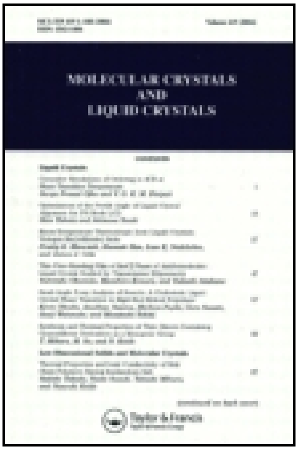

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Rutile and Layered Magnets Based on Transition Metal Complexes Containing Dicyanamide and Tricyanomethanide

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To cite this article: Mohamedally Kurmoo (2000): Rutile and Layered Magnets Based on Transition Metal Complexes Containing Dicyanamide and Tricyanomethanide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 167-176

To link to this article: http://dx.doi.org/10.1080/10587250008038261

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 167-176
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Printed in Malaysia

Rutile and Layered Magnets Based on Transition Metal Complexes Containing Dicyanamide and Tricyanomethanide

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The synthesis, characterization and the magnetic properties of $M^{II}X_2$, $Co^{II}_5(OH)_8X_2{\cdot}nH_2O$, and $M^{II}_2(OH)_3X{\cdot}nH_2O$, where M = Cu, Ni or Co and X = $N(CN)_2$ or $C(CN)_3$, are reported. Long range ferromagnetic magnetic ordering is observed for $M^{II}(N(CN)_2)_2$, M = Ni and Co and for $Ni^{II}_2(OH)_3X{\cdot}nH_2O$, while $Co^{II}_5(OH)_8X_2{\cdot}nH_2O$ exhibits ferrimagnetism. Short range ferromagnetic interaction is observed for $Co^{II}(C(CN)_3)_2$ and antiferromagnetic for $Ni^{II}(C(CN)_3)_2$. The copper compounds behave as paramagnets with small antiferromagnetic exchange interaction. The magnetic hardness spans the range of coercive fields from 400 to 12000 Oe at 2 K.

Keywords: cobalt; copper; dicyanamide; magnetism; nickel; tricyanomethanide

INTRODUCTION

There is continuing interest in the design of magnetic materials[1]. On the one hand there is a school of chemists interested in theory while on the other hand, there is a wider group of experimentalists searching for materials which exhibit long range ordering. Our own interest in the area is to create new structures by using small multitopic ligands to control structural and consequently, magnetic dimensionality[2]. In other words, ligands which have several coordination groups that can assemble moment carriers into infinite lattices. We have recently employed polycyanides[2-4] such as dicyanamide and tricyanomethanide[5] and alkyl- and aryl-dicarboxylates[6]. The latter provide a mean of tuning the exchange interaction by changing the length of the alkyl group between the two carboxylate groups. These studies have resulted in a range of materials exhibiting long range magnetic orderings at temperatures as high as 58 K and one family of metamagnets displaying an unprecedented magnetic hardness with coercive fields in excess of 5 Tesla[6]. Here, we review the structural and magnetic properties of two structural types: rutile-related structures with the ligands in bridging position and the other is layered with the ligands as spacers.

FIGURE 1 Rutile structures of $M(N(CN)_2)_2$ [2] and $M(C(CN)_3)_2$ [5].

The structure of $M(N(CN)_2)_2$[2] and $M(C(CN)_3)_2$[5] are shown in figure 1. The former adopts a simple rutile-related structure based on pseudo

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orthogonal chains of doubly bridged metals, while the latter displays two interpenetrating rutile-related networks. The metal centers in both cases adopt distorted octahedral coordination through the nitrogen atoms of the 3-connecting ligands. In the former, the shortest bridge between the metals consists of the three atom unit N≡C-N while in the latter it is a five atom unit, N≡C-C-C≡N.

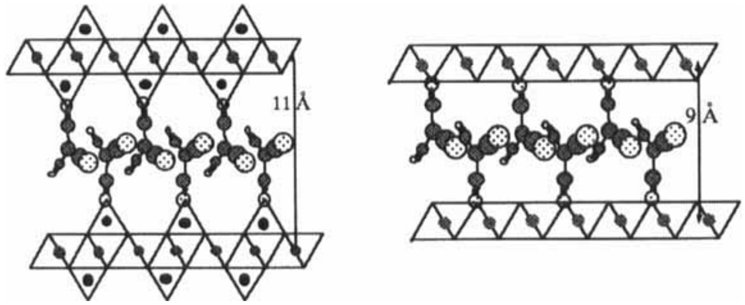

FIGURE 2 Proposed structures of $Co^{II}_5(OH)_8X_2{\cdot}nH_2O$ and $M^{II}_2(OH)_3X{\cdot}nH_2O$

