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

Polymeric Two- and Three-Dimensional Transition-Metal Networks. Crystal Structures and Magnetic Properties

Silvio Decurtins [a], Helmut W. Schmalle [a], Philippe Schneuwly [a], Rene Pellaux [a] & Jurgen Ensling [b]

[a] Institute of Inorganic Chemistry, University of Zürich, Switzerland

[b] Institute of Inorganic and Analytical Chemistry, Gutenberg-University, Mainz, Germany

Version of record first published: 24 Sep 2006.

To cite this article: Silvio Decurtins , Helmut W. Schmalle , Philippe Schneuwly , Rene Pellaux & Jurgen Ensling (1995): Polymeric Two- and Three-Dimensional Transition-Metal Networks. Crystal Structures and Magnetic Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 273:1, 167-174

To link to this article: http://dx.doi.org/10.1080/10587259508031852

Mol. Cryst. Liq. Cryst., 1995, Vol. 273, pp. 167–174
Reprints available directly from the publisher
Photocopying permitted by license only

POLYMERIC TWO- AND THREE-DIMENSIONAL TRANSITION-METAL NETWORKS. CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES

SILVIO DECURTINS,[1] HELMUT W. SCHMALLE,[1] PHILIPPE SCHNEUWLY,[1] RENE PELLAUX,[1] AND JURGEN ENSLING[2]
[1]Institute of Inorganic Chemistry, University of Zürich, Switzerland;
[2]Institute of Inorganic and Analytical Chemistry, Gutenberg-University, Mainz, Germany

Abstract A strategy for the design of molecule-based magnets consists of assembling transition-metal ions in two-dimensional (2D) or three-dimensional (3D) networks in order to maximize the interactions between the magnetic centers. While increasing the dimensionality of the compounds, an increase in T_C, the critical temperature of spontaneous magnetization should, in principal, be favoured.

We are currently studying materials that are formed by the interaction of transition-metal ions with the oxalate ligand, $C_2O_4^{2-}$, and will present a straightforward concept for building up achiral 2D and chiral 3D homo- and bimetallic networks. Whereas a variety of metal ions can be incorporated, a correlation of the magnetic behavior and the relationship to the special topology of e.g. the chiral, cubic 3-connected 10-gon net (10,3) is not yet fully understood.

INTRODUCTION

One of the strategies used to design and synthesize molecular magnets is based on the potentiality of coordination chemistry. Thereby, a broad range of synthetic possibilities is offered which the chemist may use in realizing extended transition-metal compounds as homo- and heteropolymetallic systems. We are currently following an approach which aims to assemble the transition-metal ions (spin carriers) in bidimensional (2D) and tridimensional (3D) networks in order to maximize the intramolecular interactions throughout the solid. By that, the ability of bridging multiatom ligands to mediate exchange coupling in Metal(bridging ligand)Metal units will be optimally extended at the cost of the weak intermolecular interactions.

Studying polymeric systems will put the question of the structural features into a central position. Principally, various different planar and three-dimensional networks can be derived, and following a formalistic concept, which is excellently described in the monographs of A.F. Wells,[1,2] one can easily recognize the different patterns that repeat

regularly in two, or three dimensions. Out of this manifold, we will report on two special configurations, one at a time for a 2D and a 3D network. In both cases, the nets will formally be built up by three-connected building blocks, which lead to the honeycomb plane net and the 10-gon 3D net. Once an appropriate bridging ligand system has been chosen, e.g. the oxalate ion, $C_2O_4^{2-}$, the target is to realize the polymeric nets in such a way that they properly crystallize, which in turn allows an exact structure determination.

There is undoubtly a need to have at hand specific, structurally well-defined, higher dimensional networks. Hopefully, they may act as high T_c molecule-based magnets or, in any case, as a testing ground for theoretical models for the analysis of the mechanism which leads to magnetically ordered states, as well as for an understanding of any correlations with regard to the topology of the frameworks.

THE BRIDGING LIGAND SYSTEM

The use of the oxalate ion, $C_2O_4^{2-}$, as a bridging ligand system to form chain structures of transition-metal ions, or even infinite layer compounds, as in case of lanthanide(III) ions is well established. Consequently, the ligand has principally proven its potential for building up further tailor-made frameworks. Based on this idea, the tris-chelated [M(ox)3] complexes represent negatively charged, chiral, 3-connected units which are ideally suited to act as building blocks. It may easily be shown that there exist two ways to combine these units to yield extended networks. Assembling them with the Λ and Δ chirality alternating, results unequivocally in the achiral honeycomb plane net, while combining units with only Λ or only Δ chirality delivers the chiral, three-dimensional 10-gon net. With respect to the ability of the oxalate ion to propagate the exchange interaction between the magnetic centers, we refer to published experimental and theoretical results.[3] To continue on our main theme, we have to stress the following points: How do we synthesize the polymeric, oxalate-bridged networks and how do we distinguish between the achiral 2D and the chiral 3D nets, which, by looking at the stoichiometry of the framework, are identical?

