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OXAMIDE DERIVED BIMETALLIC FERRIMAGNETS*

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Abstract New oxamide-based bimetallic ferrimagnets have been synthesized and studied. Reaction of oxamide with copper nitrate and Bu4OH in DMSO solution yields the soluble complex (Bu4N)2[Cu(C2H2N2O2)2]. Subsequent addition of nickel(II), or cobalt(II), perchlorate results in precipitation of the bimetallic materials. Magnetic susceptibility studies of both compounds show minima in the χT products, characteristic of ferrimagnetism. The minimum occurs at 45 K for the nickel-copper complex. The minimum for the cobalt-copper complex is too broad to locate accurately. The moments for both complexes reach constant values below 5 K. The cobalt-copper complex shows hysteresis at 4.2 K with a coercive field of 400 G, and exhibits long relaxation times at low temperatures.

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INTRODUCTION

The preparation of bimetallic ferrimagnetic coordination polymers has received a great deal of attention in recent years.[1] Such materials are designed so two magnetic ions of inequivalent moment, M and M', are located in an extended coordination lattice so that each ion M has only M' ions as nearest neighbors and each ion M' has only M ions for nearest neighbors. The intrinsic antiferromagnetic interaction between the M,M' pairs cannot cancel their inequivalent moments. Thus, an uncompensated moment remains in each unit cell with all the uncompensated moments in the extended lattice alligned parallel.

Two fundamental designs are used. The "brick and mortar" approach involves first enclosing a metal ion in strongly binding ligands with additional coordination sites, making the brick. The second metal ion, the mortar, is then added to coordinate to those additional sites and assemble the bricks into a polymeric lattice. This technique is well

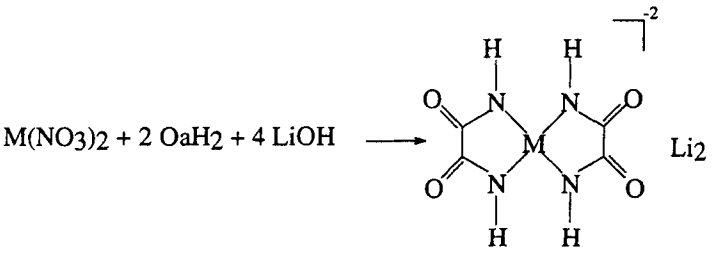
demonstrated by Kahn's use of 1,3-propylene bisoxamato-metal complexes and the related oximido bisbenzoato compounds[2] and by Coronado's work with EDTA and related chelating agents.[3] Our own initial work focused on the use of neutral bridging ligands (4-cyanopyridine, 2,2'-bipyrazine), which resulted in cationic bricks. These proved unstable to metal-exchange reactions and only bimetallic complexes with random site occupancy were isolated. This suggested the need to use more tightly coordinating anionic, chelating ligands to prevent such exchange reaction.

The second method, developed by Okawa, involves the self-assembly of metal ions of differing oxidation states into ordered bimetallic coordination polymers via a "one-pot" technique using oxalate as the binding ligand.[4] The successful use of oxalate as the bridging ligand in these system has rejected the generally accepted dogma that the ligands employed had to have different binding sites.

We reasoned that a combination of these two techniques might be possible if the dianion of oxamide were employed as the bridging ligand (we will use OaH_2 for the neutral molecule and Oa for the dianion). Kahn,[5] Verdaguer[6] and Okawa[7] have all observed strong interactions between Cu^{2+} ions through oxamide bridges with J values ranging from -60 K to -400 K. Thus, we hoped to generate a soluble oxamide-based brick and use that brick for the preparation of bimetallic ferrimagnets with strong magnetic exchange.

RESULTS AND DISCUSSION

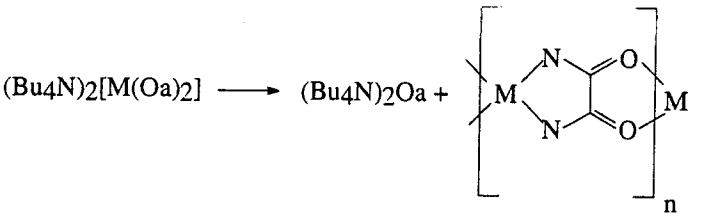
Reaction of $Cu(NO_3)_2 \bullet 3H_2O$ or $Ni(NO_3)_2 \bullet 6H_2O$ with LiOH and OaH_2 in DMSO produced the corresponding $Li_2M(Oa)_2$ complexes in high yield (Cu: quantitative, rose; Ni: 95%, yellow):



Physical data for the compounds agrees with that of the known potassium

salts.[8] The Cu complex is paramagnetic and has a room temperature χT = 0.39 cgs-emu. The Ni compound is diamagnetic, suggesting a square planer geometry. Initial attempts to use these materials to prepare bimetallic ferrimagnets failed. The compounds were not soluble in solvents other than water, in which both decompose.

