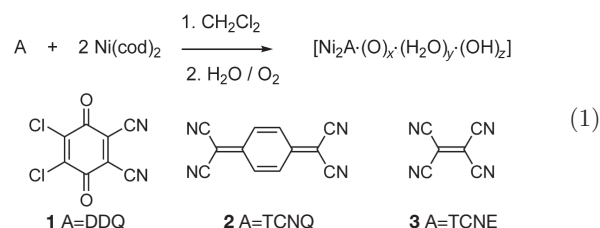# LETTERS

High-temperature metal–organic magnets

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For over two decades there have been intense efforts aimed at the development of alternatives to conventional magnets, particularly materials comprised in part or wholly of molecular components[1,2]. Such alternatives offer the prospect of realizing magnets fabricated through controlled, low-temperature, solution-based chemistry, as opposed to high-temperature metallurgical routes, and also the possibility of tuning magnetic properties through synthesis. However, examples of magnetically ordered molecular materials at or near room temperature are extremely rare[3], and the properties of these materials are often capricious and difficult to reproduce. Here we present a versatile solution-based route to a new class of metal–organic materials exhibiting magnetic order well above room temperature. Reactions of the metal (M) precursor complex bis(1,5-cyclooctadiene)nickel with three different organics A—TCNE (tetracyanoethylene), TCNQ (7,7,8,8-tetracyanoquinodimethane) or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone)—proceed via electron transfer from nickel to A and lead to materials containing Ni(II) ions and reduced forms of A in a 2:1 Ni:A ratio—that is, opposite to that of conventional (low Curie temperature) MA$_2$-type magnets. These materials also contain oxygen-based species within their architectures. Magnetic characterization of the three compounds reveals spontaneous field-dependent magnetization and hysteresis at room temperature, with ordering temperatures well above ambient. The unusual stoichiometry and striking magnetic properties highlight these three compounds as members of a class of stable magnets that are at the interface between conventional inorganic magnets and genuine molecule-based magnets.

Selected metal–cyanide-based organometallic magnets order near or above room temperature[4], although classification of these as 'molecule-based' is debatable given that the cyanide ligand is only nominally larger than the oxo (O^{2-}) bridge in conventional inorganic magnets (such as in Fe_3O_4 or CrO_2). The only molecule-based magnet which orders above room temperature[5] (transition temperature $T_c \approx 400$ K) is $V(TCNE)_x \bullet yCH_2Cl_2$ (where $x \approx 2$; $y \approx 0.5$). This pyrophoric compound is the prototypical member of a large family of low-T_c magnets based on metal (II) cations and radical anions of TCNE in a 1:2 ratio[6]. The proposed structural model is a three-dimensional coordination network[6,7] in which magnetic cooperativity arises from exchange interactions between localized spins on the metal ion and spins on the TCNE radical anion, although structural proof is still lacking. Other vanadium-based materials VR_2 (where R = radical anion) have T_c values of approximately 200 K[7,8], whereas analogous $M(TCNE)_2$ materials (where M = Fe, Co, Mn, Ni) have considerably lower (<122 K) ordering temperatures[9–11]. In general metal–TCNX (where X = E, Q) materials have a long history as conductors[12,13] and as low-temperature magnets[9–11,14], nearly all of which strictly adhere to the MR_2 stoichiometric model. The only exceptions are $Ni(TCNQ)$ and $Ni_3(TCNQ)_2$, neither of which supports magnetic ordering[15].

Here we present investigations on reactions of bis(1,5-cyclooctadiene) nickel—$Ni(cod)_2$—with the organic oxidizing agents TCNE, TCNQ and DDQ. When these reactions were carried out in the conventional 1:2 Ni:A ratio, low yields of ill-defined products were obtained. In each case, a significant amount of unreacted organic A was recovered—an observation that prompted us to explore reactions involving higher M:A ratios. Reactions involving a 2:1 Ni:A stoichiometry (the opposite of the conventional ratio) under an argon atmosphere led to immediate formation of intensely coloured and highly air-sensitive (hydrophilic/oxophilic) cloudy solutions. Subsequent controlled exposure ($\sim$2 hours) of these solutions to air led to precipitation of near-black solid materials that were isolated by filtration to afford the final products **1–3** in quantitative yield (see equation (1)). Attempts to characterize the nature of the 'intermediate species' ($Ni_{2x}A_x$) before air exposure—either in solution or the solid material obtained from it—were thwarted by the intermediate's high reactivity. Clearly the original 2:1 Ni:A stoichiometry precludes complete oxidation/coordination of all of the nickel centres; the air-exposure step fulfils these requirements for the remaining nickel centres during the reaction of the intermediate ($Ni_{2x}A_x$) with molecular oxygen (oxidant) and water (coordinating ligand) (see elemental analyses). Cyclooctadiene is the only material present in the filtrate and can be quantitatively recovered; elemental analyses of **1–3** confirm the absence of cyclooctadiene and also reveal that both the nickel and the ligands A are incorporated quantitatively into **1–3**.

