

Molecular and supramolecular Ni(II) wheels from α -benzoin oxime†

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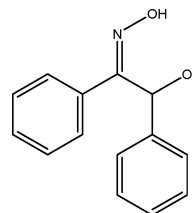
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The use of α -benzoin oxime in Ni(II) chemistry leads to the formation of a family of unusual molecular and supramolecular wheels.

The synthesis and characterisation of polymetallic clusters of paramagnetic transition metal ions is an area of intense current research since such species may display fascinating physical phenomena.¹ Indeed serendipitous self assembly has led to the discovery of, for example, single-molecule magnets,² molecular coolants³ and spin phonon traps⁴ that have inspired much beautiful chemistry and physics with exciting potential application.⁵ Introducing new preparative routes towards the synthesis of transition metal clusters is thus of interest for the discovery of completely new structural types and as a means of building up families of related compounds so that structure–property relations can be developed.⁶ Organic ligands play a crucial role in successful cluster synthesis, but their nature and variety is surprisingly restricted.⁷ In the last few years we have been exploiting the coordination ability of salicyl-oximes (R-saoH₂) to build Mn clusters, leading to the discovery of, amongst others, families of Mn₃ and Mn₆ molecules based on linked triangles.⁸ Recently we have turned our attention to the synthesis of Ni-oxime cages, and while R-saoH₂ ligands are excellent for M(III) cluster synthesis they are useless for building M(II) clusters since they form only mononuclear [M(R-saoH₂)₂] type species—a fact exploited for some time in industrial metal extraction.⁹ Our first foray into Ni-oxime chemistry produced [Ni₁₂] molecules using pyridine-2-amidoxime (IUPAC name: *N*-hydroxy-pyridine-2-carboxamidine)¹⁰ and here we extend this work to α -benzoin oxime (aboH₂, Scheme 1) and report the first members of a family of molecular and supramolecular wheels. Molecular wheels have long fascinated chemists not only for their architectural beauty but for their rich physical behaviour.¹¹ Ni(II) wheels are extremely rare¹² restricted to the species [Ni₆],^{12a-c} [Ni₈],^{12d} [Ni₁₂]^{12e-g} and [Ni₂₄],^{12h-12i} while α -benzoin oxime has been sparingly employed in transition metal coordination chemistry—



Scheme 1 The structure of α -benzoin oxime (aboH₂).

a search of the CCDC database revealing just one molybdenum dimer.¹³

Reaction of NiCl₂·6H₂O with aboH₂ and MeONa in MeOH for 3 hours, followed by Et₂O diffusion, produces the complex [Ni₈(abo)₈(Et₂O)₂(MeOH)₂(H₂O)]·2Et₂O (1·2Et₂O) in ~40% yield in 5 days, crystallising in the orthorhombic space group *Fdd2*.† The structure describes an unusual octametallc wheel in which two octahedral (Ni3, [NiO₆] coordination sphere), four square planar (Ni2 and Ni4, [NiO₂N₂] coordination sphere) and two square-based pyramidal (Ni1 and Ni5, [NiO₅] coordination sphere) Ni(II) ions alternate around the circumference (Fig. 1). A two fold axis passes through the square pyramidal Ni atoms. Each of the metal centres is connected to its nearest neighbour through one oxime group and one alkoxide, with the coordination spheres of the octahedral Ni ions completed with a MeOH molecule outside and a disordered Et₂O molecule inside the wheel. The two axial coordination sites around the square-based pyramidal atoms are occupied by a H₂O and an Et₂O molecule, respectively. The eight Ni(II) ions are nearly coplanar, with the square planar

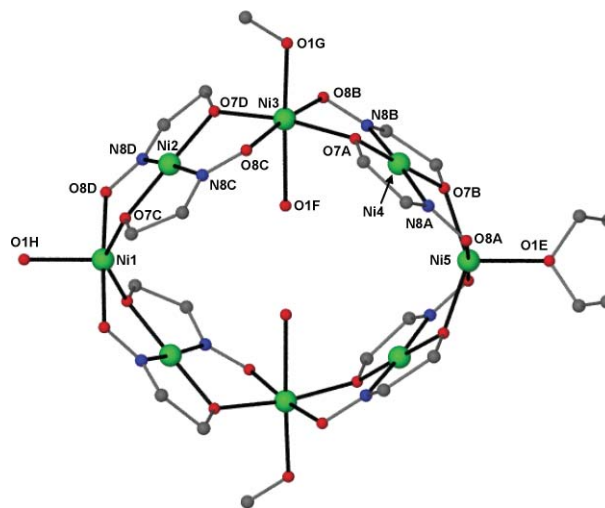


Fig. 1 The molecular structure of complex 1. Colour code: Ni = green, O = red, N = blue, C = grey. All hydrogen atoms and most carbon atoms have been omitted for clarity.

