Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Mohamedally Kurmoo & Cameron J. Kepert (1999): Magnetic Materials Containing the Dicyanamide Anion, $\{N(Cn)_2\}^-$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 693-702

To link to this article: http://dx.doi.org/10.1080/10587259908023362

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 693-702
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Magnetic Materials Containing the Dicyanamide Anion, $\{N(Cn)_2\}^-$

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The crystal structures and magnetic properties of a series of isostructural magnetic compounds, $M^{II}\{N(CN)_2\}_2$, where M = Cu (**1**), Ni (**2**), Co (**3**) and Fe (**4**) are presented. The dicyanamide bridges the metal ions in **1** – **4** to form infinite 3-D metal-organic frameworks with a rutile-type structure. Magnetic data for **1** obey the Curie-Weiss law (Θ= −2.1 K). **2** and **3** are ferromagnets with Curie temperatures (T_C) of 21 and 9 K; **4** is a canted antiferromagnet (T_N= 18.8 K). The coercive field of **4** is 17800 Oe, the largest observed for any metal-organic compound. The maximum energy product (BH) is the highest for **2** and is comparable to alloys of $SmCo_5$. We attribute the large coercive field to a combination of single ion and particle shape anisotropies.

INTRODUCTION

The cyanide and polycyanide ligands first emerged as popular connecting units for constructing magnetic materials when Mallah and coworkers[1] demonstrated that room temperature magnets can be achieved by the appropriate choice of metals in the Prussian blue family and $V(TCNE)_2$.solvent [2] were observed to be room temperature magnets. Salts of the families $M^{II}(TCNQ)_x$[3] and $M^{II}(TCNE)_x$[4] have more recently been reported to show magnetic ordering over a wide range of temperatures, although poor crystallinity has hampered their crystallographic characterization. In contrast, the highly crystalline polycy-

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anide salts $M^{II}\{C(CN)_3\}_2$ (M = Cu, Ni, Co, Fe and Mn) are dominated by antiferromagnetic interactions[5]. Amongst the different families of transition metal-polycyanide complexes, the dicyanamide represent an ideal system for study, providing a rich diversity of magnetic properties, which range from paramagnetic to canted antiferromagnetic to ferromagnetic, and being among the most crystalline for the purpose of structural characterization

Transition metal complexes of the dicyanamide and tricyanomethanide have been extensively studied by Köhler, Mrozinski, Hvastijova and Jäger[6]. Britton and Chow[7] have examined some of the early crystal structures. Robson and Batten [8] have used the multidentate character of these ligands to generate interpenetrating structures. Recently, Kini and Williams[9] have used polymeric layers of the Cu^{I}-dicyanamide anion to stabilize superconducting organic radical salts.

During an extensive study on the dicyanamide coordination complexes, we have observed exceptional magnetic properties, *for example*, a T_C of 56K and coercive fields approaching 2 Tesla. In the series of salts $M^{II}\{N(CN)_2\}_2$, where M is Cu, Ni, Co and Fe, Batten *et al.* [10], Miller [11] and ourselves [12] have independently established magnetic ordering with Curie temperatures reaching 21 K and coercive fields up to 18000 Oe[12]. We were able to tune these two parameters continuously, and as desired, by variation of the metal centers. Here we summarize the crystal structures of $M^{II}\{N(CN)_2\}_2$ (M = Cu and Co), and magnetic properties of $M^{II}\{N(CN)_2\}_2$ (M = Cu, Ni, Co and Fe).

RESULTS AND DISCUSSION

The compounds were prepared by the reaction of the metal nitrate or sulfate and sodium dicyanamide (FLUKA) in either water or ethanol. Crystals were obtained by slow recrystallization in water at room temperature. Micro size crystallites were obtained from the ethanol reaction. Experimental details of the physical measurements have been described elsewhere[12].

A summary of the crystal data are given in table I. The crystal structures of $M^{II}\{N(CN)_2\}_2$ are based on close packing of linear ribbons that propagate along *c*. Within these ribbons, the dicyanamide forms double bridges between metal ions. Adjacent ribbons are slipped by half *c*, so that the apical amide nitrogen atoms complete the 4+2 coordination on the M^{II} ions (figure 1). The structure may alternately be viewed as a single network with connectivity identical to the rutile polymorph of TiO_2, where M and dicyanamide replace the Ti and O. The asymmetry of the dicyanamide anion (and in **1**, the Jahn-Teller distortion of Cu^{II}) means that the structure is orthorhombic rather than tetragonal, and more closely related to $CrCl_2$[13].

