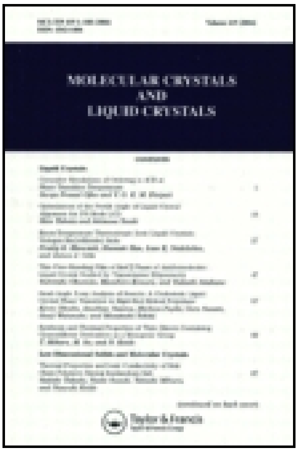

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W. M. Reiff [a] [b] & J. H. Zhang [a]
[a] Department of Chemistry, Northeastern University, Boston, Mass, 02115
[b] Xavier Univ., New Orleans, LA

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A NEW FAMILY OF LOW FIELD META-MAGNETS BASED ON ZIG-ZAG POLYMERS OF SIMPLE ENDO-BIDENTATE LIGANDS: $\{M(1,10\text{-PHENANTHROLINE OR } 2,2' \text{ BIPYRIDINE})_1Cl_2\}_\infty$ CHAINS, M = Fe^{II}, Co^{II}, Ni^{II}, Mn^{II}.

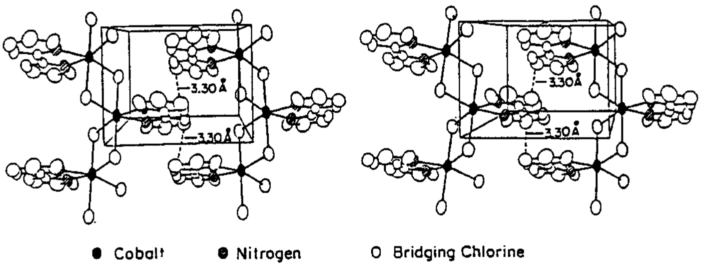
W.M. REIFF *, AND J.H. ZHANG†
Department of Chemistry, Northeastern University,
Boston, Mass 02115

Abstract Contrary to previous high field results, low field d.c. and a.c. magnetometry show that a number of the title compounds have 3D antiferromagnetic ground states and exhibit classical meta-magnetic behavior with critical fields ranging from 0.05 to 0.15 Tesla.

INTRODUCTION

Previous single crystal x-ray study (1) of Co 2,2' $(bipyridine)_1Cl_2$ and the isomorphous divalent Mn, Fe and Ni analogues shows that these materials are comprised of infinite zig-zag chains (M-M-M angles ~ 130°) of $[cis\text{-}MN_2Cl_4]$ chromophores as seen in Figure 1.

$[Co(bipy)Cl_2]_\infty$ Zig-Zag Chain Polymer
Local *cis* $[CoN_2Cl_4]$ Chromophore



Co-Co-Co < ≈ 130°   Some 20% Overlap of Adjacent Chains
Inter-Chain Stacking Interaction (3.30Å C–C Distance) Like Graphite

FIGURE 1 Zig-zag chain structure of $[Co(2,2'\text{-bipyridine})Cl_2]$

Initial d.c. susceptibility and magnetization investigations or this family (H_0 varying 0.15 to 22 Tesla) suggested 1-dimensional ferromagnetism for many of these systems with 3-dimensional ferromagnetic ground states (2), $T_{critical}$ generally $\leq$ 5K. We have now carefully reinvestigated these compounds using a combination of low field d.c. squid magnetometry ($H_0 \sim$ 1mT to 0.1T) and zero field a.c. susceptibility techniques which conclusively confirm the aforementioned 1-D chain ferromagnetism but to the contrary, classic 3D-antiferro-magnetic ground states with, as expected no out of phase or imaginary component to the a.c. susceptibility (at least for the chlorides) in the vicinity of $T_{critical}$. σ vs H curves exhibit well defined low field 0.02 to 0.06 T meta-magnetic transitions analogous to these found (3) for the new famous chain ferromagnets {M (pyridine)$_2$Cl$_2$]$_\infty$ which correspond to near linear articulation of {trans-MN_2Cl_4} chromophores seen in Figure 2, i.e., M-M-M angles ~ 180°.

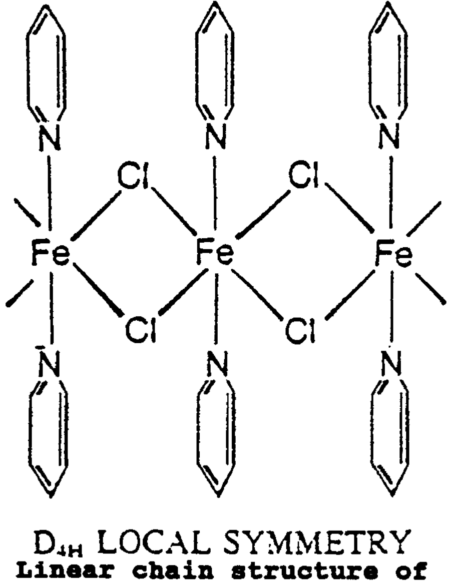


FIGURE 2 Linear chain structure of [Fe(pyridine)$_2$Cl$_2$]

The 1D-ferromagnetic effect for the present [M(bipyridine)X_2] systems is remarkable with effective moments increasing by as much as ~ 1 to 5 Bohr magnetons (depending on the metal) above the spin only value on decreasing T from ~ 80K to ~ 5K. The ultimate long range 3D-AF order is attributed to a novel interchain exchange motif wherein the bipyridine rings of adjacent chains are significantly interleaved and overlapped leading to bipyridine π-π stacking interactions at essentially the interplanar separation in graphite, i.e. ~ 3.30°A, Figure 1.