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atoms deviating by *ca.* 0.097 Å from the best least-squares plane passing through them. The closest Ni...Ni distances are almost identical, ranging from 3.153 to 3.162 Å. The wheel is “egg” shaped with the Ni...Ni distances across the diameter being 7.748, 7.849 and 9.260 Å for the octahedral, square planar and square pyramidal Ni atoms. To the best of our knowledge, **1** is only the second Ni(II) cluster containing octahedral, square pyramidal and square planar Ni(II) atoms,¹⁴ and represents only the second octanuclear Ni(II) wheel.^{12d} The molecules pack with their [Ni₈] planes approximately parallel to the *ac* plane. Despite the large number of phenyl groups around the [Ni₈] wheel, there is only a C–H...π interaction [C2A–H2A...π (C9D, C10D, C11D, C12D, C13D, C14D), H...centroid 2.98 Å, C...centroid 3.850 Å, C–H...centroid 153° (and its symmetry related)] holding the cyclic molecules together in the *ac* plane giving rise to a (4,4)-grid layer (Fig. S1†).

Addition of sodium pivalate to the reaction mixture that gave **1** followed by Et₂O diffusion produced the hexanuclear complex [Ni₆(abo)₆(aboH₂)₂(MeOH)₄].2Et₂O (**2**·2Et₂O) in ~40% yield in a week. **2**·2Et₂O crystallises in the triclinic space group *P*-1.†† A perspective view of the molecular structure of **2** is shown in Fig. 2. Four octahedral (Ni1, Ni3 and their symmetry related) and two square planar Ni(II) atoms (Ni2 and its symmetry related) and six abo²⁻ ligands have assembled to form a cyclic molecule that lies on a centre of inversion. Two abo²⁻ ligands chelate each of the square planar Ni atoms through the oximate N and the hydroxyl O atoms in a *trans* orientation giving rise to two symmetry related [Ni(abO)₂]⁺ units. Each [Ni(abO)₂]⁺ unit bridges two octahedral Ni atoms (Ni1 and Ni3) *via* the hydroxyl and the oximate O atoms, with the oximate O atoms further bridging the third and fourth octahedral Ni atoms. Each of the remaining two abo²⁻ ligands chelate to the octahedral Ni1 atom through the oximate N and the hydroxyl O atom and bridge the second octahedral Ni3 atom *via* the oximate O atom. The octahedral environment around Ni1 atom is completed by a chelating aboH₂ ligand, with the coordination sphere of Ni3 completed by two MeOH molecules. No pivalate appears in the product, but remains essential for its formation. In this arrangement, the hexanuclear cluster looks like a parallelogram rather than a wheel with the two dinuclear octahedrally coordinated Ni units being bridged by two square planar [Ni(abO)₂]⁺ units. The [Ni₆] clusters have assembled in the crystal lattice to create a **pcu** network (Fig. S2†),¹⁵ with each [Ni₆] unit interacting with six neighbouring clusters through three (and their

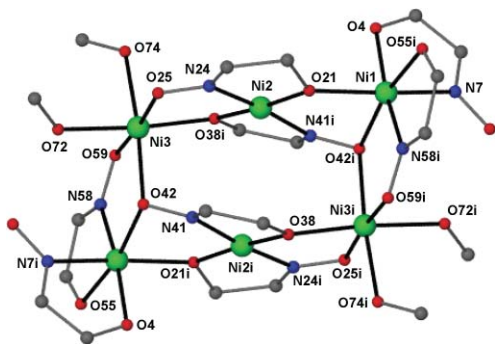


Fig. 2 The molecular structure of complex **2**. Colour code: Ni = green, O = red, N = blue, C = grey. All hydrogen atoms and most carbon atoms have been omitted for clarity.

symmetry related) C–H...π interactions [C29–H291...π (C15, C16, C17, C18, C19, C20), H...centroid 2.95 Å, C...centroid 3.847 Å, C–H...centroid 166°; C68–H681...π (C26, C27, C28, C29, C30, C31), H...centroid 2.81 Å, C...centroid 3.644 Å, C–H...centroid 147°; C70–H701...π (C60, C61, C62, C63, C64, C65), H...centroid 2.63 Å, C...centroid 3.423 Å, C–H...centroid 143°].