$$A \ + \ 2\,Ni(cod)_2 \ \xrightarrow[\text{2. H}_2\text{O / O}_2]{\text{1. CH}_2\text{Cl}_2} \ [Ni_2A \cdot (O)_x \cdot (H_2O)_y \cdot (OH)_z] \quad (1)$$

1 A=DDQ   **2** A=TCNQ   **3** A=TCNE

Elemental analyses confirm the 2:1 Ni:A ratio, as well as the presence of additional oxygen-containing species—a combination of water and oxide (O^{2-}) or hydroxide (OH^-) resulting from the hydrolysis-based work-up. Therefore, the empirical compositions of **1–3** can best be formulated as $[Ni_2A \bullet (O)_x \bullet (H_2O)_y \bullet (OH)_z]$ with residual solvent, where x, y, z depend on A and are also interdependent (see Supplementary Information for specifics). Charge-balance considerations require that the total negative charge from the ligands A and OH^-, O^{2-} balance the total positive charge on the nickel ions (see below). Efforts to pinpoint these components were thwarted by the inability to distinguish between analytically equivalent oxygen-based species (for example, $[H_2O + O^{2-}]$ versus $[2OH^-]$ in **1** or $[H_2O + O^{2-} + OH^-]$ versus $[3OH^-]$ in **2** and **3**). Powder X-ray diffraction experiments reveal all samples to be amorphous.

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The scanning transmission electron microscopy (STEM) images show all three samples to consist of irregularly shaped and sized 'grains' in the micrometre-to-submicrometre regime, with a texture like broken mud (Supplementary Information). Energy-dispersive X-ray microanalyses corroborated the elemental compositional makeup. Characteristic Ni-Kα, L$\alpha\beta$ X-rays were observed at 7.477 and 0.849 keV respectively[15]. The C, O and Cl Kα-peaks featured at 0.282, 0.523 (ref. 16) and 2.622 keV respectively. The presence of the oxygen peak in **2** and **3** supports the idea of the incorporation of oxygen-containing species from the hydrolysis-based work-up. Studies of several individual grains confirm consistent and uniform composition on this length scale. TEM images show smaller textural features estimated to be 30 ± 3 nm, but none of the images are reminiscent of well-defined nanostructures.

The infrared spectra of the Ni$_2$TCNQ- and Ni$_2$TCNE-based materials (**2** and **3**, respectively) are consistent with these organics present as radical anions: broad ν_{CN} bands were centred at 2,191 cm^{-1} in **2** and at 2,205 and 2,179 cm^{-1} in **3** (ref. 17). For **2** this is further corroborated by a δ_{C-H} feature at 824 cm^{-1} and $\nu_{C=C}$ stretches at 1,505 cm^{-1}, both traits of the π-delocalized TCNQ$^{-\bullet}$ moiety (ref. 14 and references therein). In contrast, the infrared spectrum of Ni$_2$DDQ (**1**) possesses a large bathochromic shift (>240 cm^{-1}) in its ν_{CO} compared to neutral DDQ, which is consistent with dianionic DDQ[18]. The spectra of **1–3** are consistent with the ligands A being coordinated to the nickel ions because the ν_{CN} or ν_{CO} values do not correspond to non-coordinated TCNE and TCNQ (ref. 19 and references therein) or DDQ[19,20] in any of their normal oxidation states, as is observed in their electron-transfer salts. The infrared characteristics differ from Ni(TCNX)$_2$ materials[9,11,14,21] and all exhibit 'clean', singular CN stretches, precluding the presence of degraded forms of the ligands, which would possess their own characteristic stretches. The solid-state electronic spectra corroborate DDQ as a dianion in **1** (ref. 20) through a characteristic absorption at ~400 nm, whereas **2** and **3** have low energy absorptions consistent with the presence of the TCNQ$^{-\bullet}$ and TCNE$^{-\bullet}$ moieties respectively[22].

