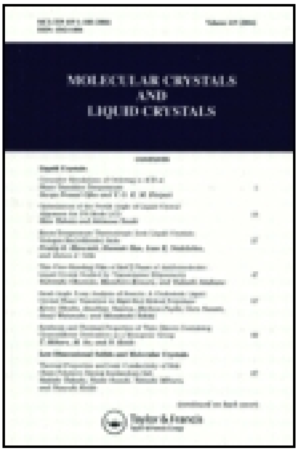

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Synthetic Design of Ferrimagnetic Materials: One Dimensional Bimetallic Coordination Polymers

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SYNTHETIC DESIGN OF FERRIMAGNETIC MATERIALS: ONE DIMENSIONAL BIMETALLIC COORDINATION POLYMERS

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Abstract An approach to the synthesis of alternating site linear chain systems using cationic bricks containing Cu(II) ions and anionic mortar is described. Bricks formed with neutral quadradentate N_4 macrocycles successfully permit the construction of ordered bimetallic chains, although the magnetic interactions are always found to be weak. Efforts to form similar systems using mono- or bi-dentate neutral ligands have thus far failed to lead to the assembly of the desired structures.

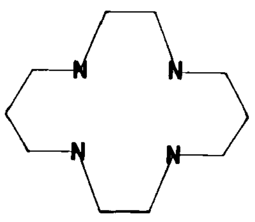
INTRODUCTION

Linear bimetallic chains continue to be of intense interest in magnetochemistry. They have proven to be a fertile testing ground for the concepts in molecular engineering, such as the "brick and mortar" procedure for preparing ordered bimetallic systems [1] and for testing the theories of exchange interactions in charge transfer systems [2]. While it is generally held that high temperature ordered ferrimagnetism is unlikely to arise from linear chains, it is probable that the ultimate success will profit from the knowledge gained from their study.

This article describes work on progress on the synthesis and characterization of new bimetallic linear chains, constructed according to the "brick and mortar" technique. Unlike the well known bimetallic chains described in the references in which anionic bricks are bridged with cationic mortar, the compounds in this paper all contain cationic bricks.

COPPER MACROCYCLIC SYSTEMS

We have formed cationic bricks by incorporating a Cu(II) ion inside a neutral quadradentate N_4 macrocyclic ligand. The macrocycles employed go by the shorthand notations cyclam (I) and TIM (II), respectively, (cyclam = 1,4,8,11-tetraazacyclotetradecane ; TIM = 2, 3, 9, 10-tetramethyl-1,3,8,10-tetraenecyclo-1,4,8,11-tetraazatetradecane). The planar units thus formed are then linked into neutral chains by tetrahedral MX_4^{2-} anions, where M is a divalent metal ion (Cu(II), Mn(II), or Co(II)) and X = Cl or Br.



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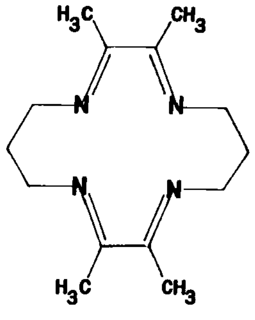

(II)

The result is the formation of chains as illustrated in Fig. 1 in which adjacent metal ions are linked by semi-coordinate halide bridges. Structurally, the Cu(cyclam)MX_4 chains are defined as possessing alternating sites linked by uniform exchange while the Cu(TIM)MX_4 chains have both alternating sites and alternating exchange.

Preliminary insight can be gained into the magnetic interactions present in these systems by studying finite oligimers which contain structural fragments similar to those found in the fully extended chains. It is possible to prepare $A_2Cu(TIM)(MX_4)_2$, where A is a monovalent cation such as Me_4N^+or Et_4N^+. Analysis of the magnetic susceptibility of these trimers reveals that the exchange through the semi-coordinate bonds is moderately strong and can be ferromagnetic (Cu/M, M=Cu compounds) as well as antiferromagnetic (Cu/Co and Cu/Mn compounds).

