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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),[1] nickel(II),[2] platinum(IV),[3] rhenium(IV),[4] or rhodium(III).[5] This addition of the N–OH moiety across the nitrile C≡N bond results in formation of an iminoether, with new C–O and N–H linkages, and the product's imino-nitrogen coordinated to the nickel.[2] 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,[6] supramolecular[7] and medicinal[8] chemistry.

Reaction of $Ni(DtoxH_2)(H_2O)_2^{2+}$ **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 $(\mathbf{2} + 3ClO_4^-)^+$ and $(2 - H + 2ClO_4^-)^+$ were found at *m*/*z* 1143 and 1043, respectively. The 1143+ peak, the most intense feature at *m*/*z* > 400, corresponds to the ion containing two nickel atoms and the ligand moiety $(Dtox/o\text{-}C_6H_4[CNH]_2)_2$. These results are similar to those observed previously for $Ni\{Dtox(NHCCH_3)_2\}(ClO_4)_2$, isolated as the product of metal-promoted covalent addition of CH_3CN to $DtoxH_2$.[2]

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.[9] The triclinic unit cell contains an enantiomeric pair of dinuclear complex cations of **2**. The two oxime groups from $Ni(DtoxH_2)^{2+}$ have added to two nitrile groups of two different $o\text{-}C_6H_4(CN)_2$ molecules and *vice versa*, resulting in four iminoether moieties (Fig. 2). The inequivalent Ni(II) atoms in the dinuclear molecule are consequently located in distorted octahedral S_2N_4 donor sets. Similar coordination and structural parameters are observed for prior NiN_2S_4 chromophores,[2,10] the coordination core metrics of **2** being comparable with those for $[Ni\{Dtox(NHCCH_3)_2\}](ClO_4)_2$.[2] 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 $o\text{-}C_6H_4(CN)_2$ with $Ni(DtoxH_2)^{2+}$ 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_6H_4–C=N fragments are quite nonplanar, the N–C–C–C dihedral angles ranging from 37 to 55° and the C–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_4 relationship) to one another; the nickel atoms are 6.00 Å apart.

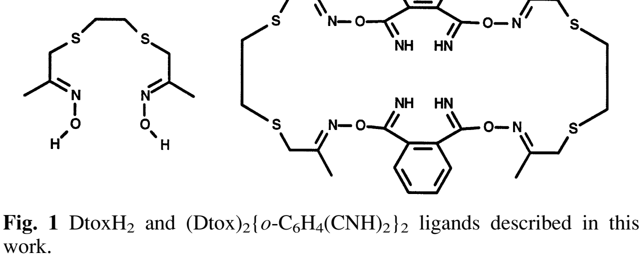

Fig. 1 $DtoxH_2$ and $(Dtox)_2\{o\text{-}C_6H_4(CNH)_2\}_2$ ligands described in this work.

The electronic spectra of **2** show two d–d transitions in nitromethane $\{\lambda_{max}$ = 832 nm [ε = 250 L mol^{-1} cm^{-1}]; $^3A_{2g} \rightarrow {}^3T_{2g}$; 561 nm [$\varepsilon$ = 77]; $^3A_{2g} \rightarrow {}^3T_{1g}(F)^{11,12}\}$ and in the solid state (833, 568 nm; $BaSO_4$ matrix), evidencing that the molecule maintains its integrity in solution.

The cathodic and anodic electrochemistry[2,12] of **2** is non-Nernstian. In CH_3CN/NEt_4ClO_4, the Ni(I) instability implied by the irreversible reduction ($E_{p,c}$ in cyclic voltammetry at −0.8 V *vs.* SCE[13]) is partly a consequence of its high coordination number,[2] while the observed oxidation ($E_{p,a}$ at +2.1 V *vs.* SCE) is attributable to ligand oxidation.[14]