Two slightly different Brucite-related structures are encountered in the layered compounds depending on the metal centers. For copper and nickel, the structure is a single M-OH layer interleaved by the cyano-ligands coordinating through only one of its cyanide groups[6,7]. All the metals adopt octahedral or distorted octahedral coordination. Consequently, they display bands in the visible absorption spectra corresponding to d-d transition characteristic for the blue and green color of divalent copper and nickel, respectively, in an oxygen crystal field. For the cobalt compounds, one in four of the metals in the Brucite layer is replaced by two tetrahedral coordinated cobalt[8]. While three sites in the tetrahedron are occupied by three OH of the layer, the fourth site is coordinated by one of the cyanide group of the ligand. These compounds are deep green due to a weak broad absorption band at ~20200 cm^{-1} originating from octahedral cobalt and two spin-orbit split sharp bands at lower energy, ~15500 and ~17000 cm^{-1}, from tetrahedral cobalt.

EXPERIMENTAL

The binary complexes, $M^{II}X_2$, were synthesized by the reaction of $M^{II}(H_2O)_6(NO_3)_2$ and $NaN(CN)_2$ or $KC(CN)_3$[9] in water and a molar ratio of 1:2.2. $Co^{II}_5(OH)_8X_2.nH_2O$ were prepared by the reaction of aqueous solution of the above binary complexes with ammonia and by the reaction of a suspension of $Co^{II}_2(OH)_3(NO_3)$ in water with $NaN(CN)_2$ or $KC(CN)_3$. $Ni^{II}_2(OH)_3X{\cdot}nH_2O$, were obtained by addition of ammonia to a solution of NiX_2. $Cu^{II}_2(OH)_3X{\cdot}nH_2O$ were obtained by exchange of the acetate group in $Cu^{II}_2(OH)_3(CH_3CO_2){\cdot}H_2O$[7] by the cyano-ligands. All compounds were correctly analyzed for C, H, N, and the metal content by thermogravimetry.

Single crystal structures were determined from data collected on a Enraf-Nonius DIP2000 (Mo Kα) diffractometer[2]. Powder XRD were performed on Seimens 500 (Co Kα) and 5000 (Cu Kα) diffractometers, and on the Neutron D2 diffractomer at ILL.

Magnetization as a function of temperature and *ac* and *dc* magnetic fields were measured by use of a SQUID (Quantum Design

MPMS). A Princeton Applied Research VSM was used to measure the hysteresis loops at T> 4.5 K. [2,6]

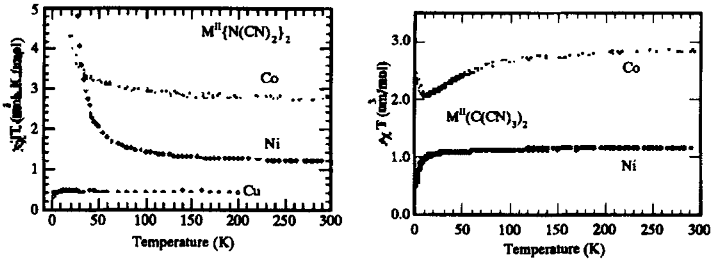

FIGURE 3 Temperature dependence of χT for the rutile compounds.

RESULTS AND DISCUSSION

The temperature dependence of the magnetic moments, represented by the product of χT (= $\mu_{eff}^2/8$), for the rutile compounds are shown in figure 3[2] and a summary of the magnetic data is given in Table 1. The copper-dicyanamide compound behaves as a paramagnet. The cobalt and nickel compounds exhibit long range ferromagnetic ordering below 9 and 21 K, respectively. These transitions were further characterized by cooling in small *ac* and *dc* fields and by specific heat, and hysteresis measurements[2]. The hysteresis loops are dependent on particle size and attain 710 and 7975 Oe at 2K for the finest particles of $Co(N(CN)_2)_2$ and $Ni(N(CN)_2)_2$, respectively. The magnetization approaching the expected saturation values gS of 2 and 3 μ_B in high field (Figure 5).

The tricyanomethanide complexes behave quite different to the dicyanamide ones; no long range magnetic ordering is observed[5a]. Both exhibit antiferromagnetic coupling, although for the cobalt complex this may be due to the lifting of degeneracy by spin-orbit coupling, stabilizing an s=1/2 state at low temperatures[10]. However, at low temperature there is sign of short range ferromagnetic coupling in $Co(C(CN)_3)_2$. Our data are consistent with those found by Batten *et al.* [5a]

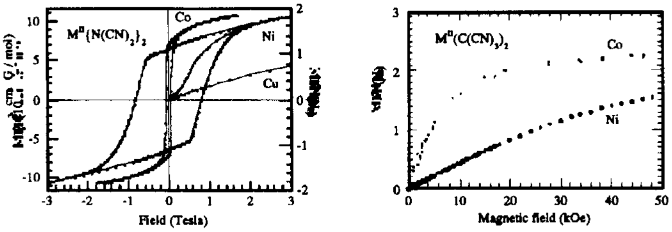

FIGURE 4 Field dependence of the magnetization for the rutile compounds.