A TWO-DIMENSIONAL HONEYCOMB NET

Taking the specific case of a negatively charged network with the stoichiometry $[Mn^{II}Cr^{III}(ox)_3]_n^{n-}$ as an example, the dominating influence of the counterion on the creation of a bidimensional net which properly crystallizes, will be emphasized.[4] Charge, size and symmetry turned out to be the crucial factors affecting the choice of

counterions, and in this case $[P(Ph)4]^+$, Ph=phenyl, fulfils the requirements for initiating a planar structure. Figure 1 shows a sector from the honeycomb plane exhibiting the trigonal environment. The counterions match nicely with the symmetry and the size of the net and it requires one cation per hole for charge balance. Additionally, Figure 2 demonstrates by use of a space-filling model (about the same orientation as Figure 1) how well one of the phenyl rings of the cations stacks in the vacancies of the planar net. These ions both direct and stabilize the honeycomb net configuration. Following these ideas, alternative counterions can be tested with the aim to vary the interlayer separation, which for the example just described is rather large (9.5 Å). A variation in this spacing will, hopefully, influence the magnetic properties.

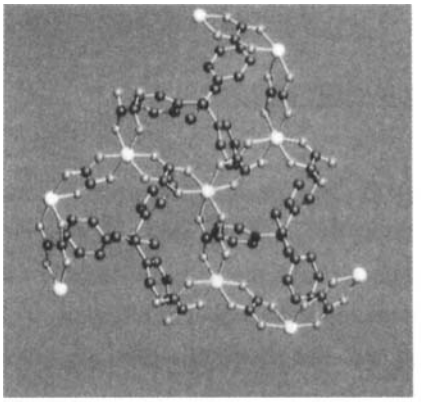

FIGURE 1 $[Mn^{II}Cr^{III}(ox)_3]_n^{n-}$ layer including the $[P(Ph)_4]^+$ cations (H-atoms omitted). See Color Plate I.

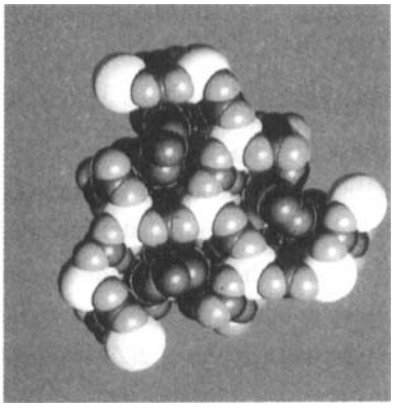

FIGURE 2 $[Mn^{II}Cr^{III}(ox)_3]_n^{n-}$ layer with a partial view of one Ph-ring (H-atoms omitted). See Color Plate II.

The temperature dependence of the spontaneous magnetization, as shown in Figure 3, exhibits a magnetic phase transition at T_C = 5.9 K. This value matches nicely the findings of Okawa and his group[5] for the powder sample of the analogous net, but with $[N(Bu)4]^+$ cations. This low T_C could be expected in view of the large separation of the magnetic layers. Based on the structural data and the availability of single crystals, magnetic measurements on oriented single crystals are planned in order to obtain information about the magnetic structure within and between the layers of the spin carriers.

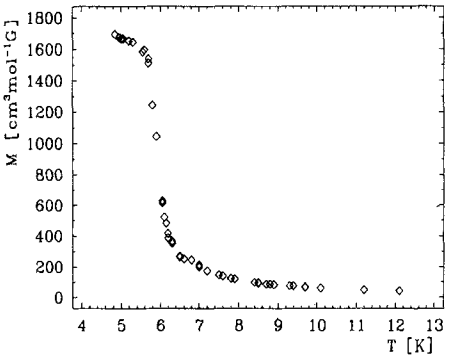

FIGURE 3 Temperature dependence of the spontaneous magnetization for $\{[P(Ph)_4][MnCr(ox)_3]\}_n$

A THREE-DIMENSIONAL 3-CONNECTED 10-GON NET (10,3)

Structural Features

In order to understand the fascinating topology of this type of 3D network, it is worthwhile to follow a formalistic scheme. By taking the $[M(ox)_3]$ units as 3-connected points, four of them (Z = 4) are required in order to have the necessary number (6) of free links to build up the 3D net. Identically oriented links repeat at intervals of (Z+1) points, so that circuits of 2(Z+1) points are formed. The structure represents a uniform net in the sense that the shortest path, starting from any point along any link and returning to that point along any other link, is a circuit of 10 points. Thereby, each point will belong to 15 different 10-gons and similarly each link to 10 different 10-gons.

