{bis(2-pyridylethyl)amino}phenolato]-bis[aquanickel(II)] dinitrate tetrahydrate

The title complex, $[\text{Ni}_2(\text{L}-\text{O}^-)(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, where $\text{L}-\text{O}^-$ is bis[2-{bis(2-pyridyl)ethyl}amino]phenol ($\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}$), is dimeric with each Ni^{2+} ion coordinated by two bridging phenolate O atoms and three N atoms of the N_3O -tetradentate ligand anion $\text{L}-\text{O}^-$. A molecule of water on each metal completes the octahedral geometry. Crystallographic inversion symmetry is present at the center of the Ni_2O_2 plane of the dimeric unit.

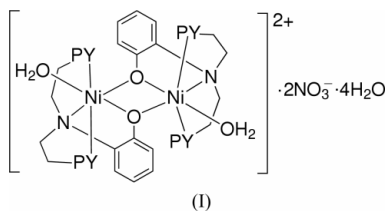
Received 18 June 2003

Accepted 9 July 2003

Online 24 July 2003

Comment

Nickel is an essential trace element present at the active sites of metalloenzymes urease (Lippard, 1995; Hausinger & Karplus, 2001), hydrogenase, carbon monoxide dehydrogenase and a few others (Wilcox, 1996). The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide. The urease active site, thus structurally characterized, has similar structural features with the dinickel(II) center, ligated by histidines and terminally bonded to water, besides a bridging water or hydroxide. Studies related to urease have both agricultural and medicinal implications. The lack of understanding of active-site structure and function prompts bioinorganic chemists to synthesize model complexes (Barrios & Lippard, 2001; Volkmer *et al.*, 1996) that help emulate the active site, both structurally (Carlsson *et al.*, 2002; Jabri *et al.*, 1995) and functionally (Barrios & Lippard, 1999). Understanding of the requirements for forming catalytic sites in biology leads the way to creating new man-made catalysts. Design of new binuclear nickel centers is useful in industry for soil nitrogen fertilization (Barrios & Lippard, 2000). We describe here the synthesis and crystal structure of a binuclear nickel(II) complex, $[\text{Ni}_2(\text{L}-\text{O}^-)(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (I), where $\text{L}-\text{O}^-$ is 2-[[bis(2-pyridyl)ethyl]amino]phenolate, whose coordination environment bears some resemblance to the active site of urease.



The structure of (I) consists of a discrete dimeric nickel(II) dication, two nitrate counter-anions and four water molecules of solvation. Each Ni^{II} atom is coordinated by two bridging phenolate O- and three N-donors from the tetradentate ligand anion, $\text{L}-\text{O}^-$, plus the binding of water at the sixth coordination site to complete the octahedral geometry about each metal ion. The crystallographic inversion symmetry at the center of the Ni_2O_2 plane makes the two Ni^{II} units geome-

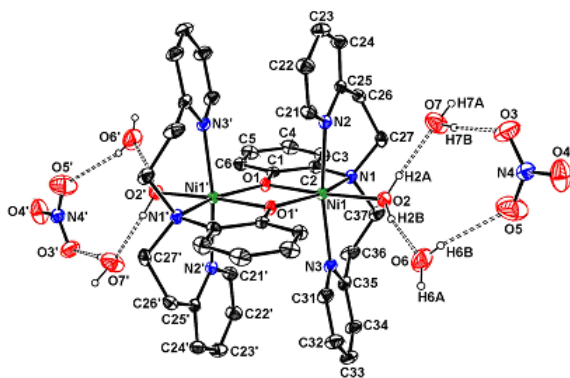


Figure 1
A view of the title compound, showing hydrogen bonding. Displacement ellipsoids are drawn at the 20% probability level.

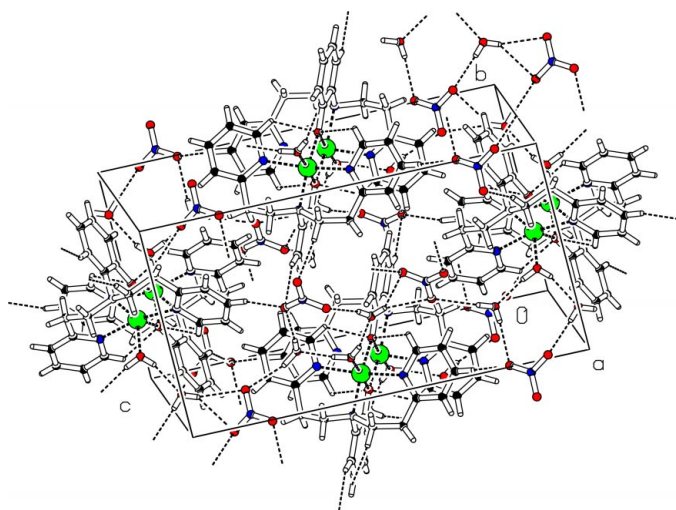


Figure 2
A packing diagram of the title compound.