TABLE I: Summary of Crystal Data for $M^{II}\{N(CN)_2\}_2$

Compound	M = Cu (**1**)	M = Cu (**1**)	M = Ni (**2**)	M = Co (**3**)
Formula	$Cu\{N(CN)_2\}_2$	$Cu\{N(CN)_2\}_2$	$Ni\{N(CN)_2\}_2$	$Co\{N(CN)_2\}_2$
Measurement	Crystal	Crystal	Powder	Crystal
Radiation	X-ray	X-ray	X-ray	X-ray
T /K	295(2)	150(2)	295(2)	150(2)
Space group	Pnnm	Pnnm	Pnnm	Pnnm
a /Å	6.120(1)	6.082(1)	5.980(1)	5.970(1)
b /Å	7.339(1)	7.288(1)	7.107(1)	7.060(1)
c /Å	7.173 (1)	7.187(1)	7.393(1)	7.406(1)
V /Å^3	322.17(8)	318.57(8)	314.2	312.15(8)
Z	2	2	2	2

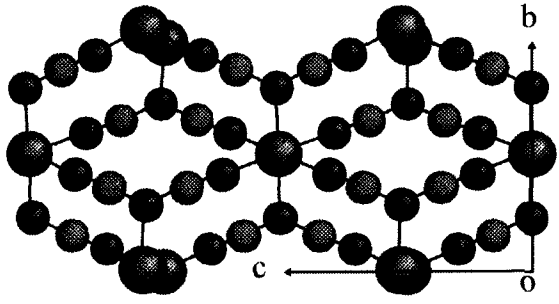

FIGURE 1 View of the structure of $Co\{N(CN)_2\}_2$ along a.

Although complexes **2** and **3** are isostructural with **1**, their crystal structures differ significantly due to the absence of a strong Jahn-Teller distortion. In **3**, the M-M distance in the chain (Cu-Cu = 7.187 Å, c-axis parameter) is increased to 7.406 Å due to an increase in the M-N_{eq} distance from 1.98 (Cu) to 2.10 Å (Co). The reverse is seen for the b-parameter, 7.288(Cu) to 7.060Å (Co), due to a decrease of the M-N_{amide} distance from 2.45 (Cu) to 2.15 Å (Co). Most importantly, the distortion away from a regular tetragonal lattice is less severe in **2** and **3** than in **1**.

A summary of the important magnetic data is given in table II and the temperature dependence of the DC and AC magnetization are shown in figures 2-4. Compounds **2** - **4** show spontaneous magnetization in very small applied magnetic field and an imaginary component in the AC susceptibilities in zero field. The Curie constants are consistent with those expected for high-spin divalent metals in octahedral coordination. The Weiss constants, Curie temperatures and critical exponents suggest that **2** and **3** are mean-field (MF) magnets. The β value for **4** is that expected for MF but the other parameters are not.

TABLE II: Summary of Magnetic Data

Compound	(1)	(2)	(3)	(4)
M, d^n, Spin (S)	Cu, d^9, 1/2	Ni, d^8, 1	Co, d^7, 3/2	Fe, d^6, 2
C (cm^3 K/mol)	0.44	1.21	2.82	3.22
Θ (K)	-2.1(4)	+22.7(2)	+9.7(6)	+3(1)
T_C(K)		21.1(4)	9.0(3)	18.8(3)
β		0.49(2)	0.49(2)	0.49(2)
γ		1.00(5)	1.00(5)	
γ'		0.98(3)	0.91(4)	0.29(1)
M(μ_B in [H/T]	1 [7T]	1.98 [5T]	2.56 [5T]	1.3 [8T]
M_{REM} (μ_B)	0	1.07	1.45	0.50
H_c (Oe) at 2K	0	7975	710	17800
$(BH)_{max}$ (MOeG)	0	26	2	16.6

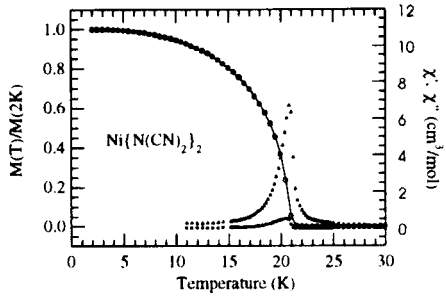

FIGURE 2 Temperature dependence of the relative magnetisation in 0.1 Oe, χ' and χ'' of $Ni\{N(CN)_2\}_2$.