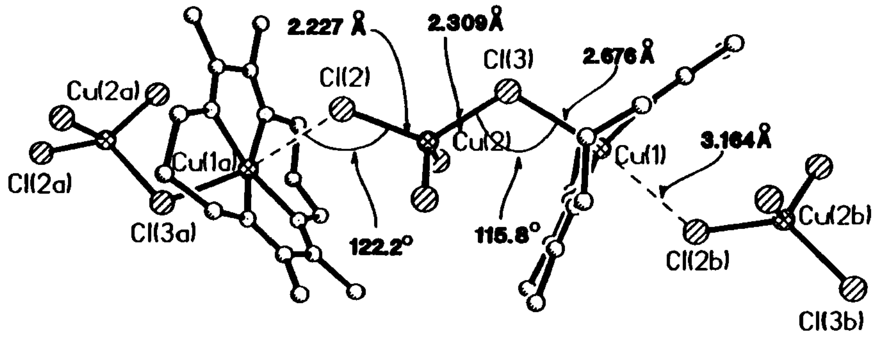

FIGURE 1 Illustration of the alternating site bimetallic chain in Cu(TIM)$CuCl_4$

The exchange interaction strengths between the central copper ion and terminal copper ions are ferromagnetic in all cases studied (A = Me_4N or Et_4N ; X = Cl, Br), ranging in energy (expressed in thermal units) from a few Kelvin for A; X = Me_4N; Br to as high as 20 K for Et_4N; Cl. Exchange between the central copper and the terminal manganese ions is weak (< 2 K) and antiferromagnetic in all cases, whereas the Cu/Co interaction is inevitably antiferromagnetic, but stronger.

Returning to the fully extended chains, we first address the $Cu(TIM)MX_4$ series. As seen in Fig. 1, the macrocyclic cation is nonplanar, due to the fact that the Cu(II) ions sits out of the plane of the N ligating atoms. As a consequence, the Cu(II) ion in the macrocycle has a distorted-square-bipyramidal geometry with unequal apical distances. This nonplanarity leads to inequivalent Cu•••Cl-Cu linkages joining adjacent metal sites, which implies an alternation of exchange parameters as well as an alternation of sites.

For both the homometallic $Cu(TIM)CuX_4$ salts (X = Cl, Br), the Curie-Weiss analysis shows the existence of dominant ferromagnetic interactions at high temperatures, with the onset of antiferromagnetic behavior at lower temperatures. This data has been interpreted in terms of a model of an alternating chain in which the exchange constants alternate sign as well as magnitude. Since the model commonly used for the analysis of alternating S=1/2 Heisenberg chains [3] is only valid for alternating *antiferromagnetic* interactions, the chloride analog has been analyzed in terms of an alternating chain of ferromagnetically coupled S=1/2 dimers with antiferromagnetic exchange between dimers. The ferromagnetic dimers were treated exactly while the interdimer coupling was approximated in the mean-field approximation [4]. The best-fit analysis [5] yielded
$J_F/k_B = +13.3$ K and $J_A/k_B = -2.6$ K .

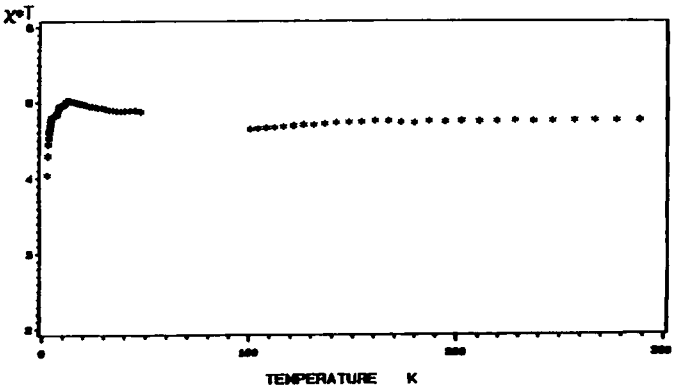

FIGURE 2 Magnetic susceptibility of $Cu(TIM)MnCl_4$, plotted as $\chi_m T$ versus T.

The magnetic susceptibility of the Cu(TIM)$MnCl_4$ system (Fig. 2) is consistent with ferrimagnetic behavior. At high temperature (> 100 K), the gradual decrease in the susceptibility product χT as T decreases indicates antiferromagnetic coupling between adjacent Cu and Mn atoms along the chain. Between 10 and 100 K, χT increases somewhat due to the onset of correlations between the magnetic unit cells. The product decreases rapidly towards zero below 10 K indicative of interchain interactions. A similar phenomenon has already been observed[6] in the ferrimagnetic chain compound FeCu(pbaOH)$(H_2O)_3 \cdot nH_2O$.

