

Inorganic Approaches to Molecular Magnets: The Bimetallic Chains

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Literature Seminar

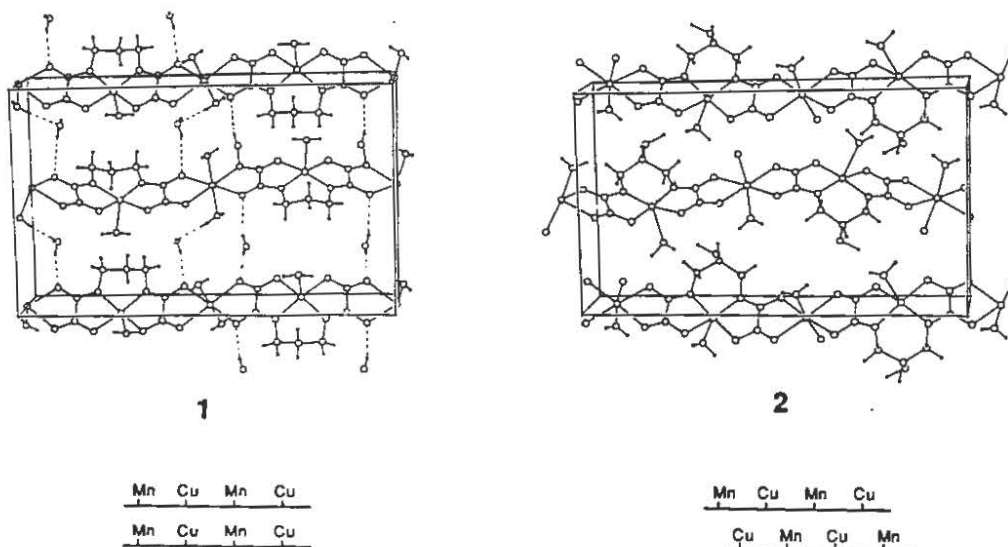
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Molecular magnets are molecular-based materials that exhibit ferromagnetic transitions. Interest in these systems has been stimulated by the desire to improve the properties of magnets. There are three types that have been characterized so far: 1) donor-acceptor charge transfer salts [1], 2) Mn(II)-nitroxide chain compounds [2], and 3) bimetallic chain compounds with bisbidentate extended ligands. Of these, the bimetallic chains have shown substantial recent promise.

In order to understand the magnetic properties of bimetallic chain compounds, it is instructive to first consider non-chain bimetallic and trimetallic compounds [3,4]. In non-chain bimetallic compounds which display ferromagnetic interactions, the two magnetic orbitals are required to be strictly orthogonal in order to stabilize high-spin multiplicity. This strict orthogonality is possible only with a few pairs of metal ions and requires high site symmetry. Accidental orthogonality may occur in some complexes with an M-X-M bridging angle close to 90° [5], but it can be destroyed easily by small structural changes. The spin state in bimetallic complexes is regular; the spin multiplicity varies monotonically with the energy of the spin state. However, when there are more than two interaction centers, the spin multiplicity may or may not vary monotonically with energy. Therefore ferromagnetic-like behavior can be obtained in compounds containing more than two metal centers ($\chi_M T$ increases upon cooling where χ_M is the molar magnetic susceptibility and T the temperature).

The greatest success in making molecular magnets has been through the synthesis of bimetallic chain compounds. The first bimetallic chain compounds, $AMn(S_2C_2O_2)_2(H_2O)_3 \cdot 4.5H_2O$, A = Cu, Ni, Pd, Pt, were made in 1981 by Verdaguer et. al [6]. These compounds consist of extended zigzag chains $-A(S_2C_2O_2)-Mn(H_2O)_3-(O_2C_2S_2)A-$ and isolated water molecules. Magnetic studies of $CuMn(S_2C_2O_2)_2(H_2O)_3 \cdot 4.5H_2O$ showed that the ferrimagnetic interactions occurred between CuMn units in the temperature range of 130K to 7.5K. Sudden decrease of $\chi_M T$ was observed around 7.5K. This behavior may be attributed to three-dimensional interchain antiferromagnetic interactions.

To further understand the requirements for obtaining better ferrimagnets, Kahn systematically studied the compounds $MnCu(pba)(H_2O)_3 \cdot 2H_2O$ **1** (pba = 1,3-propylenebis(oxamato)), $NiCu(pba)(H_2O)_3 \cdot 2H_2O$, and $MnCu(pbaOH)(H_2O)_3 \cdot 2H_2O$ **2** (pbaOH = 2-hydroxy-1,3-propylenebis(oxamato)) [7]. These compounds all consist of ordered bimetallic chains with equally spaced metal centers. Studies showed that for isostructural AB bimetallic chains with S_A and S_B spins, the larger the difference between S_A and S_B , the larger the increase of $\chi_M T$ upon cooling. The intramolecular coupling constant J_{intra} should be as large as possible for a given metal couple to extend the temperature range of ferrimagnetic interactions. Intrachain ferrimagnetic interactions were quenched by interchain antiferromagnetic interactions. To minimize these interchain interactions, the distance between chains should be as large as possible. The magnetic properties of **2** are surprisingly different from **1** at $T < 30K$ in spite of their very similar structures and almost identical magnetic properties in the 30K-300K temperature range. **1** presents one-dimensional ferrimagnetic behavior with three-dimensional antiferromagnetic interactions at low temperatures whereas **2** has a three-dimensional ferromagnetic transition at $T_c = 4.8K$. Such a difference has to be related to the packing of chains. Every other chain in **2** is displaced by slightly less than half a unit along the b axis, as shown in Scheme A, avoiding antiferromagnetic interactions. This implies that minimal interchain antiferromagnetic interactions are achieved by staggering the relative positions of the chains, which favors the ferromagnetic state.



A

Studies of $MM'(edta)(H_2O)_4 \cdot xH_2O$ compounds ($-M(H_2O)_4-M'(edta)-M(H_2O)_4-$) showed that slight differences between coupling constants, J_1 and J_2 , result in ferrimagnetic interactions even when S_M is the same as $S_{M'}$ [8], where J_1 and J_2 are the coupling constants of one metal center with two adjacent metal centers. This result enabled synthetic chemists to make alternating bimetallic chain compounds. The structures and magnetic properties of alternating chain compounds resulting from the reaction of Cu(II) dianionic precursors with Mn(II) ions were explored [9]. Two types of structures have been characterized: chains with a syn-anti configuration, and chains with an anti-anti configuration around the carboxylato bridge. Magnetic studies showed that the interactions through the carboxylato bridge are negligible when the configuration is syn-anti and detectable when the configuration is anti-anti. Another compounds containing alternating Mn(II)-Cu(II) chains, $MnCu(obbz) \cdot xH_2O$ ($x = 1, 5$), $obbz = \text{oxamidobis}(N, N'\text{-benzoato})$, showed spontaneous magnetization when $x = 1$ but orders anti-ferromagnetically around 2.3K when $x = 5$. The understanding of these differences has been hindered by the absence of the crystal structures.

Two three-dimensional magnets have been synthesized, $MnCu(pbaOH)(H_2O)_3 \cdot 2H_2O$ [7b] and $MnCu(obbz) \cdot H_2O$ [9c]. $MnCu(pbaOH)(H_2O)_3 \cdot 2H_2O$ is composed of one-dimensional ferrimagnets packed in a way to favor ferromagnetic interactions. $MnCu(obbz) \cdot H_2O$ is presently not structurally characterized but is proposed to have three dimensional network bonding.

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