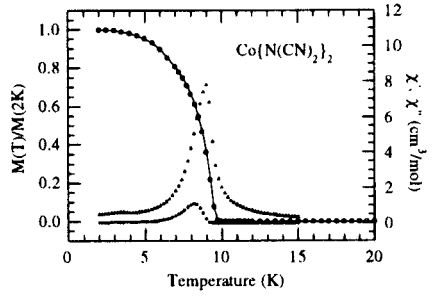

FIGURE 3 Temperature dependence of the relative magnetisation in 0.1 Oe, χ' and χ'' of $Co\{N(CN)_2\}_2$.

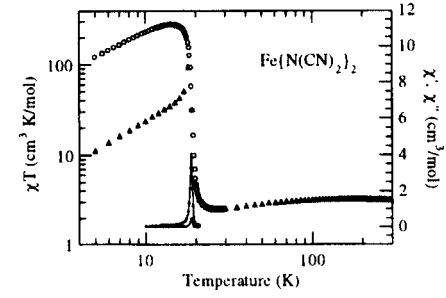

FIGURE 4 Temperature dependence of χT in 100 Oe, χ' and χ'' of $Fe\{N(CN)_2\}_2$.

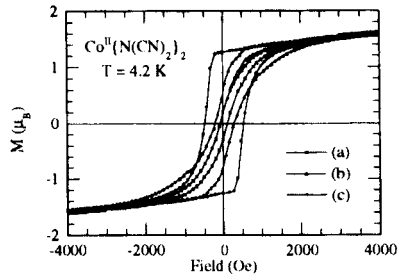

FIGURE 5 Particle size effect on the hysteresis loop of $Co\{N(CN)_2\}_2$ for (a) as grown crystals (>100μ), (b) ground crystals (1-5μ) and (c) as powder prepared from ethanol (<1μ).

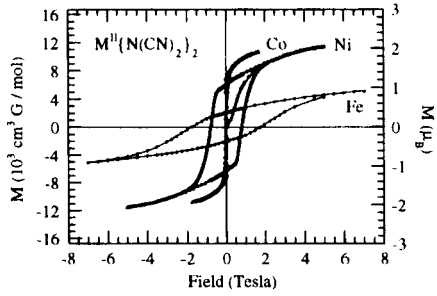

FIGURE 6 First magnetization and hysteresis for $M\{N(CN)_2\}_2$, Ni (triangles, T=2K), Co (open circles, T=4.5K) and Fe (filled circles, T=3K).

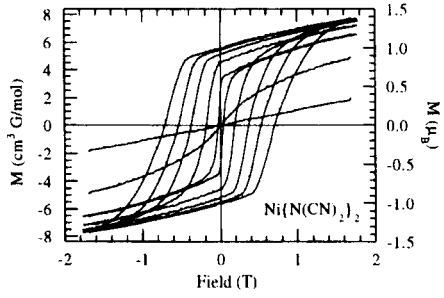

FIGURE 7 Hysteresis loops of fine particles of $Ni\{N(CN)_2\}_2$ at various temperatures.

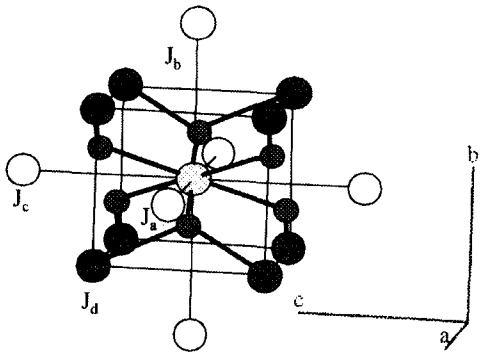

FIGURE 8 Definition of the four exchange pathways within the structure of $M^{II}\{N(CN)_2\}_2$ (only the metals and the apical nitrogen are shown for clarity)