Results

Some fairly typical results exemplifying the aforementioned observations of: (1) uncanted genuine 3D-AF ground states (2) low field meta-magnetism (3) and dominant ferromagnetism are given in Figures 3, 4, 5 and 6 for the specific case of the zig-zag chain Fe(2,2'-bipyridine)Cl_2. Powder x-ray diffractometry shows the latter to be isomorphous to Co(2,2,'-bipyridine)Cl_2, Figure 1, whose heat capacity and low field d.c. susceptibility indicate T_N=2.1K and fit well to a ferromagnetic Ising chain with $J_{(\mathrm{Intra\text{-}Chain})}/k_B$ = +7.1K. Figure 3 shows the temperature dependence of the a.c. molar susceptibility (at 1 Oe, 125Hz) for Fe(2,2'-bipyridine)Cl_2 with χ''_m clearly = 0 at T_N(4.1K)i.e., consistent with a 3D-AF ground state and no canting behavior.

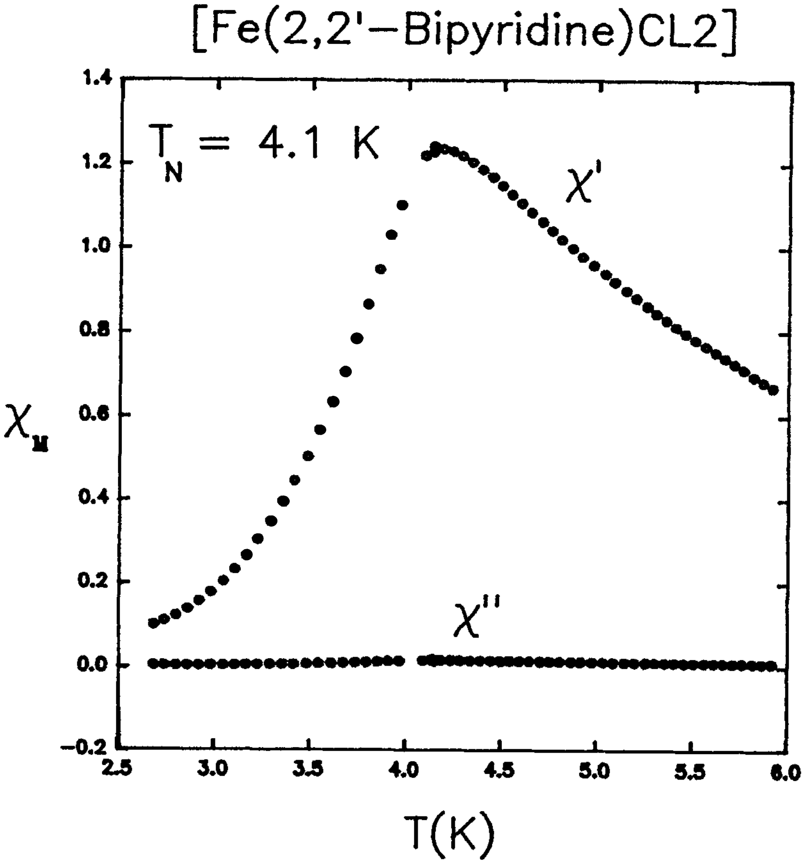


FIGURE 3 Temperature dependence of real (χ'_m) and imaginary (χ''_m) components of the a.c. susceptibility of the six coordinate iron form of [Fe(2,2'-bipyridine)Cl_2]

However, relatively small d.c. fields strongly perturb this ground state as shown in Figure 4.