We next address the Cu(cyclam)MX_4 series. In the structures for the members of this series, the Cu(II) ion sits in the plane of the four N ligating atoms (Fig. 3), which insures that the exchange pathway between each pair of metal ions is the same. While the chain contains two metal sites, the sites are linked by only one exchange constant.

The homometallic Cu(cyclam)$CuCl_4$ salt [7] shows antiferromagnetic behavior in the 4-50 temperature range. The data is well described by a uniform antiferromagnetic Heisenberg linear chain with $J/k_B = -2.1$ K.

The magnetic behavior of the bimetallic Cu(cyclam)$CoCl_4$ shows rather unexpected magnetic results. Measurements collected during initial cooling of a loosely packed sample show sudden sharp increases in the magnetic moment of the sample. This is presumably due to reorientation of the individual particles under the influence of the applied magnetic field. This behavior implies a substantial anisotropy in the magnetic behavior of the system, a not unexpected conclusion for a system containing the d^7 Co(II) ion. The Curie-Weiss plot of χ^{-1} versus temperature shows the high temperature data to extrapolate to a negative intercept, which could be due to some combination of zero-field splitting effects and antiferromagnetic exchange coupling. If zero-field splitting effects play a substantial role, this would indicate that the $m_s = \pm 1/2$ levels lie low in energy.

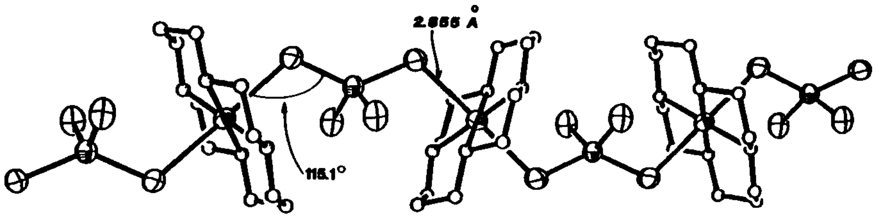

FIGURE 3 Illustration of the alternating site bimetallic chain in Cu(cylam)$CuCl_4$

It is also observed that the χT versus T decreases as T decreases. This would be consistent with the presence of an antiferromagnetically coupled alternating chain in which the moments of the Cu(II) ion and the Co(II) $m_s = \pm 1/2$ effectively cancel one another. Further studies will test this hypothesis.

NONMACROCYCLIC SYSTEMS

As indicated in the previous paper in this volume, we have also studied the possibility of forming ferrimagnetic chains using non-macrocyclic ligands originally selected for the formation of 2D structures. The first of these ligands is 4-cyanopyridine which we have found[8] forms a square planar brick enclosing the copper(II) ion, CuL_4 . Since the ligand is neutral, the copper brick is cationic and requires anionic mortar.

$$Cu(4\text{-}CNPy)_4{}^{2+} + MCl_4{}^{2-} \rightarrow Cu_{1-x}M_x(4\text{-}CNPy)_2Cl_2$$

The attempt to assemble a alternating site chain failed since the coordinating chloride ions tore apart the brick. The structure formed is that of a monosite chain, with metals bibridged by chloride ions and the organic ligands occupying the axial sites The structure corresponds to that of the well-studied series[9] of one dimensional magnets, $M(py)_2Cl_2$, where py = pyridine. Magnetic investigation[10] of the 4-cyanopyridine analogs shows that intrachain ferromagnetic interactions are found in the iron, cobalt, and nickel members while antiferromagnetic exchange dominates in the manganese and the copper compounds.

CONCLUSIONS

The "brick and mortar" approach to the synthesis of alternating site linear chain systems utilizing $M(macrocycle)^{2+}$ cations and $M'X_4{}^{2-}$ anions has been shown to be a successful design strategy. The compounds obtained appear to exhibit the desired magnetic behavior within the chains. Unfortunately, it appears that the combination of rather weak intrachain exchange coupling and relatively strong interchain interactions (which dominate the magnetic behavior at low temperatures) masks much of the interesting behavior associated with ferrimagnetic linear chains. In both macrocyclic systems, the source of the interchain interactions appears to be dipolar, since no readily recognizable superexchange pathways (such as Cl-Cl or Cl-H-N contacts) exist between chains.

The use of a non-chelating neutral ligands such as 4-cyanopyridine in the formation of a cationic brick leads to ligand redistribution upon introduction of tetrahalometallate mortar and thus fails to form the desired ferrimagnetic lattice.

ACKNOWLEDGEMENTS

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