The difference in behavior for the two different sets of compounds is most likely associated to the number of atoms in the bridge between the moment carriers. A clear correlation exists for the critical temperature and the number of atoms in the bridging unit. For pure metals (no bridging unit) T_C is greater than 1000 K, for those with one atom connector (*e.g.*: oxides) T_C can reach up to 800 K and for those with two atoms connectors (*e.g.*: cyanides of the Prussian blue family[11]) T_C is nearly 400 K. For the $M(N(CN)_2)_2$ family which has a three atoms bridge, · · · N–C≡N· · · , the highest T_C observed is 21 K[2-4]. Consequently no long range ordering is observed for the $M(C(CN)_3)_2$ family which contains the five atom bridges, · · · N≡C-C–C≡N· · · .

The two series of layered compounds with dicyanamide and tricyanomethanide behave in a similar manner. The copper compounds exhibit short range antiferromagnetic coupling and no long range ordering[7]. The nickel compounds show continuous increase of moment on lowering temperature as expected for ferromagnets, while the cobalt compounds have a minimum around 100 K, typical of ferrimagnets. Long range

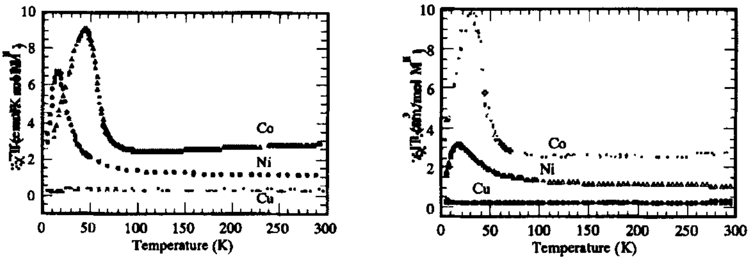

FIGURE 5 Temperature dependence of χT for $Co^{II}_5(OH)_8X_2.nH_2O$ and $M^{II}_2(OH)_3X.nH_2O$; $X=N(CN)_2$ (left) and $X=C(CN)_3$ (right).

ordering were established for the latter two sets at $T_C = 58$ K for $Co^{II}_5(OH)_8(N(CN)_2)_2{\cdot}6H_2O$, 38 K for $Co^{II}_5(OH)_8(C(CN)_3)_2{\cdot}4H_2O$, 25 K for $Ni^{II}_2(OH)_3N(CN)_2{\cdot}H_2O$ and 23 K for $Ni^{II}_2(OH)_3C(CN)_3{\cdot}H_2O$. These transitions were further confirmed by the observation of spontaneous magnetization in a small applied field of the order of 1 Oe and by the presence of both in-phase and out-of-phase components in the *ac*-susceptibilities. The short range super-exchange interaction (M-O-M) between the metals within a layer results in large effective moments which interact with neighboring layers *via* small dipolar interaction to achieve long range ordering[6].

Below the Curie temperatures, the isothermal magnetization exhibits hysteresis (Figure 6). The coercive field increases on lowering temperature and attains 12000 Oe at 2 K for $Co^{II}_5(OH)_8(N(CN)_2)_2 \cdot 6H_2O$, 1600 Oe at 4.5 K for $Co^{II}_5(OH)_8(C(CN)_3)_2 \cdot 4H_2O$, 600 Oe at 4.5 K for $Ni^{II}_2(OH)_3N(CN)_2 \cdot H_2O$ and 400 Oe at 4.5 K for $Ni^{II}_2(OH)_3C(CN)_3 \cdot H_2O$. The magnetization of the cobalt compounds reaches 3 μ_B per formula unit in agreement with the proposed structure and the expected resultant moment for a two-sublattice ferrimagnet having one sublattice with three octahedral high spin cobalt and the other with two tetrahedral cobalt. For the nickel compounds the magnetization is tending to the expected 4 μ_B.

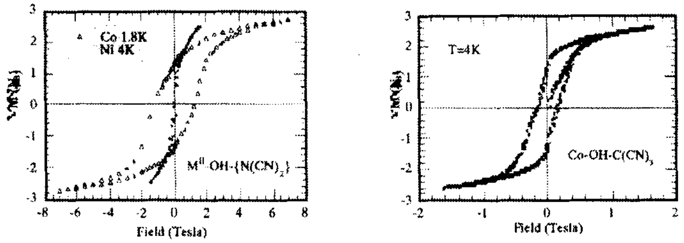

FIGURE 6 Field dependence of the magnetization of $Co^{II}_5(OH)_8X_2 \cdot nH_2O$, and $M^{II}_2(OH)_3X \cdot nH_2O$.

