

Two new oximate-bridged square-planar dinuclear nickel(II) complexes

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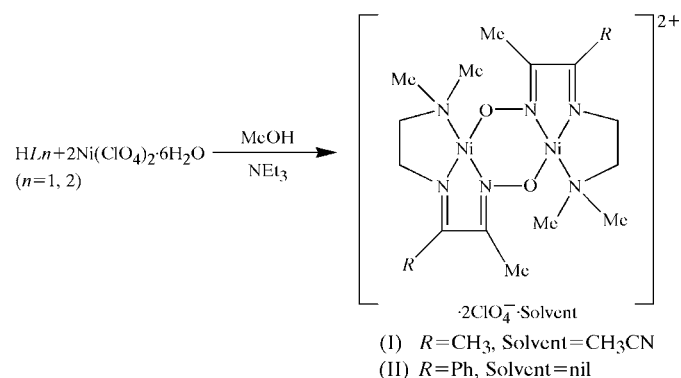
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The synthesis and characterization of two new dinuclear nickel(II) complexes, namely bis{ μ -3-[2-(dimethylamino)ethylimino]butan-2-one oximate}dinickel(II) bis(perchlorate) acetonitrile solvate, $[\text{Ni}_2(\text{C}_8\text{H}_{16}\text{N}_3\text{O})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$, (I), and bis{ μ -3-[2-(dimethylamino)ethylimino]-3-phenylpropan-2-one oximate}dinickel(II) bis(perchlorate), $[\text{Ni}_2(\text{C}_{13}\text{H}_{18}\text{N}_3\text{O})_2](\text{ClO}_4)_2$, (II), are reported. Single-crystal X-ray analyses of the complexes reveal that the nickel(II) ions are in square-planar N_3O environments and form six-membered $(\text{NiNO})_2$ metallacycles. The cation in (II) possesses crystallographically imposed inversion symmetry.

Comment

There are many nickel(II) complexes with ligands incorporating oximate donors that have been shown to stabilize the nickel(III) and nickel(IV) oxidation states at low potential (Mohanty *et al.*, 1975; Singh *et al.*, 1977; Singh & Chakravorty, 1980; Kruger *et al.*, 1991; Berkessel *et al.*, 1996). Such complexes in different oxidation states have a strong role in bioinorganic chemistry and redox enzyme systems (Lancaster, 1988; Kolodziej, 1994), and may provide the basis for models for active sites of biological systems (Parashar *et al.*, 1988; West *et al.*, 1993) or may act as catalysts (Beley *et al.*, 1986; Fujita *et al.*, 1994; Kimura *et al.*, 1994). Oximes represent a very important class of ligands in coordination chemistry (Kukushkin & Pombeiro, 1999; Chaudhuri, 2003). Recent interest in oxime ligands is mostly due to the remarkable ability of the deprotonated oximate groups to form bridges between metal ions, giving rise to polynuclear complexes of different nuclearity with different types of oximate bridges (Costes *et al.*, 1998; Colacio *et al.*, 1997; Cervera *et al.*, 1997). The vast majority of reports of oximate complexes published during the past 15 years have dealt with the synthesis and study of magnetic properties of polynuclear μ -oximate complexes (Pavlishchuk *et al.*, 2001, 2003). These complexes exhibit octahedral coordination geometry at the nickel(II) centers. Recently, Goldcamp *et al.* (2002) reported that the ligand tris(2-hydroxyiminopropyl)amine binds to the Ni^{II} ion

in multiple protonation states, yielding mononuclear and oximate-bridged dinuclear complexes. The dinuclear complex of the fully deprotonated ligand in acetonitrile undergoes oxidation by O_2 , and this system oxidizes PPh_3 with incorporation of oxygen from O_2 . With a similar system, Edison *et al.* (2004) reported substrate oxidation by the first $\text{Ni}^{\text{II}} + \text{O}_2$ reaction that does not proceed *via* irreversible ligand oxidation. We report here the synthesis and X-ray structure of two oximate-bridged square-planar dinuclear nickel(II) complexes, (I) and (II).