The oxidation state of nickel was probed by X-ray photoelectron spectroscopy. The binding energies found for the Ni $2p_{3/2}$ peaks in **1–3** are 856.5, 856.4 and 856.3 eV respectively, values in the expected range for chemically stable Ni(II) centres bound to organo- moieties[15]; ruling out nickel (0), for which the Ni $2p_{3/2}$ peaks are typically around 853 eV (ref. 23). Charge-balance considerations therefore require anionic components additional to the organic anion A^{n-}, probably metal-coordinated OH$^-$ or O^{2-}, supported by elemental analyses.

Compounds **1–3** are readily attracted in bulk to external magnets, under ambient conditions. Quantitative magnetic studies were performed with a superconducting quantum interference device (SQUID) magnetometer. Figure 1 presents the field-cooled temper-
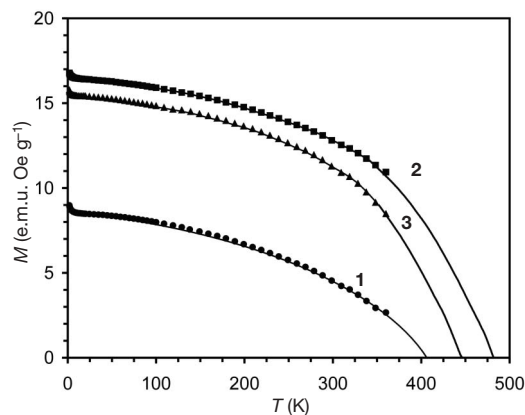
Table 1 | Magnetic parameters for 1–3

Compound	T_c (K)	H_c (Oe)	M_r (e.m.u. Oe g^{-1})	M_{sat} (e.m.u. Oe g^{-1})
1	405	12.9	0.46	32.2
2	480	14.0	5.49	68.6
3	440	12.4	3.69	52.9

ature dependence of magnetization, the $M(T)$ profiles, for **1–3**. Critical temperatures (T_c values) were estimated to be 405 K (**1**), 480 K (**2**) and 440 K (**3**) from the onset points ($M(T) \rightarrow 0$), derived by extrapolation[6–8,11]. These T_c values are more than one order of magnitude larger than those reported for Ni(TCNX)$_2$-based magnets[9,11,14,21] and are clearly dependent on the organics A.

Magnetization versus field plots at 300 K reveal that all three compounds exhibit spontaneous magnetization and distinctive hysteresis (Fig. 2a, b), substantiating long-range bulk magnetic ordering at ambient temperature. Spontaneous magnetization behaviour (Fig. 2b), expressed in gram-magnetization (employed because of unknown structure), in the field-dependent plots was typical of real magnets. Qualitatively, all three samples have visibly different attractive responses to an external magnet. Coercive fields (H_c) and remanent magnetization (M_r) of **1–3** at 300 K are tabulated (Table 1). Interestingly, the remanence of **1**, which contains a spin-inactive DDQ dianion, is an order of magnitude smaller than that of **2** or **3**, both of which contain spin-active ($S=1/2$) radical anions. On the basis of the observed coercive fields (10–15 Oe), all three compounds are soft magnets[3]. The temperature dependence of the M_{sat} values for isothermals between 1.8–100 K, and particularly their shapes in the M versus H plots, (Supplementary Information) can be attributed to a glassy magnetic state[14,24] (see below) owing to spin disorder or frustration inherent in these materials, which is less prominent at higher temperatures (>100 K) approaching or above freezing temperatures. Unexpectedly, however, the M_{sat} values abnormally increase in the low-temperature $M(H)$ measurements. The possibility that the overall magnetization may consist of contributions from two different magnetic regimes—one magnetically ordered and one consisting of non-correlated spins—cannot be ruled out, although the disordered
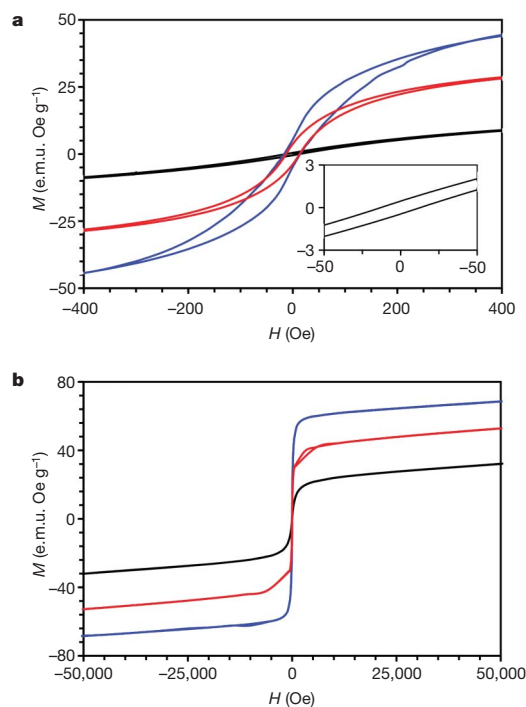