The solubility of the materials was greatly improved by changing the geganion to Bu_4N^+. Reaction of $Cu(NO_3)_2 \bullet 3H_2O$ or $Ni(NO_3)_2 \bullet 6H_2O$ with Bu_4NOH and OaH_2 in DMSO gave quasi-stable solutions of the corresponding products, $(Bu_4N)_2[M(Oa)_2]$. Upon standing, DMSO solutions of both $(Bu_4N)_2$-$[Cu(Oa)_2]$ (deep red) and $(Bu_4N)_2[Ni(Oa)_2]$ (orange) decompose to give the homopolymers (Copper - olive green;[9] Nickel - yellow):



Solutions of the Ni complex decomposed fairly rapidly at first, but the Cu complex was sufficiently stable to use in the preparation of bimetallic compounds. The solution of $(Bu_4N)_2[Cu(Oa)_2]$ was treated with $Ni(ClO_4)_2$, or $Co(ClO_4)_2$ in DMSO and gave reddish precipitates of $Ni[Cu(Oa)_2]$ (1), or $Co[Cu(Oa)_2]$ (2), in >95% yield.

$$(Bu_4N)_2[Cu(Oa)_2] + M(ClO_4)_2 \longrightarrow M[Cu(Oa)_2](H_2O)_n$$

$$M = Ni, Co$$

Magnetic susceptibility data for $Ni[Cu(Oa)_2]$ were collected over the temperature range 1.5-300 K. Figure 1 shows the χT product as a function of T over the temperature range 5 K to 275 K. Figure 2 shows both χ vs T and χT vs from a second data collection over the temperature range 1.5 K to 70 K.

The minimum in χT near 45 K, characteristic of ferrimagnetic interactions, is clearly seen in Fig. 1. Even at room temperature, the χT value has still not reached a maximum, suggesting strong interactions. A peak in χT appears at 10 K and the susceptibility appears to level off below 3 K (Fig. 2). High field magnetization studies (-20 T to +20 T) show no significant hysteresis at either 4.2 K, or 2.8 K.

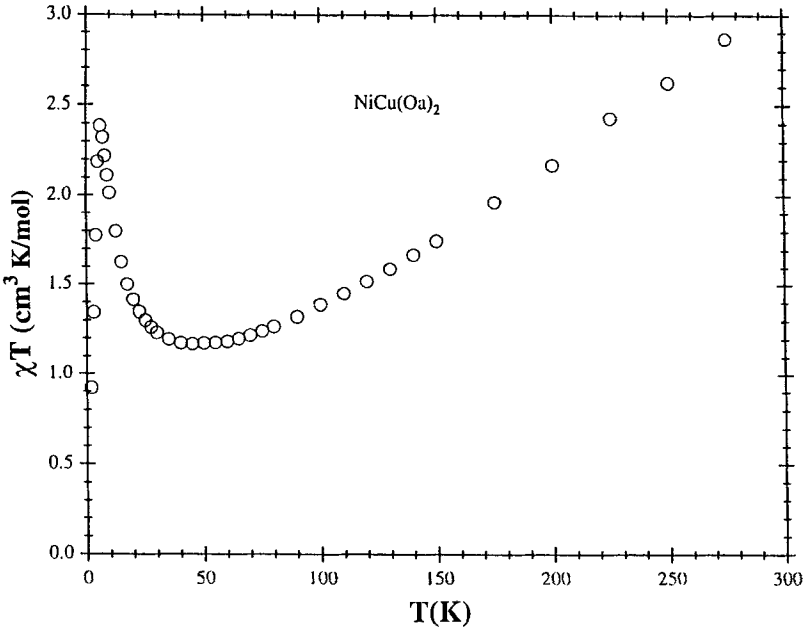


FIGURE 1 χT as a Function of T for $Ni[Cu(Oa)_2]$ (1)