Complex (I) (Fig. 1 and Table 1) consists of a dinuclear $[\text{Ni}_2^{\text{II}}(\mu\text{-L1})_2]^{2+}$ cation {L1 is 3-[2-(dimethylamino)ethylimino]butan-2-one oximate}, two perchlorate anions, and one molecule of acetonitrile located 2.5118 (17) Å from atom Ni1. Complex (II) (Fig. 2 and Table 2) is composed of a dinuclear $[\text{Ni}_2^{\text{II}}(\mu\text{-L2})_2]^{2+}$ cation {L2 is 3-[2-(dimethylamino)ethylimino]-1-phenylpropan-2-one oximate} and two perchlorate anions. The cations represent the first examples of oximate-bridged square-planar dinickel(II/III) complexes. Each cation involves two dianionic ligands and two nickel(II) cations. The coordination geometries around each nickel(II) ion in (I) and (II) are best described as distorted square-planar N_3O environments. One amine N, one imine N, one oxime N and one oximate O atom satisfy the square-planar coordination geometry of each nickel(II) ion.

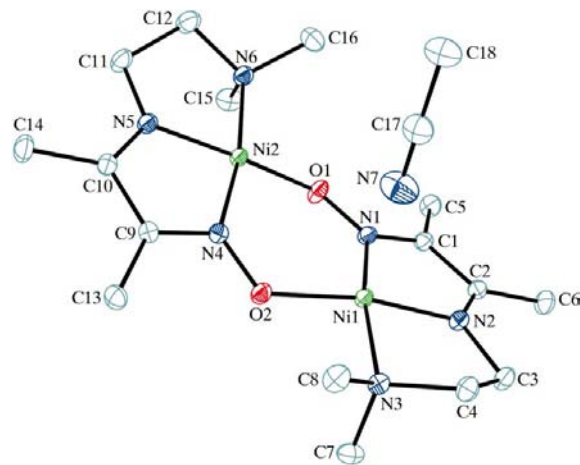


Figure 1

A displacement ellipsoid diagram of (I), showing the cation and acetonitrile solvent molecule. H atoms have been omitted for clarity and ellipsoids are shown at the 50% probability level.

Around atom Ni1 of (I), the four donor atoms alternate above and below the mean plane by 0.02 Å. Atom Ni1 is displaced 0.138 Å from this plane towards acetonitrile atom N7. The atoms coordinated to Ni2 show greater deviation than those around Ni1, alternating by 0.0887 (6) Å above and below the mean plane. Atom Ni2 is displaced 0.0718 (6) Å from this plane. The angle between these two planes is 22.2°.

In complex (II), the deviations from the plane of the four donor atoms are approximately 0.0127 (2) Å, alternating above and below the plane. Atom Ni1 lies 0.0116 (2) Å out of the mean basal plane. Because of crystallographically imposed inversion symmetry, the coordination planes of the two metal centers are coincident.

In both (I) and (II), three N atoms of each ligand are coordinated to one metal center, forming two five-membered (N–Ni–N) chelate rings. The average chelate bite angles for the five-membered rings in (I) and (II) are in the ranges 82.74 (5)–85.88 (6) and 82.99 (17)–85.67 (17)°, respectively. In complexes (I) and (II), a central six-membered dimetallic chelate ring (Ni1/N1/O1/Ni2/N4/O2 and Ni1/N1/O1/Ni1A/N1A/O1A, respectively), is formed through the coordination of oxime N and oximate O atoms to each nickel(II) ion in a *trans* arrangement. The average C–N and N–O distances of the $-(\text{CH}_3)\text{C}=\text{N}-\text{O}-$ oximate groups are 1.318 (17) and 1.338 (15) Å, respectively, in (I) and 1.313 (6) and 1.326 (5) Å, respectively, in (II). These distances are consistent with the deprotonated form of oxime functional groups (Bera *et al.*, 2006; Gupta Sreerama & Pal, 2002; Birkelbach *et al.*, 1997; Pal *et al.*, 1986). The $\text{C}=\text{N}_{\text{imine}}$ distances are significantly shorter than the $\text{C}=\text{N}_{\text{oximate}}$ distances in both complexes. The intradimer Ni···Ni distances are 3.6021 (3) Å in (I) and 3.6530 (2) Å in (II), which are consistent with that in the octahedral dinickel(II) complex reported by Goldcamp *et al.*

