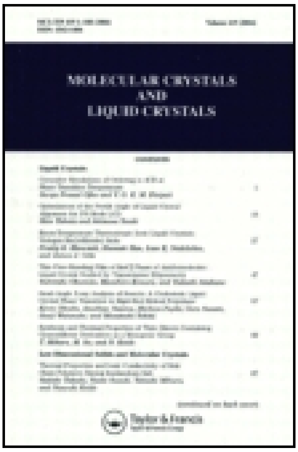

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A Recurrent Novel Motif For 3-Dimensional Magnetic Exchange Interactions in Chain Structures Containing Endo-Bidentate α-Di-Imine Ligands: π-π Overlap Interactions

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A RECURRENT NOVEL MOTIF FOR 3-DIMENSIONAL MAGNETIC EXCHANGE INTERACTIONS IN CHAIN STRUCTURES CONTAINING ENDO-BIDENTATE α-DI-IMINE LIGANDS: π-π OVERLAP INTERACTIONS

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Abstract

Weakly associated five coordinate monomers based on high-spin trivalent iron α-di-imine complexes are found to exhibit surprisingly strong magnetic exchange interactions that lead to easily discerned 1-and 3-dimensional antiferromagnetic exchange and ordering effects respectively.

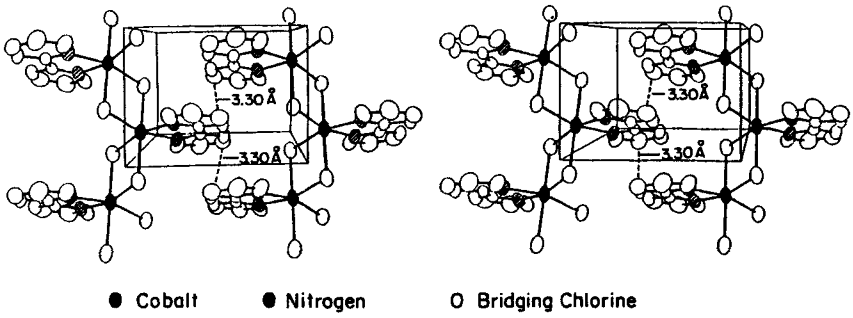
Introduction

For a number of years, we have been interested in the magnetic properties of low dimensionality molecular magnetic materials based on transition metal complexes of simple α-di-imine ligands such 1,10 orthophenanthroline, 2,2'-bipyridine and 2-(pyridin-2-yl) benzothiazole. The synthetic strategy is to prepare formally coordinatively unsaturated materials by using 1:1 metal to ligand preparation reaction stoichiometries to obtain materials corresponding to the empirical formula $[M^{II}LX_2]$ or $[M^{III}LX_3]$, X=halide or pseudo-halide. The coordinative unsaturation is presumably overcome via *halogen or pseudo-halogen bridging* among the foregoing units leading to articulation of distinctly non-linear or zig-zag chains in some cases.

We find (1) that precisely the foregoing behavior occurs for the M(2,2'bipyridine)Cl_2 and 1,10-orthophenanthroline series. See Figure 1 for the case of Co(2,2'-bipyridine)Cl_2 where such chains interleave and inter-act via π-π overlap stacking interactions.

$[Co(bipy)Cl_2]_\infty$ Zig-Zag Chain Polymer

Local *cis* $[CoN_2Cl_4]$ Chromophore



Co-Co-Co $< \approx$ 130° Some 20% Overlap of Adjacent Chains

Inter-Chain Stacking Interaction (3.30 Å C—C Distance) Like Graphite

FIGURE 1 Zig-zag chain structure of [Co(2,2'-bipyridine)Cl_2] with its *two bridging chlorine atoms*

On the other hand, for the trivalent metal analogues, e.g., [Fe (2-pyridin-2-yl benzothiazole)Cl_3] (A) and the related [Fe(1,10-phenanthroline Cl_3] and [Fe(2,2' bipyridine)Cl_3], there is no halogen bridging. That is, a combination of single crystal x-ray diffraction and Mossbauer spectroscopy shows that these ferric materials consist of novel chains or *five coordinate monomeric units* connected *only* by π-π stacking interactions of the overlapping di-imine ligands and perhaps weak Cl-Cl contacts. This situation contrasts strongly with that for Mn(2,2', -bipyridine)Cl_3 whose single chlorine atom bridging leads to six coordinate manganese (III) chromophores in zig-zag chains (2) as pictured in Figure 2.

