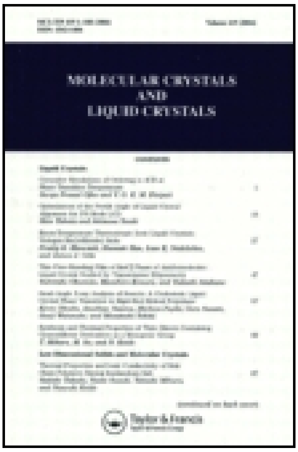

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Mark M. Turnbull [a], Christopher P. Landee [a], Todd C. Soesbe [a] & Roger D. Willett [b]

[a] Departments of Chemistry and Physics, Clark University, Worcester, MA, 01610, USA

[b] Department of Chemistry, Washington State University, Pullman, WA, 99164, USA

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SYNTHETIC DESIGN OF FERRIMAGNETIC MATERIALS: TWO AND THREE DIMENSIONAL BIMETALLIC COORDINATION POLYMERS

MARK M. TURNBULL[a], CHRISTOPHER P. LANDEE[a], TODD C. SOESBE[a] AND ROGER D. WILLETT[b]
a) Departments of Chemistry and Physics, Clark University, Worcester, MA 01610 USA b) Department of Chemistry, Washington State University, Pullman, WA 99164 USA

Abstract A synthetic design and rationale for the preparation of ferrimagnetic two- and three-dimensional bimetallic coordination polymers is presented. Preliminary results of the attempted synthesis of such lattices using 4-cyanopyridine, bipyrazine and 1,4,8,11-tetraazacyclotetradecane are discussed with emphasis on reasons for their inability to generate the desired systems.

INTRODUCTION

Molecularly based materials having novel magnetic and optical properties have received a great deal of attention during the past ten years, especially insulating ferrimagnets. Much of this interest has arisen by analogy to metal oxide ferrimagnets such as the spinel ferrites. These classical ferrimagnets respond strongly to external magnetic fields and are transparent in the microwave region. As such, they can modify the state of polarization of electromagnetic radiation passing through them, through the Faraday effect, and have been widely used in the microwave industry as isolators, circulators, switches and modulators for the past three decades.[1] However, their mixed-valence nature renders them opaque in the visible region. In contrast, molecular based magnetic materials that resemble traditional coordination complexes are expected to be transparent to a range of wavelengths in the visible/near ir and present the possibility of magneto-optical control of visible light and even magneto-optical data storage.[2]

We are interested in the preparation of a family of site specific bimetallic two-dimensional coordination polymers. The complexes will be designed so the magnetic ions M and M′ are located in the lattice such that each ion M has only M′ ions as nearest neighbors and M′ has only M ions for nearest neighbors. The intrinsic antiferromagnetic interaction between the M,M′ pairs cannot cancel their inequivalent moments and thus an uncompensated moment remains in each unit cell with all uncompensated moments parallel. At a temperature proportional to the strength of the interaction between the M,M′ pairs the layers will undergo a transition to long range ferrimagnetic order. The ordering temperature could be raised by linking the layers together into a three dimensional array.

There is an advantage to attempting the design and preparation of a ferrimagnetic material rather than a ferromagnetic one. The strict requirement for orthogonality between magnetic orbitals in a ferromagnetic system requires rigorous control of coordination geometry about the magnetic ions and bond angles throughout the system. Thus, relatively minor distortions within a system containing a single magnetic species will lead to antiferromagnetic interactions and loss of net magnetization results. Conversely, if the system is designed around an expected antiferromagnetic interaction between inequivalent moments the "accidental" creation of a ferromagnetic system only serves to increase the net magnetization. We describe below our general synthetic scheme for the preparation of two- and three-dimensional ferrimagnetic materials and some preliminary results of this ongoing study.

DESIGN PRINCIPLES

Our fundamental design is based on a "brick and mortar" approach.^{3} This requires the preparation of two complexes, ML_n and $M'L'_m$, which can be subsequently assembled into the desired two- or three-dimensional lattice. The species ML_n and $M'L'_m$ should be constructed with a number of guidelines in mind. 1) The "brick", ML_n, should be a complex where the M-L bonds are sufficiently stable to prevent the exchange of metal ions when the $M'L'_m$ "mortar" is introduced. It is imperative that these systems be rigorously site specific, or else antiferromagnetic defects will occur (adjacent MM, or M′M′ ions resulting in complete cancellation of net moment). 2) The ML_n and $M'L'_m$ complexes should ideally be a cation-/anion pair to promote assembly of the lattice. Coulombic repulsion will make it difficult, at best, to coordinate cationic M′ ions to cationic ML_n clusters. This type of a system would also require non-coordinating geganions which may disrupt formation of the desired lattice. The practical result of this is that L or L′ must be an anionic ligand.