Despite forming an isostructural series, there is considerable variation in the magnetic properties of **1** - **4**. An interesting question is to what differences may account for **1** being paramagnetic, **2** and **3** being ferromagnetic, and **4** being a canted antiferromagnet. For compounds having the rutile structure Goodenough[14] has proposed a phase diagram which consists of four possible ground states depending on the ratio of the exchange interactions (figure 8). In the present rutile-type structure there are four independent nearest-neighbor magnetic exchange interactions (figure 8): eight equivalent super-exchange (J_d, d for diagonal) via M(1)-N(1)-C(1)-N(2)---M(1)' (M...M' of 5.94 Å), two equivalent direct (J_a) along *a* at 5.98 Å, two (J_b) along *b* at 7.11 Å and a further two which are a combination of direct and super-exchange (J_c) along *c* at 7.34 Å. Within this structure type the magnetic ground state and Curie temperature, and therefore the magnitudes and signs of the magnetic exchange interactions are found to depend greatly on the M-N coordination distances and on the degree of structural distortion. The absence of any clear relationship between the Curie temperature and the metal spin state for the different transition metals provides further evidence for the fine dependence of the magnetic behavior on

the structure rather than the metal spin state alone. The relatively weak magnetic exchange in **1** is likely to reflect a severe weakening of the J_d interaction due to the Jahn-Teller distortion of the Cu^{II} ion, and indicates that the other exchange interaction are weak. Furthermore, this observation suggests that it is the approximate orthogonal super-exchange pathway, J_d, that is highest in magnitude for **2** - **4**. We propose that it is a strong and positive J_d in both **2** and **3** that is responsible for the moderate temperature ferromagnetism in these materials.

As expected, the field dependence of the magnetization of **1** takes the form of the J=1/2 Brillouin function. The hysteretic behavior (magnetization *vs* field) below the Curie temperatures for compounds **3** is shown in figure 5. An important particle size effect is observed, the shape of the loop changes from being rounded as expected for multi-domain particles to square on approaching single domain, and the coercive field increases for the smallest particles. Similar effect is observed for **2** and **4**; those for the smallest particles are shown in figure 6. The isothermal magnetization versus field has been recorded for **2** - **4** for every degree below the transition temperatures. The results are shown for the case of **2** in figure 7. In each case, we noted an increase of the coercive fields and remnant magnetization as the temperature is lowered. The remnant magnetization increases in a manner similar to the magnetization in a very small field (figures 2 and 3). The large coercive fields and gradual monotonic increase of the magnetization characterize these materials as hard magnets.

The saturation magnetization of **4** is 1.3 μ_B, approximately a third of the expected value ($4\mu_B$ for high spin Fe^{II} assuming spin only and g=2). This large discrepancy in M_{sat}, the slow increase of M with H, the sharper and lower value of χ' and the low value of γ' are consistent with the behavior of a canted antiferromagnet. From the magnitude of the magnetization, a rough estimate for the canting angle is ~25°.

Given that we have almost square hysteresis loops it is of interest to calculate the maximum energy products (BH) and compare them with those of known hard magnets. The values we obtained are 2, 26 and 16.6 MGOe/mol for **2** - **4**, respectively. Although these values are at temperatures that are too low for any practical use, they are close to those of alloys of $SmCo_5$ [15] This is an important breakthrough in this field as it shows promise of achieving better performance magnets from molecular systems. Furthermore, the shape anisotropy to reduce the demagnetizing fields is 'generic', being based purely on the molecular structure (the packing of one dimensional rods) and does not need to be optimized through manufacturing processes.

Conclusion

The dicyanamide anion is well suited to aligning divalent transition metals in such a way that their magnetic orbitals are approximately orthogonal. The reaction proceeds though a self assembly of the M^{II} and the $N(CN)_2^-$ to give tetragonally distorted octahedra, the $N(CN)_2^-$ adopting an unprecedented triple coordination. The magnetic ground states of metal salts of this anion depend on the electronic configurations and on the geometry-dependent balance between ferromagnetic and antiferromagnetic interactions. The hardness of these metal-organic magnets is a result of the synergy of parallel alignment of the magnetocrystalline anisotropy and the shape anisotropy.

Acknowledgements

This work was supported by the CNRS-France. CJK thanks Christ Church, Oxford, for a Junior Research Fellowship.

Note added in proof: Similar observation was reported by Murray *et al.* and Miller *et al.* at this conference.

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