a

b

Figure 2 | Magnetic hysteresis loops for **1** (black line), **2** (blue line), and **3** (red line) at 300 K. **a**, ± 400 Oe. Inset shows expansion of the loop for **1**. **b**, $\pm 50,000$ Oe.

Figure 1 | Temperature dependence of field-cooled (25 Oe) magnetization for 1–3. Solid lines are extrapolations.

non-correlated spin-glass $V(TCNE)_2 \bullet 0.5CH_2Cl_2$ molecule-based magnet[25] shows similar trends in M_{sat}. This behaviour reflects a deviation from properties reminiscent of conventional magnets.

Alternating current (a.c.) susceptibility measurements also support magnetic ordering well above room temperature. Figure 3 presents a.c. data for **3** as a representative example. Both $\chi'(T)$ (in-phase) and $\chi''(T)$ (out-of-phase) plots are frequency-dependent with peak (freezing) temperatures shifting to higher values with increasing frequencies; this trend in the χ' data is suggestive of glassy magnetic behaviour[14]. For a given frequency, the lack of multiple peaks supports the existence of a single magnetic phase[21]. The incomplete saturation in the $M(H)$ plots is also consistent with the postulated glassy state[24], although degrees of glassiness can vary as a function of crystallographic disorder[24], spin frustration arising from specific spin topology[14], residual solvent and temperature[25].

Electron transfer chemistry between $Ni(cod)_2$ and A appears to be a key requirement in the formation of **1–3**. Reactions of $Ni(cod)_2$ with poor oxidizing agents like 1,4-benzoquinone and 1,4-naphtho-quinone lead to low yields of products that do not exhibit magnetic ordering. The corresponding reaction with duroquinone yields non-magnetic discrete π-sandwich complexes[26] and no reaction occurs with p-anthraquinone. The use of coordinating solvents like tetra-hydrofuran or acetonitrile thwarts the formation of **1–3**, perhaps through solvent coordination to nickel[25]. Conceivably, the dissociation of cyclooctadiene with pre-coordination between the organic acceptor and Ni leads to an intermediate which facilitates electron transfer[7,8].

The X-ray photoelectron spectroscopy studies (see above) rule out sources of nickel (0) (whether bulk nickel ($T_c = 627\,K$) or nickel nanoparticles, which are superparamagnetic, with blocking temperatures dependent upon surface species and size/aggregation effects[27]) as the dominant source of the magnetism. The use of $Ni(cod)_2$ to produce Ni nanoparticles requires special conditions (for example, sonochemical decomposition[28]) that afford different types of magnetic materials[29]. Pure nickel oxide (NiO) and nickel hydroxide

$(Ni(OH)_2)$ are antiferromagnets ($T_N = 523\,K$ and 24.8 K respectively) and therefore cannot justify the origin of the magnetism in **1–3**. Nickel oxide nanoparticles are dissimilar to **1–3** because their properties are dependent upon finite size effects and fit behaviour defined as superantiferromagnetic or superparamagnetic[30]. In contrast, the magnetic properties of **1–3** are reproducible from sample to sample without any discernible size-dependence.