3) The ligand L used in formation of the brick should have two inequivalent binding sites. The bidentate ligand will aid in formation of the polymeric lattice and the inequivalence of the binding sites should promote specificity in location of the metal ions. Although this is a desired property, it is not an absolute requirement. A lattice containing a chloride bridged alternating chain will be presented later.

The number of available (uncoordinated) binding sites on the ligands in the brick may determine the dimensionality of the lattice formed on addition of mortar. A number of ferrimagnetic chains have been developed by Kahn using bricks with two free binding sites based on 1,3-propylene bisoxamato-metal complexes or a related oximido bisbenzoato compound.[4] These materials exhibit ferrimagnetic behavior along the chains and show characteristic minima in χT ranging from 83-120 K. Similar ferrimagnetic chains have been prepared by Coronado using EDTA and related chelating agents.[5] Both of these methods suffer the limitation of being one-dimensional materials. Interactions between the chains determine the ultimate ordered state and these are invariably weak, leading to low T_c's. It is also very difficult to control the sign of the interchain interactions through chemical methods. Kahn has done a remarkable job in finding systems with ferromagnetic interactions between the chains. There appears to be no systematic pathway to high temperature ferrimagnets using one-dimensional materials.

Bricks with four, or six, available coordination sites in either a square planar or octahedral array will lend themselves to the assembly of either two- or three-dimensional coordination lattices respectively. Unlike isolated linear chains, two-dimensional magnets undergo phase transitions to states of long-range order at temperatures which are proportional to the interlayer exchange constant.

A classic, although non-magnetic example of the desired two dimensional bimetallic lattice is found in the Hofmann clathrates which have the general formula $[M(NH_3)_2][Ni(CN)_4]\cdot 2G$ where M may be a wide variety of 2+ metal ions and G is a neutral organic "guest" molecule. These compounds extend the idea of Kahn's brick into a two dimensional lattice via the square planar tetracyanonickelate anion. The nitrogen termini of the cyano groups provide the four desired coordination sites for linking the bricks via M'^{2+} mortar. Of course, the square planar Ni^{2+} ion is diamagnetic and so ferrimagnetic interactions are not possible.

PRELIMINARY RESULTS

Our initial attempts to create ferrimagnetic layer compounds have focused on the preparation of cationic bricks (bricks formed from neutral ligands). An investigation of the literature showed that 4-cyanopyridine (4-CNPy) can coordinate selectively through either the pyridine nitrogen[6,7] or the nitrile nitrogen[8], making it a potential ligand for these systems. Reaction of 4-CNPy with $Cu(ClO_4)_2$ in 95% ethanol gave $Cu(4\text{-}CNPy)_4(ClO_4)_2(H_2O)$:

$$Cu(ClO_4)_2 \cdot 6(H_2O) + 4\ 4\text{-}CNPy \longrightarrow Cu(4\text{-}CNPy)_4(ClO_4)_2(H_2O)$$

Recrystallization from aqueous solution gave single crystals suitable for X-ray analysis. The compound is a distorted octahedron with the 4-CNPy ligands in the equatorial plane coordinated through the pyridine nitrogens (ave Cu-N = 2.05 Å), and a H_2O molecule occupying an axial site (Fig. 1a). The other axial site is occupied by a semi-coordinate bond to the nitrile nitrogen of the next unit (C-N = 2.65Å), making a one-dimensional chain (Fig. 1b) (ClO_4's have been removed for clarity).

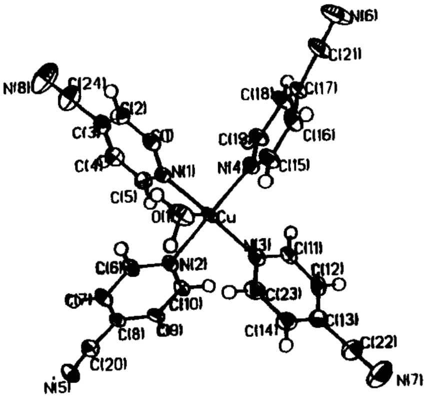

Fig. 1a

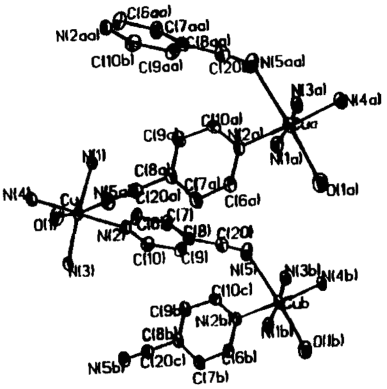

Fig. 1b

Attempts to link the $Cu(4\text{-}CNPy)_4{}^{2+}$ bricks through the nitrile nitrogens into a two-dimensional layer by addition of $M'Cl_4{}^{2-}$ anionic units lead to destruction of the brick and rearrangement of the complex into halide bibridged linear chains with random site occupancy by the metal ions (see the following paper for more detail):