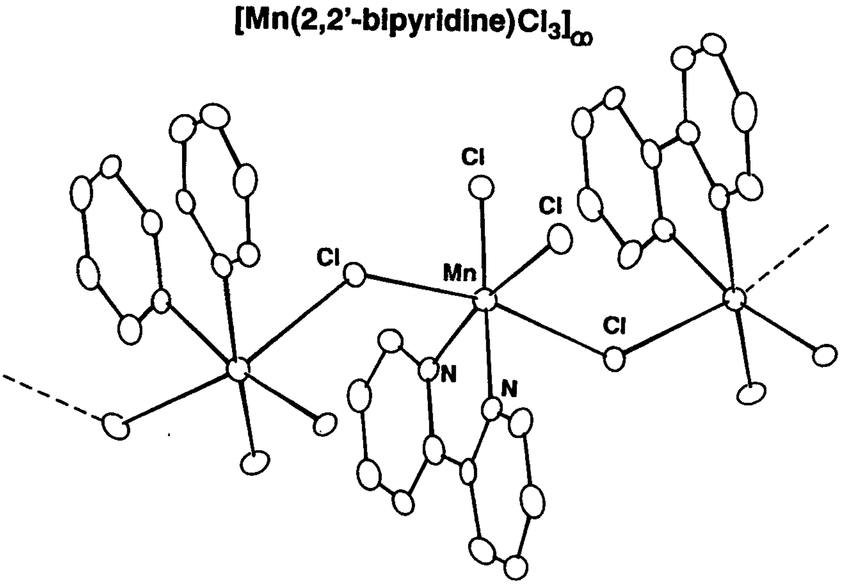
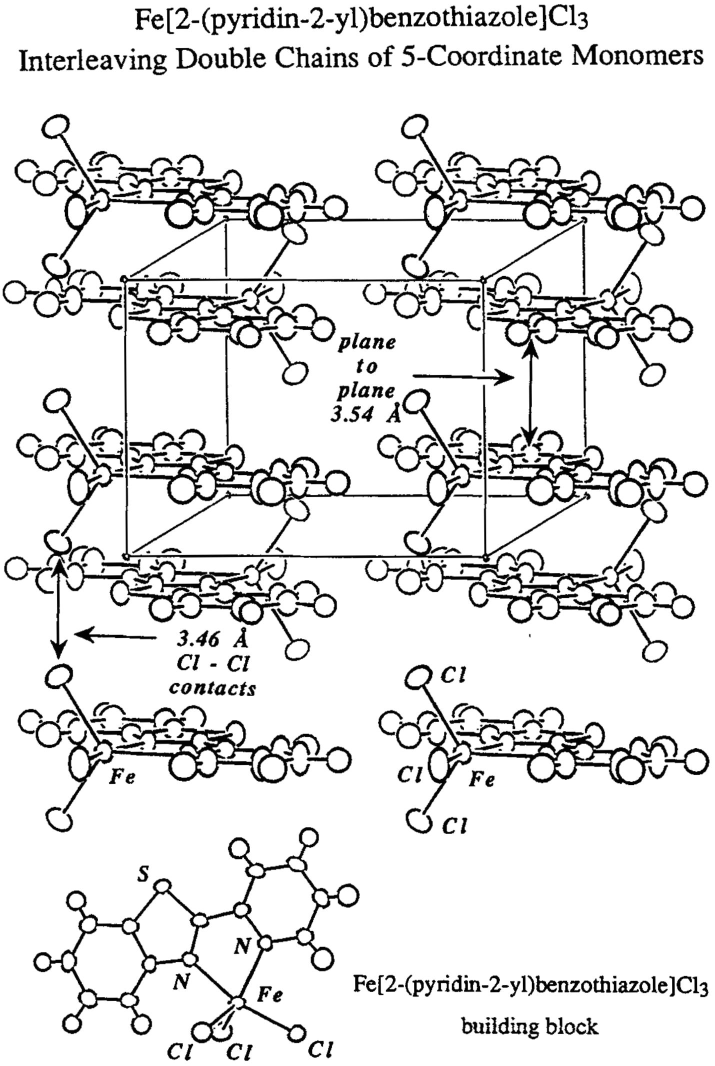

$[Mn(2,2'\text{-bipyridine})Cl_3]_\infty$

FIGURE 2 Zig-zag chain structure of $[Mn(2,2'\text{-bipyridine})Cl_3]$ with its *single bridging chlorine atom* after Perlepes et al (Ref 2)

The individual linear chains and their overlap for compound (A) are shown in Figure 3.