Again, the task was to set the experimental conditions in such a way that the crystallization of this 3D, chiral configuration would be favoured. As before, charge, size and symmetry of the counterion plays the dominant role. While investigating the photochemical behavior of these oxalate complexes,[6] it turned out that the tris-chelated bipyridine complexes $[M(bpy)_3]^{2+}$ fulfil all the criteria in an ideal way. Figure 4 demonstrates very nicely how this tris-chelated cations fit into the vacancies of the 3D 10-gon net. According to the space group symmetry, $P4_332$ or $P4_132$, they are located at sites with symmetry 32 (Wyckoff letter a) which corresponds perfectly to their chiral molecular point group symmetry. Following the argument that the charge and the steric demand of the counterions are the crucial factors in determining the 3D arrangement, an alternative synthetic approach towards these 3D networks may be considered. Recently, we confirmed this hypothesis, and with a straightforward one-pot reaction involving all

of the components, homo- and bimetallic (10,3) nets could be prepared. Also, both types of stoichiometries, namely $[M^{II}_2(ox)3]$ or $[M^{I}M^{III}(ox)3]$, can be obtained with the same kind of counterions.[7] Naturally, the bimetallic compounds yield a structure with lower symmetry, so they have to be described in the space group $P2_13$.

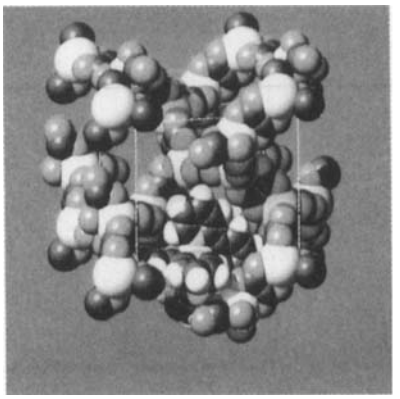

FIGURE 4 3D $[M^{II}_2(ox)_3]_n^{2n-}$ type network with one $[M^{II}(bpy)_3]^{2+}$ cation. See Color Plate III.

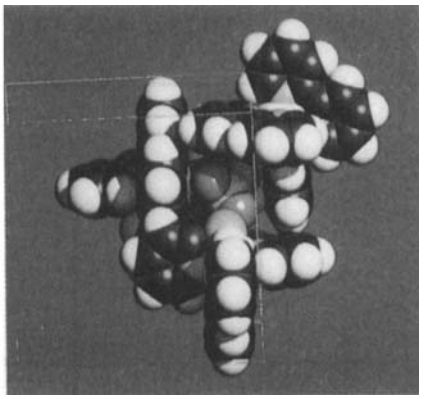

FIGURE 5 Three $[M^{III}(bpy)_3]^{3+}$ enclosing a $(ClO_4)^-$ anion. See Color Plate IV.

The versatility of this specific 3D configuration is not yet exhausted. A further remarkable structural feature is discernible when looking exclusively at the close packing of the tris-chelated bipyridine complexes. Three of them together constitute, with their interligand pockets, a cubic shaped cavity. This cavity has been found unoccupied in the presence of divalent cations and not even any water of crystallization is enclosed. Contrary to that finding, when using trivalent tris-chelated bipyridine complexes, an enhanced accumulation of attractive coulomb-forces results in the enclosure of small anions. Figure 5 depicts the experimental finding,[8] that $(ClO4)^-$ anions will fill quite perfectly the cubic vacancies. For illustrative purposes, the front bipyridine ligand is only partly shown in this Figure.

Primarily, this structural versatility brings about an additional free parameter for the overall charge balance. Further studies in this area are in progress.