$$Cu(4\text{-}CNPy)_4(ClO_4)_2(H_2O) + M'Cl_4^{2-} \longrightarrow [Cu_xM'_{1-x}(4\text{-}CNPy)_2Cl_2]_n$$

The $Cu(4\text{-}CNPy)_4^{2+}$ brick was insufficiently stable with respect to metal ion exchange. In an effort to increase the stability of the cationic unit, we changed to the chelating ligand bipyrazine. Like bipyridine, bipyrazine (bpz) binds to a wide variety of metal ions[9] and the $Ru(bpz)_3^{2+}$ ion has been shown to coordinate $[Fe(CN)_5]_n^{3-}$ (n = 1-6) to the N-4 positions of the bipyrazine rings.[10] Thus encouraged we attempted the synthesis of $Cu(bpz)_2Cl_2$. Reaction of $CuCl_2$ with excess bpz in 95% ethanol gave $Cu(bpz)Cl_2$ as the sole product in >90% yield.

$$CuCl_2 + xs\ bpz \longrightarrow [Cu(bpz)Cl_2]_n$$

Powder x-ray diffraction shows the compound to be isomorphous with the previously characterized bipyridine complex $[Cu(bpy)Cl_2]_n$. Single crystal studies of $[Cu(bpy)Cl_2]_n$ reveal a zig-zag chain of Cu^{2+} ions, bibridged by chlorides, with the bipyridine ligands occupying the remaining sites of a pseudo-octahedron.[11] The equivalency of the metal sites and the Cu-Cu linkages made this complex unsuitable for the preparation of ferrimagnetic materials. However, similar reaction with $FeCl_2$, $CoCl_2$ and $MnCl_2$, or with $CuCl_2$ in refluxing ethanol, lead to a series of compounds with the same stoichiometry, but of a different phase according to x-ray powder diffraction and ir spectra. The possibility that these compounds had rearranged to the alternating site coordination isomer $[M(bpz)_2MCl_4]_n$ was discarded when the Mossbauer spectrum of the Fe complex revealed only a single site in the molecule. These materials show a range of magnetic interactions and their structure is still under investigation.

We believe that the bridging character of the chloride anions prevented formation of the desired $Cu(bpz)_2^{2+}$ brick, so we changed to a non-coordinating geganion. Reaction of $M(ClO_4)_2$ with bpz in 95% ethanol at room temperature gave the corresponding tris(bipyrazine) complexes:

$$M(ClO_4)_2\cdot 6H_2O + 3bpz \longrightarrow M(bpz)_3(ClO_4)_2 \quad M = Cu, Ni, Co, Mn$$

The general structure of these complexes makes them suitable as bricks for formation of a three-dimensional lattice. The uncoordinated nitrogens in the pyrazine rings point nearly toward the vertices of an octahedron. A series of metathesis reactions were run to determine the stability of the bricks with respect to metal ion exchange. Addition of one molar equivalent of $Cu(ClO_4)_2$ to slurries of the other $M(bpz)_3^{2+}$ complexes in ethanol showed quantitative exchange of Cu^{2+} ion into the chelating site of the brick:

$$M(bpz)_3(ClO_4)_2 + Cu^{2+} \xrightarrow[M\,=\,Ni,\ Co,\ Mn]{} Cu(bpz)_3(ClO_4)_2 + M^{2+}$$

This selectivity suggested that a self-assembling lattice might be formed by the reaction of a 1:1 mixture of $CuCl_2$ and $MnCl_2$ with three equivalents of bpz. Combination of the reagents formed a light green slurry which remained unchanged after 48 hours in refluxing absolute ethanol. We recovered a light green powder which gave an acceptable combustion analysis for $CuMn(bpz)_2Cl_4$:

$$CuCl_2 + MnCl_2 + 3\ bpz \longrightarrow CuMn(bpz)_2Cl_4$$

One equivalent of bipyrazine was recovered from the filtrate. Powder x-ray diffraction patterns and IR spectra show this material to be different from the earlier copper complex $[Cu(bpz)Cl_2]_n$, but isostructural with the Mn, Fe, and Co complexes. Temperature vs. susceptibility measurements yielded $C = 5.1$ and $\theta \approx -10$ K. The isomorphous nature of this sample with the iron complex suggests that only one metal site exists and it is therefore most likely randomly occupied, eliminating the possibility of ferrimagnetic interactions.