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

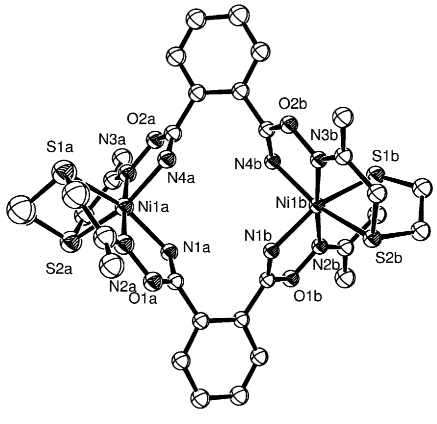

Fig. 2 ORTEP plot of the structure of the complex cation of **2**. H-atoms and non-core atom labels are omitted, and thermal ellipsoids are shown at the 20% level for clarity. Selected bond lengths (Å): Ni(1a)–N(2a) 2.005(6); Ni(1a)–N(3a) 1.997(6); Ni(1a)–N(4a) 2.039(5); Ni(1a)–N(1a) 2.037(4); Ni(1a)–S(2a)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

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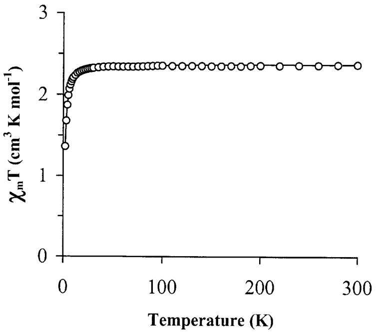

Fig. 3 Temperature dependence of the magnetic susceptibility of the dinuclear macrocycle **2**, plotted as χT *vs.* T. The solid line is the least-squares fit, with $g = 2.18(1)$, $\mathcal{N}\alpha$ set to 0.0001 cm^3 mol^{-1}, $R^2_{(\chi)} = 4 \times 10^{-5}$.

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[15,16] based on $\mathcal{H} = -2JS_1\cdot S_2$ consistently indicates a very weak antiferromagnetic coupling between the two Ni(II) ($-2J = 0.6 \pm 0.2$ cm^{-1}), although reliable separation of the zero-field splitting contribution for nickel(II) (*ca.* -1 cm^{-1} in this fit) is not possible in situations like this.

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9 A solution of DtoxH$_2$, Ni(ClO$_4$)$_2$·6H$_2$O and *o*-C$_6$H$_4$(CN)$_2$ (0.85 mmol of each) in 2 mL of MeNO$_2$ was allowed to stand for two weeks at ambient temperature, after which Et$_2$O addition yielded an oily blue mass, which was solidified by trituration with cold Et$_2$O. Yield (after recrystallization *via* Et$_2$O diffusion into an MeNO$_2$ solution): 485 mg (88%). $C_{32}H_{46}Cl_4N_8Ni_2O_{23}S_4$: Calc. (found): C, 29.6 (29.6); H, 3.55 (3.55); N, 8.63 (8.62); Ni, 9.1 (9.1)%. IR (cm^{-1}, in KBr): 1680sh, m; 1650m (νC=N oxime and imine). The crystals formed *via* Et$_2$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 × 0.18 × 0.16 mm crystal at 296 K on a Bruker SMART 6K CCD diffractometer with a Rigaku Rotating anode (Cu filament, $\lambda = 1.54178$ Å, absorption coefficient = 4.874 mm^{-1}) generator equipped with Gobel mirrors at settings of 50 kV and 100 mA. The ω–2θ scan routine, with $2.32 \leq \theta \leq 66.81°$ and $-12 \leq h \leq 13$, $-14 \leq k \leq 12$, $-22 \leq l \leq 23$, gave 12315 data (7493 unique, $R_{int} = 0.0283$, 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 $P\bar{1}$, $a = 11.9847(2)$, $b = 12.1783(2)$, $c = 19.8496(4)$ Å, $\alpha = 99.031(1)$, $\beta = 100.509(1)$, $\gamma = 104.562(1)°$, $V = 2693.66(8)$ Å^3, $R = 0.0759$, $R_w = 0.2157$ ($I > 2\sigma_I$). 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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