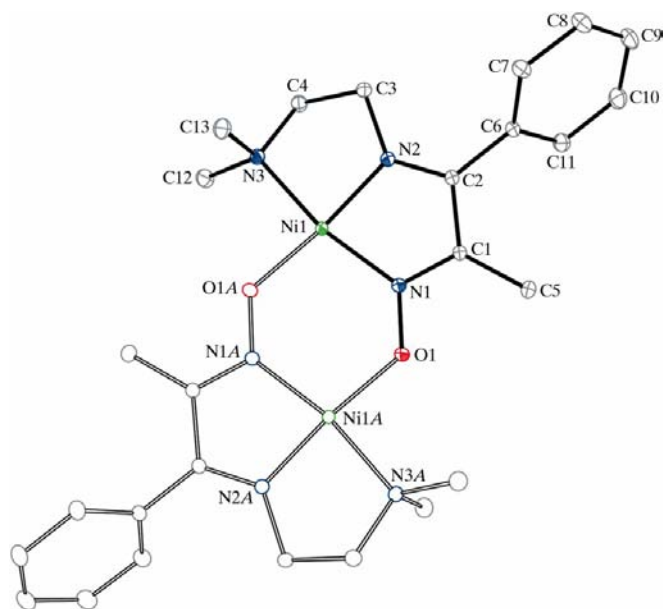


Figure 2

A displacement ellipsoid plot of the cation of (II). Ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

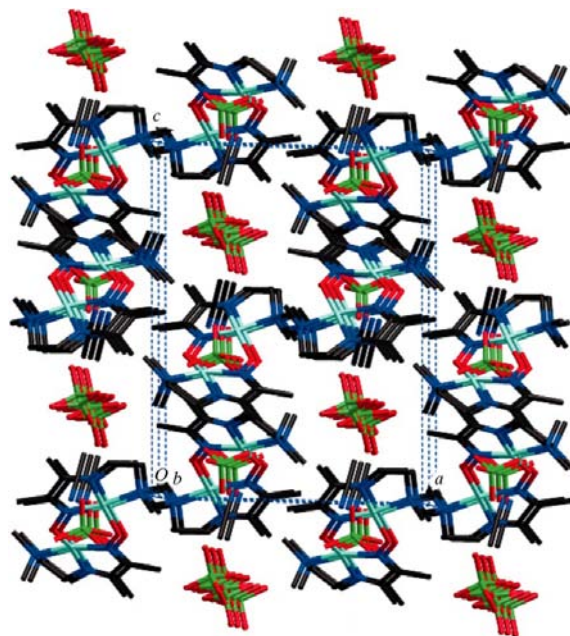


Figure 3

The packing for (I), illustrating channels for solvent motion.

(2002) but larger than those in other square-planar dinickel(II) systems (Rispen *et al.*, 1996; Brooker *et al.*, 2000; Aukauloo *et al.*, 1999).

An interesting feature of the crystal structure lies in the packing of (I) (Fig. 3). In the structure of (I), the geometry of the perchlorate groups shows some typical disorder. The disordered perchlorate anions fill the channels that run parallel to the *b*-axis direction. The other perchlorate anions occupy pockets surrounded by cations. Within the channels, the uncoordinated acetonitrile molecule makes a 2.5118 (17) Å contact with atom Ni1. The Ni–N–C contact angle is 172.74 (17)°. There are no such channels in (II).