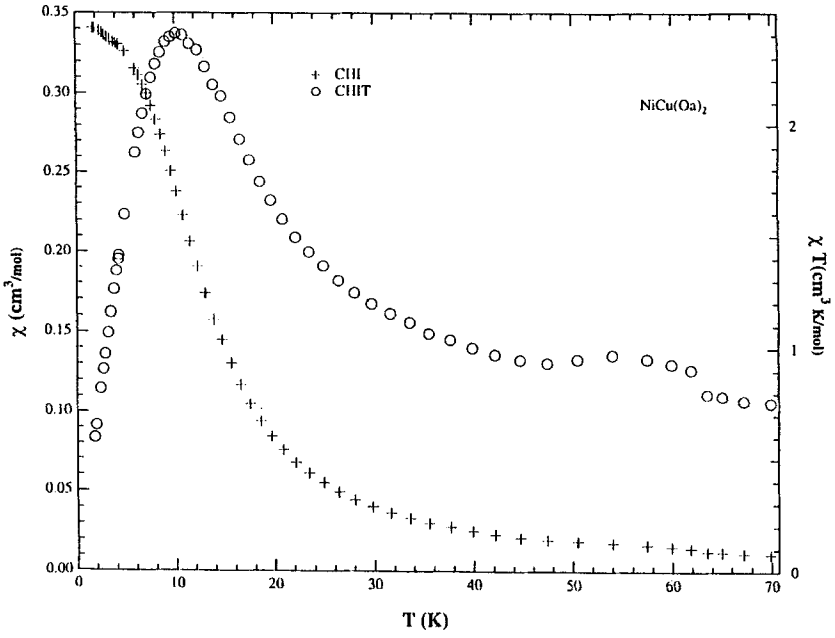


FIGURE 2 χ (+) and χT (o) as a Function of T for $Ni[Cu(Oa)_2]$ (1)

Data for $Co[Cu(Oa)_2]$ (2) shows a very broad minimum in χT as a function of T (Fig. 3). The value of χT is 1.4 at 350 K and decreases by about 7% to 1.3 at 100 K. A sharp increase in χT is seen at lower temperatures reaching a peak near 7 K, somewhat lower in temperature than that observed for 1. High field magnetization studies show significant hysteresis for 2, with a coersive field of 400 Oe at 4.2 K.

Both compounds 1 and 2 exhibit significant relaxation times at low temperatures (near 5 K and below). Figure 4 shows χ vs T data for three cases; zero field-cooled (ZFC), field-cooled (FC), and non-equilibrium field-cooled (nFC). The ZFC data were collected by cooling the sample to 4.2 K, then applying the field and waiting until the moment had stabilized (about one hour) before collecting data.

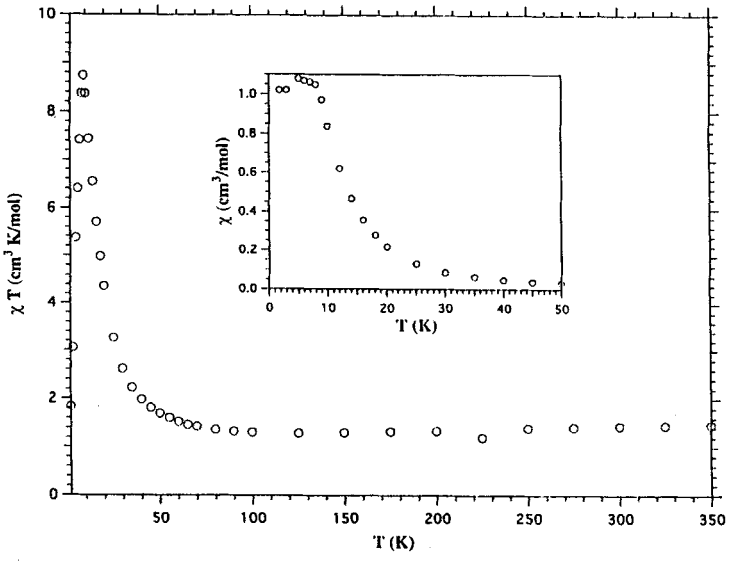


FIGURE 3 χ and θT as a Function of T for $Co[Cu(Oa)_2]$ (2)

The FC data were collected by cooling the sample to 4.2 K in a 3000 Oe field and waiting until the moment had stabilized before collecting data (again, about one hour). The nFC data were obtained by cooling the sample to 4.2 K in a 3000 Oe field and beginning data collection immediately. The correspondence between the FC and ZFC data at low temperature suggests a unique ground state, but the long relaxation times evident from the nFC data show that there must be other low energy align-

ments as well. Alternatively, the long relaxation times may be indicative of some disorder in the metal ion site occupancy. If there is some disorder in the site-occupancy, that could also account for the hysteresis effects observed.