Encouraged that the $Cu(bpz)_3^{2+}$ brick was stable with respect to the other M^{2+} ions, we attempted to assemble the desired lattice using $MnCl_4^{2-}$ as our mortar:

$$Cu(bpz)_3(ClO_4)_2 + MnCl_4^{2-} \longrightarrow CuMn(bpz)_2Cl_4 + bpz + 2\ ClO_4^-$$

Once again we observed formation of a complex containing only two bpz molecules which was isomorphous, by ir and powder x-ray, to the previous monometallic species. Temperature vs. susceptibility measurements yielded $C \approx 6.1$ and $\theta \approx -35$ K. The difference in the magnetic properties, especially the high value of C, suggests that the second material is not 1:1 Cu to Mn, but rather contains an excess of Mn^{2+} ions. It is clear that although the $Cu(bpz)_3{}^{2+}$ brick may be stable to metal ion exchange in solution, this is only true in the absence of coordinating anions.

Our final attempt, to date, at cross-linking cation/anion pairs involves the reaction of $Cu(cyclam)Cl_2$ with $MnCl_2$ [14-ane-N_4 = 1,4,8,11-tetraazacyclotetradecane]:

$$Cu(cyclam)Cl_2 + MnCl_2 \longrightarrow [Cu(cyclam)MnCl_3(H_2O)_2]Cl$$

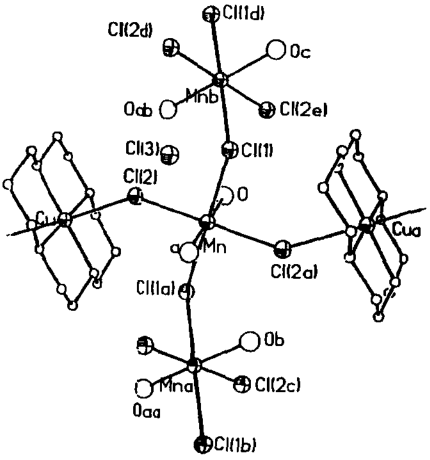

Fig. 2a

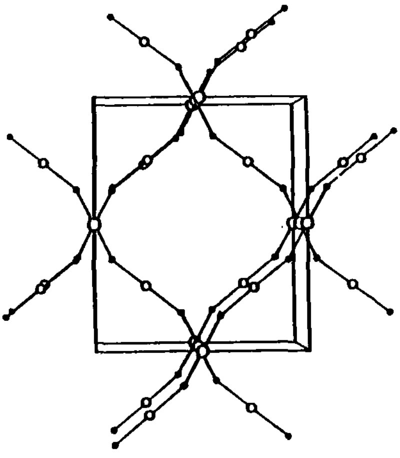

Fig. 2b

The x-ray structure reveals that rather than having formed the desired two-dimensional lattice with Cl^- ions bridging the metals, -Cu-Cl-Mn-Cl- chains are formed which are further cross-linked via perpendicular Mn-Cl-Mn bridges (see Fig. 2a) with two H_2O molecules filling out the Mn octahedral coordination sphere. The geometry about the -Mn-Cl-Mn-Cl- chains (passing into the page, Fig. 2b) is such that adjacent -Cu-Cl-Mn-Cl- chains are mutually perpendicular, generating a three-dimensional network. Unfortunately, antiferromagnetic exchange in the homometallic -Mn-Cl- chains is expected to lead to net order as a 3D-antiferromagnet even though the -Cu-Cl-Mn-Cl- chains may be ferrimagnetic.

CONCLUSIONS

The stability of our ML_n brick has proven to be the chief hinderance to assembling the desired two- and three-dimensional bimetallic lattices. The systems have been unstable with respect to metal ion exchange when neutral ligands with one (as in 4-CNPy) or two (as in bpz) binding sites are used for coordination to the brick metal ion. The tetradentate macrocycle provided the necessary brick stability, but left only two vacant coordination sites, limiting the ferrimagnetic interactions to one dimension. Clearly, future systems will need to be based upon ligands with multiple binding sites to the central ion as in the macrocycle, but must also incorporate external binding sites in the proper symmetry and number to allow extension of the bimetallic lattice into two- and three-dimensions.

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