Targeting the interesting $[M^{II}M^{III}(ox)3]_n^{n-}$ combination, we sought an univalent cation which also is able to initiate the 3D net configuration. To this end we tested a cyclometallated Rh(III) complex, namely $[Rh^{III}(ppy)_2(bpy)]^+$, ppy=phenylpyridine. Despite the fact that the 3-fold symmetry in this complex is not fully apparent, various

combinations were tested. In all cases, the samples proved to be difficult to crystallize in a proper manner, so that a structure determination could not be accomplished. Only by examining the X-ray powder diffraction data, as shown in Figure 6, could the existence of the 3D type structure be verified. Thereby, the structurally defined 3D compound with the metal combination $Li^{I}Cr^{III}$ (**3**), could be compared with the polycrystalline samples of $Cd^{II}Cr^{III}$ (**1**) and $Cu^{II}Cr^{III}$ (**2**) metal stoichiometries.

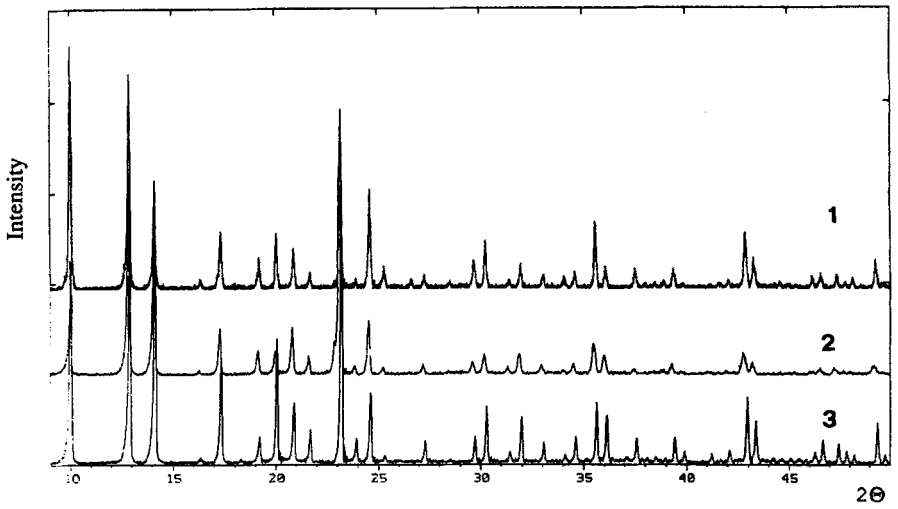

FIGURE 6 X-ray powder diffractogram for the network stoichiometries $[Cd^{II}Cr^{III}(ox)_3]$ (**1**), $[Cu^{II}Cr^{III}(ox)_3]$ (**2**) and the 3D $[Li^{I}Cr^{III}(ox)_3]$ network (**3**).

Magnetic Susceptibility Measurements

The result from the synthetic approach with the cyclometallated Rh(III) complex enables us to compare the magnetic susceptibility data from $[M^{II}_2(ox)_3]$ stoichiometries with the data of a $[M^{II}M^{III}(ox)_3]$ composition. In the former case, samples with M^{II}=Mn, Fe, Cu reveal an antiferromagnetic behavior. The Weiss constant, Θ, obtained from a fit of the temperature dependence of X_m^{-1} within the temperature range of 100-300 K to the Curie-Weiss law are -33 K, -28 K and -51 K respectively. The expected maximum in the susceptibility versus temperature curve is most clearly seen for the Mn^{II}_2 compound at a value of 17 K.[7]

Figure 7 exhibits the thermal variation of the molar magnetic susceptibility X_m and of the X_mT product for the $[Cu^{II}_2(ox)_3]$ stoichiometry.

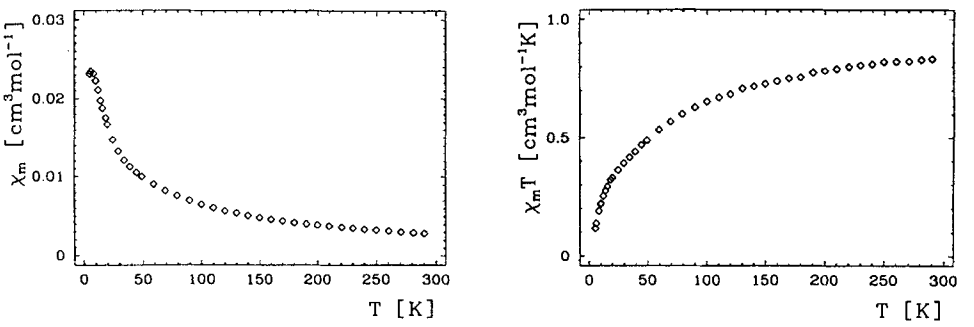

FIGURE 7 Temperature dependence of X_m and X_mT for $\{[Ru(bpy)_3][Cu^{II}_2(ox)_3]\}_n$

In contrast, the $[Cu^{II}Cr^{III}(ox)_3]$ network has ferromagnetic properties. Figure 8 presents the thermal variation of the X_mT function and of the inverse molar magnetic susceptibility X_m^{-1}. Now a positive Weiss constant, Θ=+12 K, results and most importantly, as shown in Figure 9, a spontaneous magnetization occuring at 6 K clearly demonstrates the magnetic ordering. The magnetization versus field curve, measured at 4.7 K, is also shown in the same Figure. The saturation magnetization reaches at 20 kG only a value of 2.5 Nß per CuCr pair, which is far too low for a fully ferromagnetic coupling of a 1/2 - 3/2 spin system.

