

## A new class of macrocyclic complexes formed *via* nickel-promoted macrocyclisation of dioxime with dinitrile

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*o*-Phthalonitrile couples with chelating dioxime on nickel(II), with formation of a dinuclear nickel(II) macrocyclic complex—the first representative of a new class of imine-appended macrocycles.

Recent reports describe metal-promoted coupling of oximes and nitriles by vanadium(V),<sup>1</sup> nickel(II),<sup>2</sup> platinum(IV),<sup>3</sup> rhenium(IV),<sup>4</sup> or rhodium(III).<sup>5</sup> This addition of the N–OH moiety across the nitrile C≡N bond results in formation of an imino-ether, with new C–O and N–H linkages, and the product's imino-nitrogen coordinated to the nickel.<sup>2</sup> Such coupling potentially provides an attractive pathway for generation of a new class of imine-appended macrocyclic ligands by reaction of appropriate dinitriles with dioximes. The contemporary development of metal macrocycles continues unabated, because of their importance in biomimetic,<sup>6</sup> supramolecular<sup>7</sup> and medicinal<sup>8</sup> chemistry.

Reaction of Ni(DtoxH<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> **1**, with 1,2-dicyanobenzene resulted in formation of the binuclear complex **2**, of the macrocyclic ligand shown in Fig. 1—the first representative of this new class of macrocycles. In the FAB mass spectrum of its tetraperchlorate salt, peaks for the molecular ions (**2** + 3ClO<sub>4</sub><sup>−</sup>)<sup>+</sup> and (**2** − H + 2ClO<sub>4</sub><sup>−</sup>)<sup>+</sup> were found at *m/z* 1143 and 1043, respectively. The 1143<sup>+</sup> peak, the most intense feature at *m/z* > 400, corresponds to the ion containing two nickel atoms and the ligand moiety (Dtox/*o*-C<sub>6</sub>H<sub>4</sub>[CNH]<sub>2</sub>)<sub>2</sub>. These results are similar to those observed previously for Ni{Dtox(NHCCH<sub>3</sub>)<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub>, isolated as the product of metal-promoted covalent addition of CH<sub>3</sub>CN to DtoxH<sub>2</sub>.<sup>2</sup>

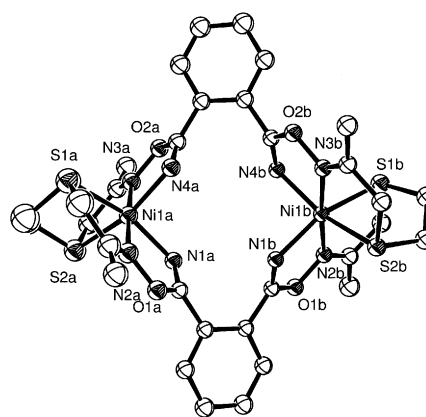
Deep blue crystals of the above perchlorate salt of **2**, as the trihydrate, were obtainable from nitromethane by vapour diffusion of ether or liquid diffusion of mesitylene.<sup>9</sup> The triclinic unit cell contains an enantiomeric pair of dinuclear complex cations of **2**. The two oxime groups from Ni(DtoxH<sub>2</sub>)<sup>2+</sup> have added to two nitrile groups of two different *o*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub> molecules and *vice versa*, resulting in four imino-ether moieties (Fig. 2). The inequivalent Ni(II) atoms in the dinuclear molecule are consequently located in distorted octahedral S<sub>2</sub>N<sub>4</sub> donor sets. Similar coordination and structural parameters are observed for prior NiN<sub>2</sub>S<sub>4</sub> chromophores,<sup>2,10</sup> the coordination core metrics of **2** being comparable with those for