trically equivalent. The two pyridyls (N2 and N3) on each Ni^{II} are located *trans* to each other, while arylamino atom N1 is *cis* to the pyridyl groups. The angles at the metal subtended by the *cis* and *trans* ligand deviate by at least 13.5 and 20.4°, respectively, from the ideal values of 90 and 180°, indicating distortion from regular octahedral geometry. The largest deviations are O1–Ni1–O1ⁱ = 76.52 (11)° and O1ⁱ–Ni1–N1 = 159.58 (11)°. Interestingly, the Ni–N_{pyridyl} distances are identical, 2.189 (3) Å, in contrast to the Ni–N_{aryl} distance of 2.122 (3) Å. The Ni^{II}–O_{phenoxo} bridge is asymmetric as revealed by Ni1–O1 and Ni1–O1ⁱ distances of 2.014 (3) and 2.107 (2) Å, respectively. The binuclear center is characterized by a metal–metal separation of 3.235 (1) Å and a μ -phenoxo Ni1–O1–Ni1ⁱ bridge angle of 103.48 (11)° (see Table 1). The metal–metal and metal–ligand distances compare favorably to a variety of dinuclear Ni complexes having Ni₂O₂ units formed by phenolic macrocyclic ligands (Adams *et al.*, 2000; Koga *et al.*, 1998; Nanda *et al.*, 1998).

The notable feature of the structure is the aqua coordination on each Ni^{II} atom; the water molecules are disposed *trans* with respect to the μ -phenoxo O atoms. The coordinated

water molecules both participate in strong hydrogen-bonding interactions with the four uncoordinated water molecules (Fig. 1). The nitrate counter-anions also form moderately strong intermolecular hydrogen bonds with the uncoordinated water molecules (see Table 2 and Fig. 2).

Experimental

The ligand 2-[[bis(2-pyridyl)ethyl]amino]phenol, L–OH, was synthesized following a literature procedure (Murthy *et al.*, 1993). To a solution of Ni(NO₃)₂·6H₂O (0.565 g, 19 mmol) in MeOH (8.0 ml) was added a mixture of predissolved ligand L–OH (0.62 g, 19 mmol) and NEt₃ (0.27 ml, 19 mmol), resulting in the formation of a clear green solution. After stirring this for 1 h, slow solvent evaporation produced X-ray quality crystals of (I) (0.75 g) in 79% yield. UV–vis [MeOH, λ_{max} , nm (ϵ , M^{−1} cm^{−1}): 388 (78), 639 (35), 1095 (36). IR (Nujol, cm^{−1}): 3440 (s, O–H), 1270 (s, C–O), 1088 (s, ClO₄[−]). Magnetic moment (Evans, MeOH): 2.54 B.M./Ni at 296 K. ¹H NMR (MeOH, 400 MHz, room temperature): δ −16.94, −12.13, 14.84, 18.14, 22.27, 26.666, 29.68, 39.66, 40.15, 63.

Crystal data

[Ni₂(C₂₀H₂₀N₃O)₂(H₂O)₂]
(NO₃)₂·4H₂O
M_r = 986.32
Monoclinic, *P*2₁/*c*
a = 10.902 (4) Å
b = 10.613 (4) Å
c = 19.505 (8) Å
 β = 103.32 (3)°
V = 2196.0 (15) Å³
Z = 2