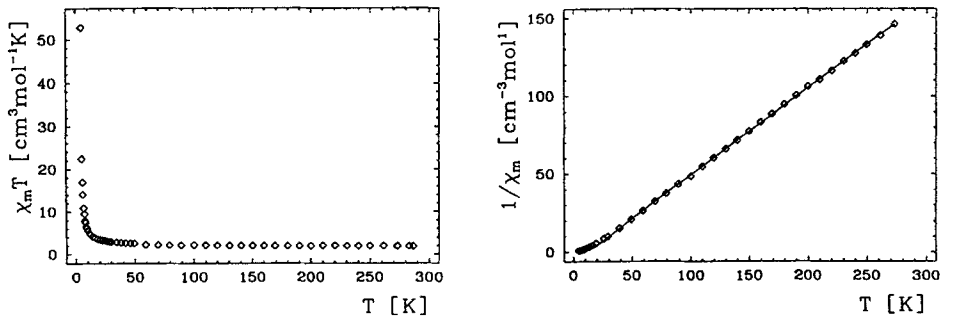

FIGURE 8 Temperature dependence of X_mT and X_m^{-1} for $\{[Rh(ppy)_2(bpy)][Cu^{II}Cr^{III}(ox)_3]\}_n$

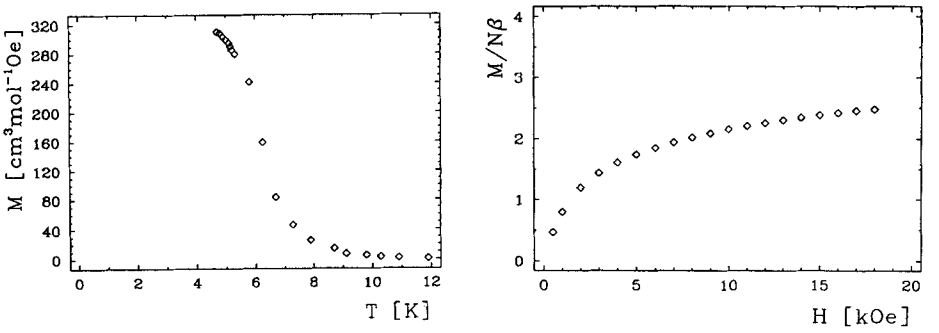

FIGURE 9 Temperature and field dependence of the magnetization M for $\{[Rh(ppy)_2(bpy)][Cu^{II}Cr^{III}(ox)_3]\}_n$

PERSPECTIVES

Based on the chemical versatility and on the structural knowledge of the 3D compounds with $[M^{II}_2(ox)_3]$ network stoichiometry, it will be a target to understand their magnetic structures and to rationalize the rather low critical temperature of the observed antiferromagnetic ordering. Further synthetic studies are in progress, in order to find 3D compounds with a $[M^{II}M^{III}(ox)_3]$ network stoichiometry, which above all will produce a better crystallization behavior.

ACKNOWLEDGMENT

Financial support by the Swiss National Science Foundation is acknowledged.

REFERENCES

1. A. F. Wells, Structural Inorganic Chemistry (Clarendon Press, Oxford, 1984).
2. A. F. Wells, Three-dimensional nets and polyhedra (Wiley-Interscience, New York, 1977).
3. O. Kahn, Molecular Magnetism (VCH Publishers, Weinheim, 1993), Chap. 8-11.
4. S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gütlich, and, A. Hauser, Inorg. Chim. Acta, 216, 65 (1994).
5. H. Tamaki, Z.J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, and H. Okawa, J. Am. Chem. Soc., 114, 6974 (1992).
6. S. Decurtins, H. W. Schmalle, P. Schneuwly, and H. R. Oswald, Inorg. Chem., 32, 1888 (1993).
7. S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling, and P. Gütlich, J. Am. Chem. Soc., in press.
8. S. Decurtins et al., to be submitted to Inorg. Chem.