Fe[2-(pyridin-2-yl)benzothiazole]Cl_3
Interleaving Double Chains of 5-Coordinate Monomers

FIGURE 3 Chain structure of [Fe(2-pyridin-2-yl benzothiazole)Cl_3] in which there is *no chlorine atom bridging*

Nevertheless, these "loosely associated" ferric ion based materials exhibit surprisingly strong magnetic exchange behavior e.g., for (A), T_N~7.3K and T(χ-max-1D)~13.8K) and a rich variety of magnetism. X-ray structure determinations show that the related materials [Fe(1,10phenan-throline)Cl_3CH_3OH]CH_3OH (B) and [Fe(2,2'-bipyridine)$Cl_3 \cdot CH_3OH$] (C) exhibit similar details, in particular the π-π stacking interactions in addition to hydrogen bonding among Cl and CH_3OH units.

Results

Some a.c. susceptibility data taken at 1 Oe and 125 Hz and bearing on the 3-dimensional magnetic ground state of (A) are given in Figure 4 for a polycrystalline sample.

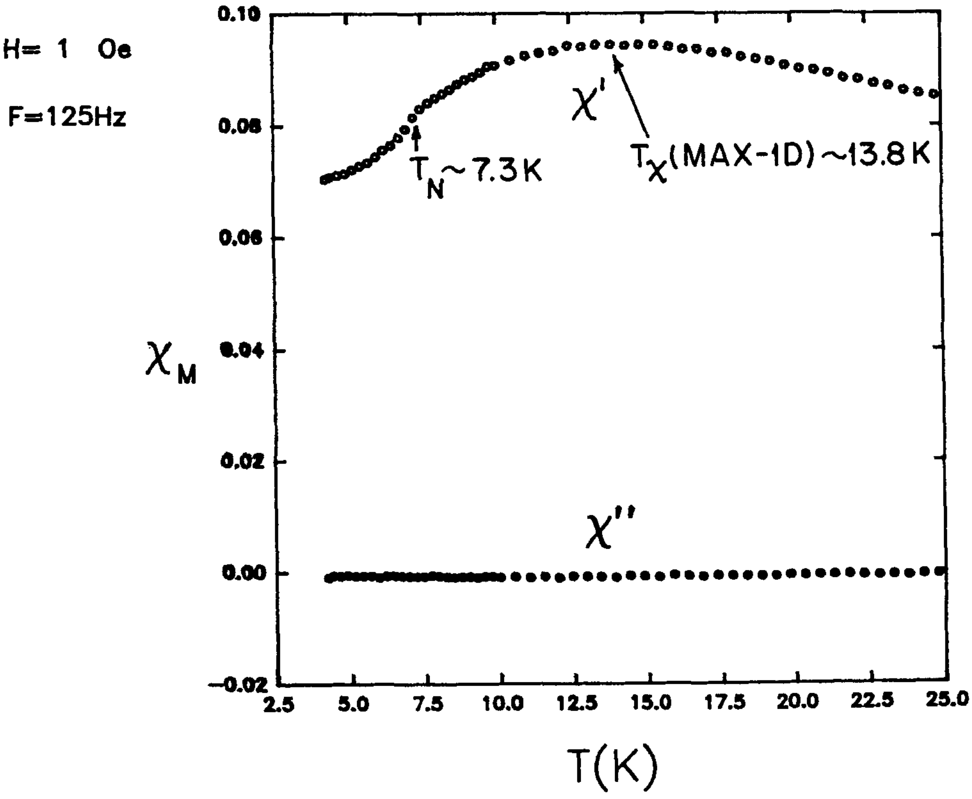


FIGURE 4 A.C. susceptibility data for *[Fe(2-pyridin-2-yl) benzothiazole)Cl_3]*

It is clear that there is no out of phase signal (χ''_m) thus confirming an uncanted 3D-A.F. ground state for this chain of five coordinate monomers. The temperature dependence of the Mossbauer spectra of (A) suggests $T_{critical}$ ~ 7.6K in essential agreement with d.c. and a.c. susceptibility results. The complete details for compounds (A), (B) and (C) including their syntheses, x-ray structures and temperature dependence of Mossbauer spectra will be published elsewhere subsequently (3).

Summary

Suffice it to say for now that rather weak molecular interactions, namely π-π stacking or at most in some cases additional hydrogen bonding can lead to strong magnetic exchange behavior for high-spin trivalent iron mono-α-di-imine complexes. *Supported by the NSF Division of Materials Research.

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