D_x = 1.492 Mg m^{−3}
Mo *K* α radiation
Cell parameters from 25
reflections
 θ = 10–15°
 μ = 0.93 mm^{−1}
T = 293 (2) K
Block, green
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω –2 θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
*T*_{min} = 0.737, *T*_{max} = 0.830
4064 measured reflections
3850 independent reflections
2879 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.040
 θ_{max} = 25.0°
h = 0 → 12
k = 0 → 12
l = −23 → 22
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.053
wR(*F*²) = 0.145
S = 1.05
3850 reflections
313 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0867P)^2 + 2.0357P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\text{max}}$ = 1.04 e Å^{−3}
 $\Delta\rho_{\text{min}}$ = −0.78 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Ni1–O1	2.014 (3)	Ni1–N2	2.189 (3)
Ni1–O1 ^{iv}	2.107 (2)	Ni1–N3	2.189 (3)
Ni1–O2	2.065 (3)	Ni1–Ni1 ^{iv}	3.235 (1)
Ni1–N1	2.122 (3)	O1–O1 ⁱ	2.552 (3)
O1–Ni1–O2	176.48 (13)	N2–Ni1–N3	168.11 (12)
O2–Ni1–O1 ^{iv}	104.93 (13)	O1 ^{iv} –Ni1–N1	159.58 (11)
O1–Ni1–O1 ^{iv}	76.52 (11)	O1 ^{iv} –Ni1–N3	90.16 (11)
N1–Ni1–N2	90.57 (12)	Ni1–O1–Ni1 ^{iv}	103.48 (11)

Symmetry code: (iv) 1 − *x*, −*y*, 1 − *z*.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2A···O7	0.83 (6)	1.90 (6)	2.726 (6)	173 (6)
O2—H2B···O6	0.73 (6)	2.01 (6)	2.717 (7)	163 (6)
O6—H6A···O4 ⁱ	0.75 (9)	2.38 (9)	3.101 (10)	161 (10)
O6—H6B···O5 ⁱⁱ	0.73 (8)	2.20 (8)	2.909 (11)	163 (10)
O7—H7A···O4 ⁱⁱⁱ	0.91 (10)	2.26 (10)	3.071 (8)	149 (9)
O7—H7B···O3 ⁱⁱⁱ	0.73 (6)	2.19 (7)	2.909 (8)	172 (7)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, y - 1, z$; (iii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms attached to aromatic C atoms were fixed at distances of 0.93 Å, while those attached to methylene C atoms were fixed at distances of 0.93 Å. H atoms of the coordinated water and lattice water molecules, having hydrogen-bonding interactions with coordinated water molecules, were refined isotropically. The $U_{\text{iso}}(\text{H})$ values for the riding atoms were fixed at $1.1U_{\text{eq}}(\text{C})$. The highest peak in the difference map was 1.15 Å from the Ni atom. This is presumed to be a spurious peak probably due to imperfections in the absorption correction.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) *PLUTON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

References

- Adams, H., Fenton, D. E., Haque, S. R., Heath, S. L., Ohba, M., Okaw, H. & Spey, S. E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1849–1856.
- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Barrios, A. M. & Lippard, S. J. (1999). *J. Am. Chem. Soc.* **121**, 11751–11757.
- Barrios, A. M. & Lippard, S. J. (2000). *J. Am. Chem. Soc.* **122**, 9172–9177.
- Barrios, A. M. & Lippard, S. J. (2001). *Inorg. Chem.* **40**, 1250–1255.
- Carlsson, H., Haukka, M. & Nordlander, E. (2002). *Inorg. Chem.* **41**, 4981–4983.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Hausinger, R. P. & Karplus, P. A. (2001). *Urease*, in *Handbook of Metalloproteins*, edited by K. Wieghardt, R. Huber, T. L. Poulos & A. Messerschmidt, pp. 867–879. London: John Wiley and Sons Ltd.
- Jabri, E., Carr, M. B., Hausinger, R. P. & Karplus, A. (1995). *Science*, **268**, 998–1004.
- Koga, T., Furutachi, H., Nakamura, T., Fukita, N., Ohba, M., Takahashi, K. & Okawa, H. (1998). *Inorg. Chem.* **37**, 989–996.
- Lippard, S. J. (1995). *Sci. Perspect.* **268**, 996–997.
- Murthy, N. N., Mahroof-Tahir, M. & Karlin, K. D. (1993). *J. Am. Chem. Soc.* **115**, 10404–10405.
- Nanda, K. K., Addison, A. W., Paterson, N., Sinn, E., Thompson, L. K. & Sakaguchi, U. (1998). *Inorg. Chem.* **37**, 1028–1036.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1999). *PLUTON for Windows*. Utrecht University, The Netherlands.
- Volkmer, D., Hommerich, B., Klaus, G., Haase, W. & Krebs, B. (1996). *Inorg. Chem.* **35**, 3792–3803.
- Wilcox, D. E. (1996). *Chem. Rev.* **96**, 2435–2458.