Switching from NiCl₂·6H₂O to Ni(ClO₄)₂·6H₂O under the same reaction conditions as in **1**, produces orange block crystals of [NaNi(abO)(aboH)(MeOH)₃] (**3**) in ~45% yield in 4 days. Complex **3** crystallises in the triclinic space group *P*-1, with two independent molecules in the unit cell. The monoanion and the dianion of the aboH₂ ligand chelate around a square planar Ni(II) atom (Ni1 and Ni10) through the hydroxyl O and the oximic N atoms in *cis* orientation. The deprotonated oximic O atom of the abo²⁻ ligand and the oximic OH group of the aboH⁻ ligand form an intramolecular hydrogen bond (O23–H231...O6, H...O 1.58 Å, O...O 2.431 Å, O–H...O 170°; O123–H1231...O106, H...O 1.57 Å, O...O 2.422 Å, O–H...O 172°). The deprotonated hydroxyl O atoms of the Ni bound abo²⁻ and aboH⁻ ligands chelate one Na atom. The square pyramidal environment around the Na atom is completed with three MeOH molecules. Two of the Na coordinated MeOH molecules are hydrogen bonded to the two hydroxyl O atoms of the second independent heteronuclear dimer to form the tetranuclear assembly (**3**)₂ (O39–H391...O119, H...O 1.92 Å, O...O 2.731 Å, O–H...O 176°; O41–H411...O102, H...O 1.90 Å, O...O 2.733 Å, O–H...O 177°; O139–H1391...O19, H...O 1.92 Å, O...O 2.716 Å, O–H...O 174°; O141–H1411...O2, H...O 1.90 Å, O...O 2.715 Å, O–H...O 176°) (Fig. 3a). Two neighboring (**3**)₂ units

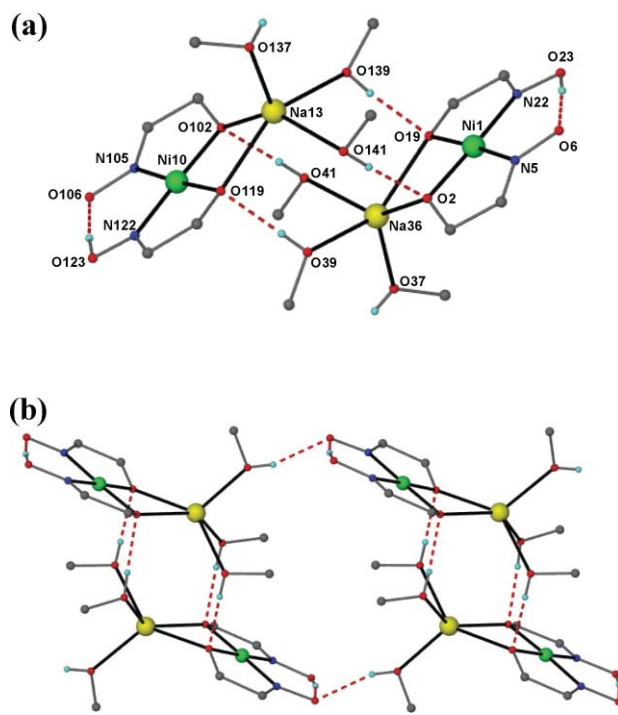


Fig. 3 (a) The molecular structure of (**3**)₂ and (b) the supramolecular wheel made of two (**3**)₂ assemblies. Colour code: Ni = green, Na = yellow, O = red, N = blue, C = grey, H = cyan. Most hydrogen and carbon atoms have been omitted for clarity.