TABLE 1 Summary of magnetic data

Compound	C (cm^3K/mol)	Θ (K)	T_C(K)	H_{coer} (Oe)
$Cu(N(CN)_2)_2$	0.44	-2		
$Ni(N(CN)_2)_2$	1.21	23	21	7975
$Co(N(CN)_2)_2$	2.82	10	9	710
$Ni(C(CN)_3)_2$	1.17	-5		

$Co(N(CN)_3)_2$	2.90	-13		
$Cu_2(OH)_3(N(CN)_2)$	0.77	-2		
$Ni_2(OH)_3(N(CN)_2)$	2.50	+25	25	600
$Co_5(OH)_8(N(CN)_2)_2$	13.45	-58	58	12000
$Cu_2(OH)_3(C(CN)_3)$	0.80	-45		
$Ni_2(OH)_3(C(CN)_3)$	2.42	+24	23	400
$Co_5(OH)_8(C(CN)_3)_2$	13.60	-15	38	1600

CONCLUSION

Dicyanamide and tricyanomethanide, have been used to synthesize novel magnetic compounds. Dicyanamide is found to be an active three atom pathway for long range ferromagnetic ordering in the rutile-related $M(N(CN)_2)_2$. On the other hand, the polycyanides have been used as innocent spacers between metal-hydroxide layer which derive their long range magnetic ordering via dipolar interaction between large effective moment within the layer.

ACKNOWLEDGEMENTS

This project was funded the CNRS. I am grateful to A. Derory, R. Poinsot and Dr M. Richard-Plouet (Strasbourg) for technical assistance and to Dr C. Kepert (Univ. of Sydney) and Dr C. Mathonière (ICMCB, Bordeaux) for many useful discussions.

References

[1] see (a) *Proceedings of the International Conference on Molecule Based Magnets*, O. Khan (ed.), *Mol. Cryst. Liq. Cryst.*, **334–335** (1999); (b) O. Kahn (ed.), *Magnetism. A supramolecular function*, NATO ASI series **C484** (Kluwer Academic Publishers, Dordrecht, 1996).

[2] (a) M. Kurmoo and C.J. Kepert, *New J. Chem.*, **22,** 1515 (1998); (b) S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D. J. Price, *J. Chem. Soc., Dalton Trans.*, 2987 (1999); (c) M. Kurmoo and C.J. Kepert, *Mol. Cryst. Liq. Cryst.*, **334,** 693 (1999); M. Kurmoo, *this proceeding.*

[3] (a) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 439 (1998); (b) K. S. Murray, S. R. Batten, B. Moubaraki, D. J. Price and R.

Robson, *Mol. Cryst. Liq. Cryst.*, **335,** 1025 (1999); (c) P. Jensen, S. R. Batten, G. D. Fallon, B. Moubaraki, K. S. Murray and D. J. Price, *Chem. Commun.*, 177 (1999).

[4] (a) J. L. Manson, C. R. Kmety, Q. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, **10,** 2552 (1998); (b) J. L. Manson, C. R. Kmety, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, **38,** 2552 (1999).

[5] (a) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *J. Chem. Soc., Dalton Trans.*, 2977 (1999) ; (b) H. Hoshino, K. Iida, T. Kawamoto and T. Mori, *Inorg. Chem.;* **38,** 4229 (1999).

[6] M. Kurmoo, *J. Mater. Chem.*, **9,** 2595 (1999); *Mater. Chem.*, **11,** 3370 (1999); *Phil. Trans.* **A 357,** 3041 (1999) ; *Mol. Cryst. Liq. Cryst.*, **334,** 693 (1999).

[7] M. Kurmoo, P. Day, A. Derory, C. Estournès, R. Poinsot, M. J. Stead and C. J. Kepert, *J. Solid State Chem.*, **145,** 452 (1999).

[8] (a) R. Allmann, *Z. Kristallogr.*, **126,** 417 (1968), (b) W. Stählin and H. R. Oswald, *Acta Crystallogr. Section B*, **26,** 860 (1970), (c) P. Benard, J. P. Auffredic and D. Louer, *Thermochemica Acta*, **232,** 65 (1994).

[9] S. Trofimenko, E. L. Little Jr. and H. F. Mower, *J. Org. Chem.*, **27,** 433 (1962).

[10] B. N. Figgis, *Introduction to Ligand Fields*, John Wiley (1966).