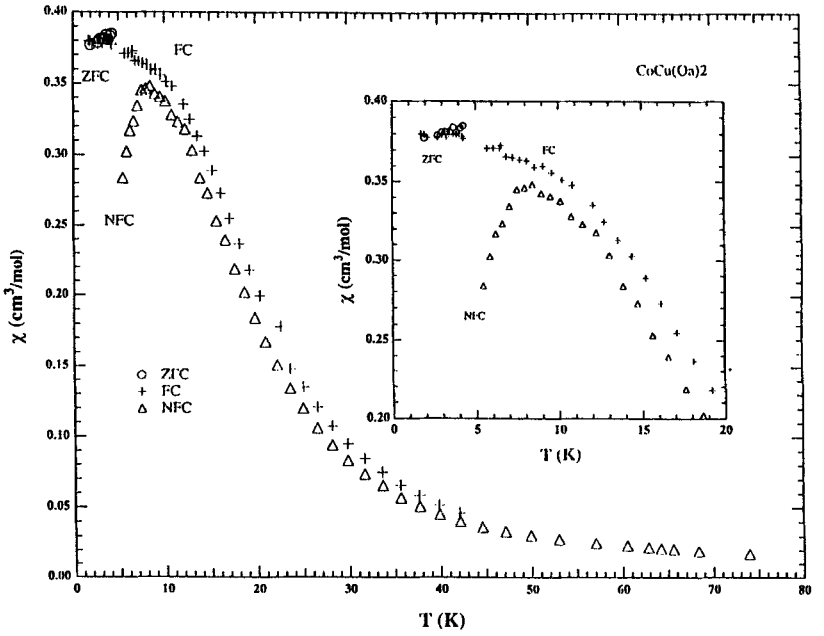


FIGURE 4 χ as a Function of T for $Co[Cu(Oa)_2]$ (2): zero field cooled (o), field cooled (+) and non-equilibrium field cooled (Δ)

The lower stability of the soluble nickel brick $(Bu_4N)_2[Ni(Oa)_2]$ prevented its use in making a related family of ferrimagnetic compounds. However, addition of solid $Li_2[Ni(Oa)_2]$ to an aqueous solution of $Cu(ClO_4)_2$ gave a green-brown precipitate:

$$Li_2[Ni(Oa)_2] + Cu(ClO_4)_2 \xrightarrow{H_2O} Cu[Ni(Oa)_2](H_2O)_n$$

While we have yet to fully characterize the product 3, preliminary magnetic data suggests an interesting result, quite different from its isomer 1. Figure 5 shows χ and χT as a function of T for 3.

The material shows no evidence of interactions above 15 K and has a paramagnetic $\chi_m T$ value of 0.47, very nearly that for isolated Cu_{2+} ions. A plot of $1/\chi$ versus T yields a Curie-Weiss θ near zero, confirm-

ing the absense of interactions. We believe this may result from generation of an oxamide bridged Cu^{2+}-Ni^{2+} chain, where the Ni^{2+} ions are in a square planar environment as they are in the starting material, $Li_2[Ni(Oa)_2]$. This would yield a chain where the paramagnetic Cu^{2+} ion are insulated from each other by the diamagnetic Ni^{2+} ions, accounting for both the observed Curie constant and the lack of interactions.

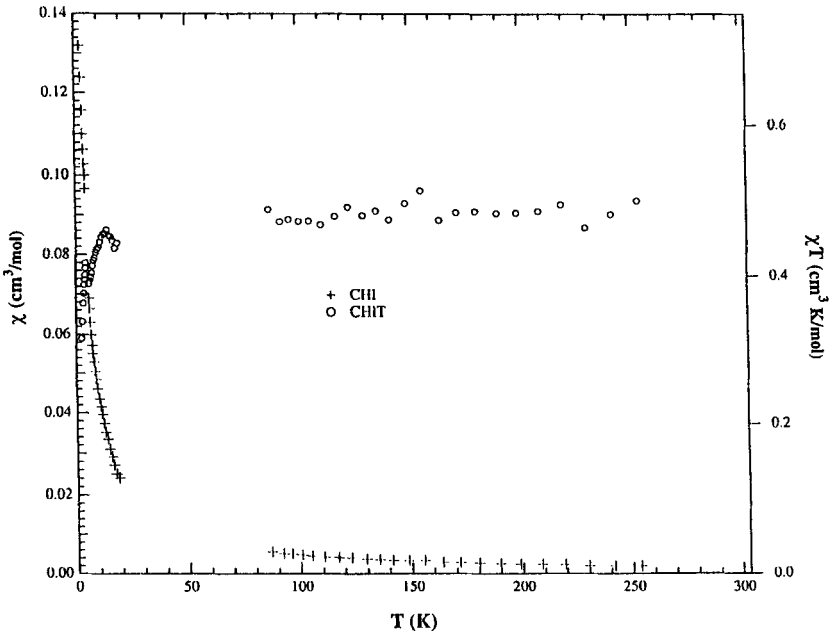


FIGURE 5 χ and χT as a Function of T for $Cu[Ni(Oa)_2]$ (3)

CONCLUSIONS

It is clear that ferrimagnetic, bimetallic coordination polymers of oxamide can be prepared, although the intractability of these materials (principally their insolubility and our inability to obtain single crystals) has prevented a detailed analysis of their structures. The lack of interactions in $Cu[Ni(Oa)_2]\bullet nH_2O$ leads us to believe that the coordination geometry about the "brick ion" in these compounds is square planer. Further work is in progress to elucidate the exact structure of these compounds and to increase the lattice dimensionality through the use of macrocyclic analogues of oxamide.

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