assemble through an O–H...O hydrogen bond that involves the O–H group of the third (Na-coordinated) MeOH molecule and the deprotonated oximic O atom of the abo^{2-} ligand of a neighbouring (3_2) assembly, to form a cyclic assembly (O37–H371...O106, H...O 2.09 Å, O...O 2.783 Å, O–H...O 148°; O137–H1371...O6, H...O 2.06 Å, O...O 2.829 Å, O–H...O 157°) (Fig. 3b). The latter hydrogen bonding pattern between the (3_2) assemblies is propagated in the lattice to produce a tape of cyclic assemblies (Fig. 4). All tapes are running parallel to the (0 1 –1) line with each further bridged through C–H... π interactions [C11–H111... π (C130, C131, C132, C133, C134, C135), H...centroid 2.78 Å, C...centroid 3.672 Å, C–H...centroid 159°; C111–H1111... π (C30, C31, C32, C33, C34, C35), H...centroid 2.76 Å, C...centroid 3.624 Å, C–H...centroid 153°; C115–H1511... π (C30, C31, C32, C33, C34, C35), H...centroid 2.91 Å, C...centroid 3.742 Å, C–H...centroid 148°] to four neighbouring tapes creating a **pcu** rod-packing¹⁶ (Fig. S3†).

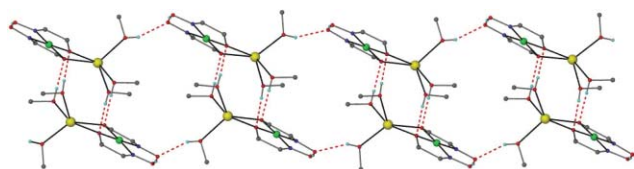


Fig. 4 The tape of the supramolecular wheels along the 0 1 –1 line. Colour code as in Fig. 3. Most hydrogen and carbon atoms have been omitted for clarity.

The initial use of α -benzoin oxime in the coordination chemistry of a first row transition metal has produced an unusual family of molecular and supramolecular wheels. $[\text{Ni}_8]$ is only the second example of an octametallc Ni(II) wheel and represents a rare example of a Ni(II) cluster exhibiting octahedral, square pyramidal and square planar coordination environments; $[\text{Ni}_6]$ is only the fourth example of a hexametallc Ni(II) wheel. The molecular structure of **1** and **2** and the supramolecular structure of **3** therefore suggests that abo^{2-} may be predisposed to form wheel-like structures with other metal ions; and in particular with other M(II) ions. Synthetic efforts are thus underway to produce the analogous Mn(II), Fe(II), Co(II) and Cu(II) wheels to further exploit the potentially exciting coordination chemistry of α -benzoin oxime.

Notes and references

‡ **1**: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 1.0 mmol), aboH_2 (0.227 g, 1.0 mmol) and CH_3ONa (0.108 g, 2 mmol) were dissolved in 25 cm^3 of MeOH and stirred for 3 hours. After filtration and Et_2O diffusion, red crystals were

formed in ~37% yield after 6 days. Elemental analysis (%) calculated for $\text{Ni}_8\text{C}_{122}\text{H}_{118}\text{N}_8\text{O}_{21}$: C 58.57, H 4.75, N 4.48; Found: C 59.11, H 4.91, N 4.87. **2**: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 1.0 mmol), aboH_2 (0.45 g, 2.00 mmol), $\text{NaO}_2\text{CCMe}_3$ (0.124 g, 1.0 mmol) and CH_3ONa (0.108 g, 2 mmol) were dissolved in 25 cm^3 of MeOH and stirred for 3 hours. After 3 filtrations and Et_2O diffusion, crystals were formed in ~40% yield after 5 days. Elemental analysis (%) calculated for $\text{Ni}_6\text{C}_{116}\text{H}_{108}\text{O}_{20}\text{N}_8$: C 60.94, H 4.76, N 4.90; Found: C 61.20, H 5.12, N 4.98. **3**: $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.365 g, 1.00 mmol), aboH_2 (0.45 g, 2.00 mmol) and CH_3ONa (0.216 g, 4 mmol) were dissolved in 25 cm^3 of MeOH, stirred for 3 hours and then filtered. X-ray quality crystals were obtained upon slow evaporation of the mother liquor in ~42% yield after 4 days. Elemental analysis (%) calculated for $\text{NiNaC}_3\text{H}_3\text{N}_2\text{O}_7$: C 59.17, H 5.61, N 4.45; Found: C 59.32 H 5.72, N 4.57.

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