Experimental

For the preparation of (I), a methanol solution (20 ml) of *N,N*-dimethylethylenediamine (0.40 ml, 3.8 mmol) and butane-2,3-dione monooxime (0.38 g, 3.8 mmol) was stirred at room temperature. After stirring for an hour, a methanol solution (20 ml) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.38 g, 3.8 mmol) and NEt_3 (0.52 ml, 3.8 mmol) were added successively. After complete addition, a dark-orange-red compound was seen separating from the solution. The whole reaction mixture was stirred for another hour at room temperature. The solvent was evaporated in air. The orange-red precipitate was filtered off using a glass frit and washed with ethanol and hexane. Recrystallization from acetonitrile/dichloromethane gave needle-shaped crystals. The products were dried *in vacuo* over fused CaCl_2 (yield 1.11 g, 85%). Analysis calculated for $\text{C}_{18}\text{H}_{35}\text{Cl}_2\text{N}_7\text{Ni}_2\text{O}_{10}$: C 30.98, H 5.05, N 14.05, Ni 16.75%; found: C 30.67, H 4.97, N 14.27, Ni 16.86%. ^1H NMR (d_6 -DMSO): δ 3.53–3.65 (*m*, 4H, CH_2 attached to imine N), 2.65–2.69 (*m*, 4H, CH_2 attached to amine N), 2.19 (*s*, 6H, imine CH_3), 2.27 (*s*, 6H, oxime CH_3), 1.92 (*s*, 12H, amine CH_3). FT-IR (cm^{-1} , KBr disk): ν 3429 (*b*), 2924 (*m*), 1632 (*s*), 1583 (*s*), 1537 (*s*), 1475 (*s*), 1237 (*s*), 1091 (*s*), 963 (*s*), 714 (*s*). Molar conductance, Λ_M (MeCN solution): 190.34 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. UV-vis spectra [λ_{max} , nm (ϵ , $\text{l mol}^{-1} \text{cm}^{-1}$)] (MeCN solution): 556 (290), 395 (8770), 341 (8565), 225 (18 750).

Complex (II) was prepared in a similar manner to (I) using 1-phenylpropane-1,2-dione 2-oxime (yield 1.38 g, 92%). Analysis calculated for $C_{26}H_{36}Cl_2N_6Ni_2O_{10}$: C 39.98, H 4.64, N 10.76, Ni 14.96%; found: C 39.53, H 4.77, N 10.57, Ni 14.75%. 1H NMR (d_6 -DMSO): δ 7.21–7.65 (*m*, 10H, C_6H_5), 3.47–3.65 (*m*, 4H, CH_2 attached to imine N), 2.68–2.78 (*m*, 4H, CH_2 attached to amine N), 2.22 (*s*, 6H, oxime CH_3), 1.90 (*s*, 12H, amine CH_3). FT-IR (cm^{-1} , KBr disk): ν 3425 (*b*), 2936 (*m*), 1627 (*s*), 1587 (*s*), 1520 (*s*), 1447 (*s*), 1234 (*s*), 1094 (*s*), 924 (*s*), 722 (*s*). Molar conductance Λ_M (MeCN solution): $194.46 \Omega^{-1} cm^2 mol^{-1}$. UV-vis spectra [λ_{max} , nm (ϵ , $l mol^{-1} cm^{-1}$)] (MeCN solution): 563 (225), 387 (6240), 343 (7550), 231 (20 435).