A structural model for these materials is still lacking, but the compositional and magnetic data argue against the model developed for the MA_2 magnets[6–8], and the existence of several NiA_2 materials with T_c values < 50 K suggest that the materials described here have a different (and new) structural basis. The spectroscopic features suggest that the organic ligands are σ-bound (via the nitrile or carbonyl groups) to the nickel. The distinct magnetic properties of **1**, **2** and **3** strongly suggest that the organic anions are not merely present to achieve charge compensation but are integral to the magnetic structure of these materials.

The predictive value of the redox and coordination chemistry suggests that it should be possible to produce a wider range of analogous magnets by careful consideration of other organic ligands, and that the intriguing high-temperature magnetic properties of **1–3** could be further modified.

METHODS

See the Supplementary Information for general information on spectroscopy (Fourier transform infrared, ultraviolet–visible, XPS), magnetic and scanning TEM equipment/measurements, and for spectroscopic, EDX, XPS, scanning TEM images, elemental analyses, and magnetic characterization data for **1–3**.

General. Bis(1,5-cyclooctadiene) nickel (0) {$Ni(cod)_2$} was purchased from Strem Chemicals, stored in a glove-box freezer ($-30\,°C$) and used as received. All glassware was thoroughly pre-dried in an oven at $170\,°C$ before use. Dichloromethane was freshly distilled under argon before use. DDQ, TCNQ and TCNE were purchased from Aldrich and also used as received.

Synthesis. In a representative experiment performed on a Schlenk line, we added 0.337 g (1.225 mmol) $Ni(cod)_2$ as a solid (weighed in dry box and taken out in a tightly sealed vial just before adding) to a vigorously stirred solution of 0.125 g (0.612 mmol) of TCNQ dissolved in 100 ml dichloromethane (DCM), under a high flow of argon at room temperature. An immediate and intense colour change from yellow to deep-green/black was observed upon mixing and after a few minutes the solution became cloudy/opaque to transmitted light. The reaction flask was immediately secured with a septum and the reaction was stirred for an additional 3.5 h while reducing the flow of argon to a normal rate. Following this, the reaction mixture was exposed to air for ~2 h and stirred at a moderate rate. The solution was then suction filtered using a normal water-jet aspirator and the precipitate was thoroughly washed with DCM, and dried in vacuum to produce a dark-coloured solid (**2**) with a quantitative yield of 0.237 g. For **1**; A = DDQ (0.125 g, 0.551 mmol); $Ni(cod)_2$ (0.303 g, 1.102 mmol). Yield of **1**: 0.230 g. For **3**; A = TCNE (0.100 g, 0.781 mmol); $Ni(cod)_2$ (0.430 g, 1.563 mmol). Yield of **3**: 0.242 g

Figure 3 | Temperature dependence of the a.c. susceptibility of 3 at different frequencies. a, In-phase (χ'); **b**, out-of-phase (χ''). 0.1 Hz, red squares; 1.0 Hz, purple diamonds; 10.0 Hz, green triangles; 117.04 Hz, blue circles; 946.97 Hz, brown squares.

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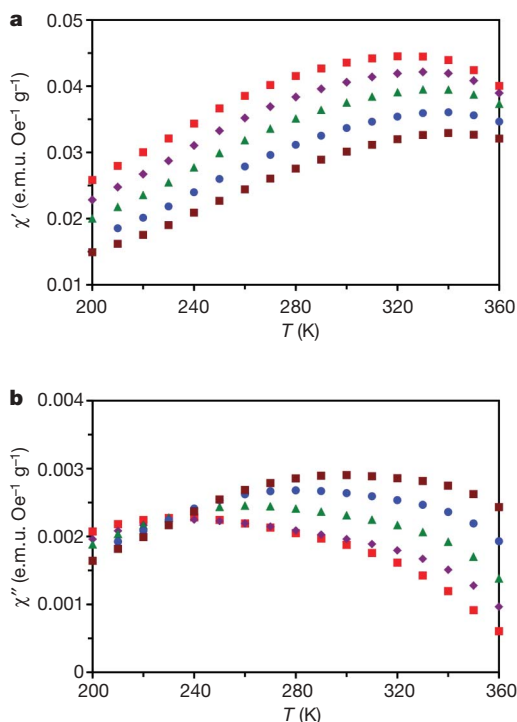
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