[Ni{Dtox(NHCCH<sub>3</sub>)<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub>].<sup>2</sup> Examination of molecular models reveals that imine-N coordination is an important factor associated with formation of the dinucleating macrocycle: the mononuclear product from coupling *o*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub> with Ni(DtoxH<sub>2</sub>)<sup>2+</sup> in 1 : 1 molar ratio would have structural/geometric properties which render mononucleative hexadentacy of the ligand impossible. Even in **2**, the N=C–C<sub>6</sub>H<sub>4</sub>–C=N fragments are quite nonplanar, the N–C–C–C dihedral angles ranging from 37 to 55° and the C–C–C ones from 10 to 20°. The chirality of the individual molecular cations is associated with a conformational twist of the macrocycle into a 'figure-8', so that in the enantiomer depicted in Fig. 2, each Ni is held in a left-handed loop which provides its four endocyclic donor atoms. The macrocycle is slightly flattened, so that its two coordination octahedra are twisted 12° from being at right-angles (*S*<sub>4</sub> relationship) to one another; the nickel atoms are 6.00 Å apart.

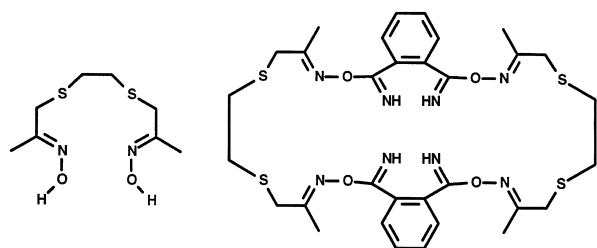
The electronic spectra of **2** show two d–d transitions in nitromethane {λ<sub>max</sub> = 832 nm [ε = 250 L mol<sup>−1</sup> cm<sup>−1</sup>]; <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>; 561 nm [ε = 77]; <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F)<sup>11,12</sup>} and in the solid state (833, 568 nm; BaSO<sub>4</sub> matrix), evidencing that the molecule maintains its integrity in solution.

The cathodic and anodic electrochemistry<sup>2,12</sup> of **2** is non-Nernstian. In CH<sub>3</sub>CN/NET<sub>4</sub>ClO<sub>4</sub>, the Ni(II) instability implied by the irreversible reduction (*E*<sub>p,c</sub> in cyclic voltammetry at −0.8 V vs. SCE<sup>13</sup>) is partly a consequence of its high coordination number,<sup>2</sup> while the observed oxidation (*E*<sub>p,a</sub> at +2.1 V vs. SCE) is attributable to ligand oxidation.<sup>14</sup>

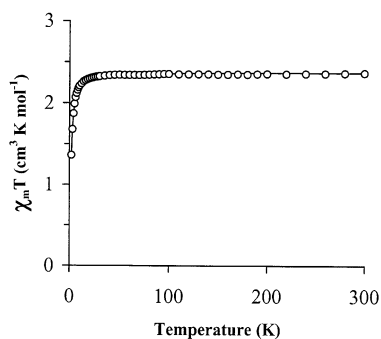
Because the dinuclear cation of **2** entails a conjugated –N=C–C=C–C=N– bridge between the nickel(II) atoms, there is the



**Fig. 2** ORTEP plot of the structure of the complex cation of **2**. H-atoms and non-core atom labels are omitted, and thermal ellipsoids are shown at the 20% level for clarity. Selected bond lengths (Å): Ni(1a)–N(2a) 2.005(6); Ni(1a)–N(3a) 1.997(6); Ni(1a)–N(4a) 2.039(5); Ni(1a)–N(1a) 2.037(4); Ni(1a)–S(2a) 2.479(2); Ni(1a)–S(1a) 2.435(2); Ni(1b)–N(3b) 2.032(4); Ni(1b)–N(2b) 2.022(4); Ni(1b)–N(1b) 2.047(4); Ni(1b)–N(4b) 2.072(4); Ni(1b)–S(1b) 2.4618(16); Ni(1b)–S(2b) 2.4506(16).



**Fig. 1** DtoxH<sub>2</sub> and (Dtox)<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(CNH)<sub>2</sub>}<sub>2</sub> ligands described in this work.