Compound (I)

Crystal data

$[Ni_2(C_8H_{16}N_3O)_2](ClO_4)_2 \cdot C_2H_5N$ $V = 2770.89 (12) \text{ \AA}^3$
 $M_r = 697.85$ $Z = 4$
 Monoclinic, $P2_1/n$ Mo $K\alpha$ radiation
 $a = 13.1320 (3) \text{ \AA}$ $\mu = 1.62 \text{ mm}^{-1}$
 $b = 12.2045 (3) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $c = 17.2959 (5) \text{ \AA}$ $0.23 \times 0.22 \times 0.14 \text{ mm}$
 $\beta = 91.6220 (14)^\circ$

Data collection

Bruker D8-APEXII CCD 290302 measured reflections
 diffractometer 14483 independent reflections
 Absorption correction: multi-scan 12536 reflections with $I > 2\sigma(I)$
 (TWINABS; Blessing, 1995; $R_{int} = 0.075$
 Sheldrick, 2004)
 $T_{min} = 0.708$, $T_{max} = 0.806$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$ 375 parameters
 $wR(F^2) = 0.095$ H-atom parameters constrained
 $S = 1.06$ $\Delta\rho_{max} = 0.84 \text{ e \AA}^{-3}$
 14483 reflections $\Delta\rho_{min} = -0.48 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Ni1–N2	1.8519 (12)	Ni2–N5	1.8420 (12)
Ni1–O2	1.8660 (10)	Ni2–O1	1.8471 (10)
Ni1–N1	1.8888 (13)	Ni2–N4	1.8866 (13)
Ni1–N3	1.9598 (13)	Ni2–N6	1.9531 (14)
N2–Ni1–O2	169.20 (5)	N5–Ni2–O1	168.98 (5)
N2–Ni1–N1	82.55 (6)	N5–Ni2–N4	82.93 (5)
O2–Ni1–N1	101.43 (5)	O1–Ni2–N4	101.81 (5)
N2–Ni1–N3	85.17 (6)	N5–Ni2–N6	86.59 (6)
O2–Ni1–N3	89.64 (5)	O1–Ni2–N6	88.85 (5)
N1–Ni1–N3	166.31 (5)	N4–Ni2–N6	169.34 (5)

Compound (II)

Crystal data

$[Ni_2(C_{13}H_{18}N_3O)_2](ClO_4)_2$ $V = 1541.48 (11) \text{ \AA}^3$
 $M_r = 780.93$ $Z = 2$
 Monoclinic, $P2_1/n$ Mo $K\alpha$ radiation
 $a = 12.5432 (5) \text{ \AA}$ $\mu = 1.46 \text{ mm}^{-1}$
 $b = 8.9714 (4) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $c = 13.7277 (5) \text{ \AA}$ $0.45 \times 0.44 \times 0.32 \text{ mm}$
 $\beta = 93.745 (2)^\circ$

Data collection

Bruker D8-APEXII CCD 124421 measured reflections
 diffractometer 14182 independent reflections
 Absorption correction: multi-scan 12434 reflections with $I > 2\sigma(I)$
 (SADABS; Blessing, 1995; $R_{int} = 0.027$
 Sheldrick, 2004)
 $T_{min} = 0.54$, $T_{max} = 0.63$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$ 211 parameters
 $wR(F^2) = 0.063$ H-atom parameters constrained
 $S = 1.03$ $\Delta\rho_{max} = 0.71 \text{ e \AA}^{-3}$
 14182 reflections $\Delta\rho_{min} = -0.81 \text{ e \AA}^{-3}$

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Ni1–O1 ⁱ	1.8348 (4)	Ni1–N1	1.8827 (4)
Ni1–N2	1.8439 (4)	Ni1–N3	1.9442 (4)
O1 ⁱ –Ni1–N2	174.274 (17)	O1 ⁱ –Ni1–N3	88.804 (17)
O1 ⁱ –Ni1–N1	102.525 (17)	N2–Ni1–N3	85.674 (17)
N2–Ni1–N1	82.999 (17)	N1–Ni1–N3	168.671 (17)

Symmetry code: (i) $-x + 1, -y, -z + 2$.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Sheldrick, 2003); program(s) used to solve structure: *XS* (Sheldrick, 2001); program(s) used to refine structure: *XL* (Sheldrick, 2001); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *XCIF* (Sheldrick, 2001) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3024). Services for accessing these data are described at the back of the journal.

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