**Fig. 3** Temperature dependence of the magnetic susceptibility of the dinuclear macrocycle **2**, plotted as  $\chi T$  vs.  $T$ . The solid line is the least-squares fit, with  $g = 2.18(1)$ ,  $N\alpha$  set to  $0.0001 \text{ cm}^3 \text{ mol}^{-1}$ ,  $R^2_{(\chi)} = 4 \times 10^{-5}$ .

possibility for a magnetic exchange interaction, despite the rather long pathway. Indeed, although **2** behaves as a paramagnet from ambient temperature down to below 50 K, the magnetic moment becomes suppressed below *ca.* 25 K (Fig. 3). Application of models<sup>15,16</sup> based on  $\mathcal{H} = -2JS_1S_2$  consistently indicates a very weak antiferromagnetic coupling between the two Ni(II) ( $-2J = 0.6 \pm 0.2 \text{ cm}^{-1}$ ), although reliable separation of the zero-field splitting contribution for nickel(II) (*ca.*  $-1 \text{ cm}^{-1}$  in this fit) is not possible in situations like this.

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- A solution of DtoxH<sub>2</sub>, Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and *o*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub> (0.85 mmol of each) in 2 mL of MeNO<sub>2</sub> was allowed to stand for two weeks at ambient temperature, after which Et<sub>2</sub>O addition yielded an oily blue mass, which was solidified by trituration with cold Et<sub>2</sub>O. Yield (after recrystallization *via* Et<sub>2</sub>O diffusion into a MeNO<sub>2</sub> solution): 485 mg (88%). C<sub>32</sub>H<sub>46</sub>Cl<sub>4</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>23</sub>S<sub>4</sub>: Calc. (found): C, 29.6 (29.6); H, 3.55 (3.55); N, 8.63 (8.62); Ni, 9.1 (9.1)%. IR (cm<sup>-1</sup>, in KBr): 1680sh, m; 1650m (νC=N oxime and imine). The crystals formed *via* Et<sub>2</sub>O or mesitylene diffusion are isostructural, although the latter were of better (though not good) quality. X-Ray data were collected for a  $0.35 \times 0.18 \times 0.16 \text{ mm}$  crystal at 296 K on a Bruker SMART 6K CCD diffractometer with a Rigaku Rotating anode (Cu filament,  $\lambda = 1.54178 \text{ \AA}$ , absorption coefficient =  $4.874 \text{ mm}^{-1}$ ) generator equipped with Gobel mirrors at settings of 50 kV and 100 mA. The  $\omega$ - $2\theta$  scan routine, with  $2.32 \leq \theta \leq 66.81^\circ$  and  $-12 \leq h \leq 13$ ,  $-14 \leq k \leq 12$ ,  $-22 \leq l \leq 23$ , gave 12315 data (7493 unique,  $R_{\text{int}} = 0.0283$ , 7493 utilised). Data reduction utilised the SAINT program system, and the structure was solved by full-matrix least-squares refinement on  $F^2$  using SHELXTL Version 5.030, absorption being corrected using the SADABS routine. *Crystal data*:  $M = 1298.2$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.9847(2)$ ,  $b = 12.1783(2)$ ,  $c = 19.8496(4) \text{ \AA}$ ,  $\alpha = 99.031(1)$ ,  $\beta = 100.509(1)$ ,  $\gamma = 104.562(1)^\circ$ ,  $V = 2693.66(8) \text{ \AA}^3$ ,  $R = 0.0759$ ,  $R_w = 0.2157$  ( $I > 2\sigma$ ). Disorder of the perchlorates prevented location of the H-atoms of the adjacent water molecules, for which the O...O distances suggest H-bonding. CCDC reference number 157872. See <http://www.rsc.org/suppdata/cc/b1/b111191b/> for crystallographic data in CIF or other electronic format.
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