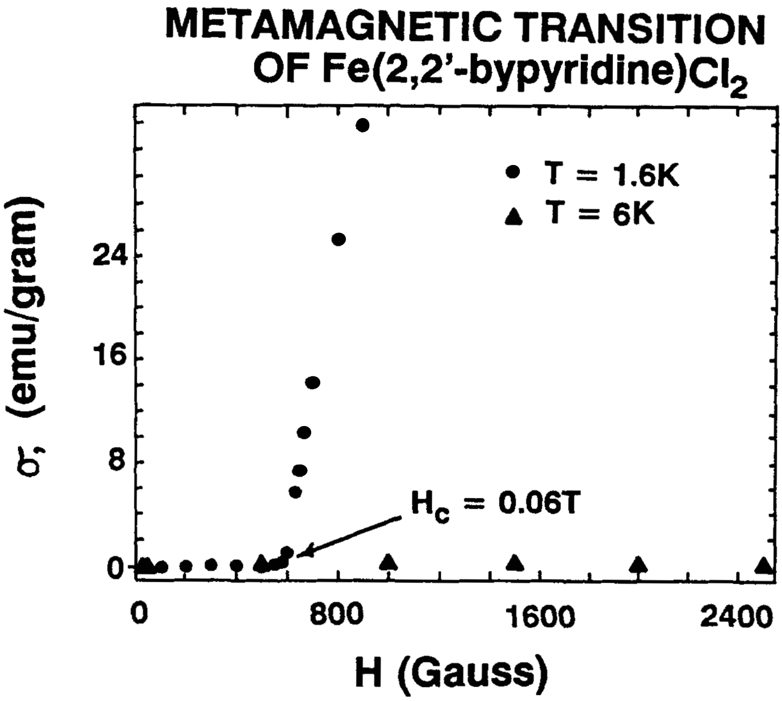


FIGURE 4 **Isothermal magnetization (σ) versus applied field above and below T_N for the six coordinate iron form of [Fe(2,2'-bipyridine)Cl_2]**

Here at 6.0K (i.e., $T > T_N$), one sees the linear field dependence of magnetization behavior expected of a simple, rapidly relaxing paramagnet. On the other hand at 1.64K($T<T_N$), an abrupt rise in specific magnetization occurs corresponding to a meta-magnetic transition at $H_{critical}$~600G (0.06T). This should be compared to similar data (4) for the linear chain ferro-magnet [Fe(pyridine)$_2$Cl$_2$ for which $H_{critical}$ = 700 Gauss. Finally, we refer to Figures 5

and 6, plots of molar moment and reciprocal molar susceptibility vs. temperature for Fe(2,2'bipyridine)Cl_2.

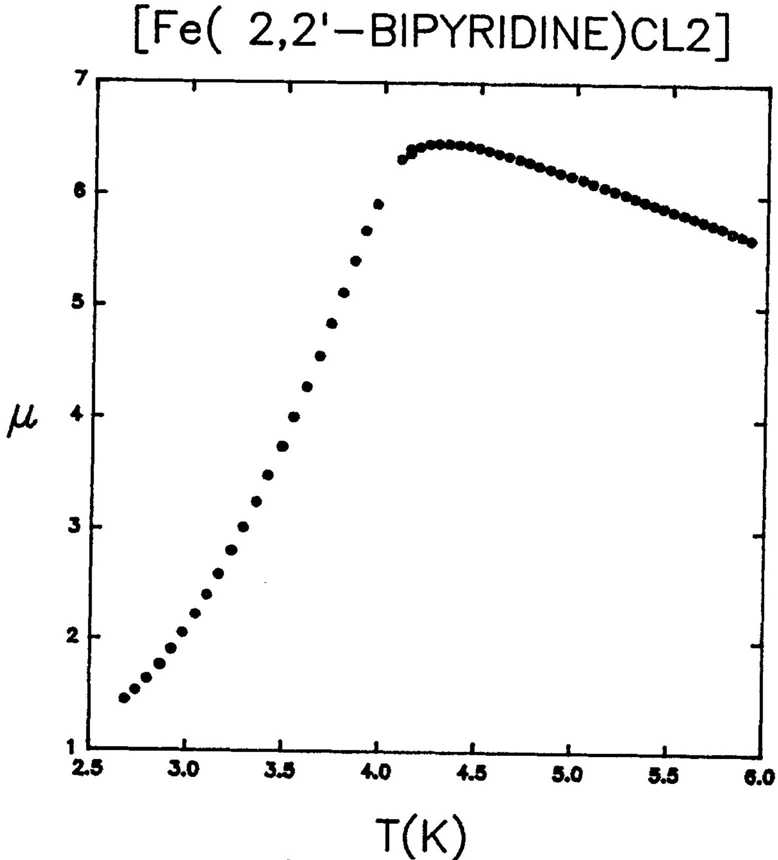


FIGURE 5 Magnetic moment (μ) versus temperature for the six coordinate iron form of [Fe(2,2'-bipyridine)Cl_2]

The strong ferromagnetic effect above T_N is obvious in view of expected spin only behavior of high-spin Fe^{II} leading to $\mu_{s.o.}$ √24(4.9 B.M.). With orbital contributions considered, the moment of high spin Fe^{II} typically ranges from 5.1 to 5.4 B.M. These values are to be compared to observed moments as large as 6.4 B.M. at 4.1K. Consistent with these results is the positive paramagnetic Curie temperature, Θ =+4.3K Figure 6, a reflection of the dominant (intra-chain) ferromagnetic interaction even though the material ultimately 3D orders antiferro-magnetically owing to weaker inter chain exchange interactions.

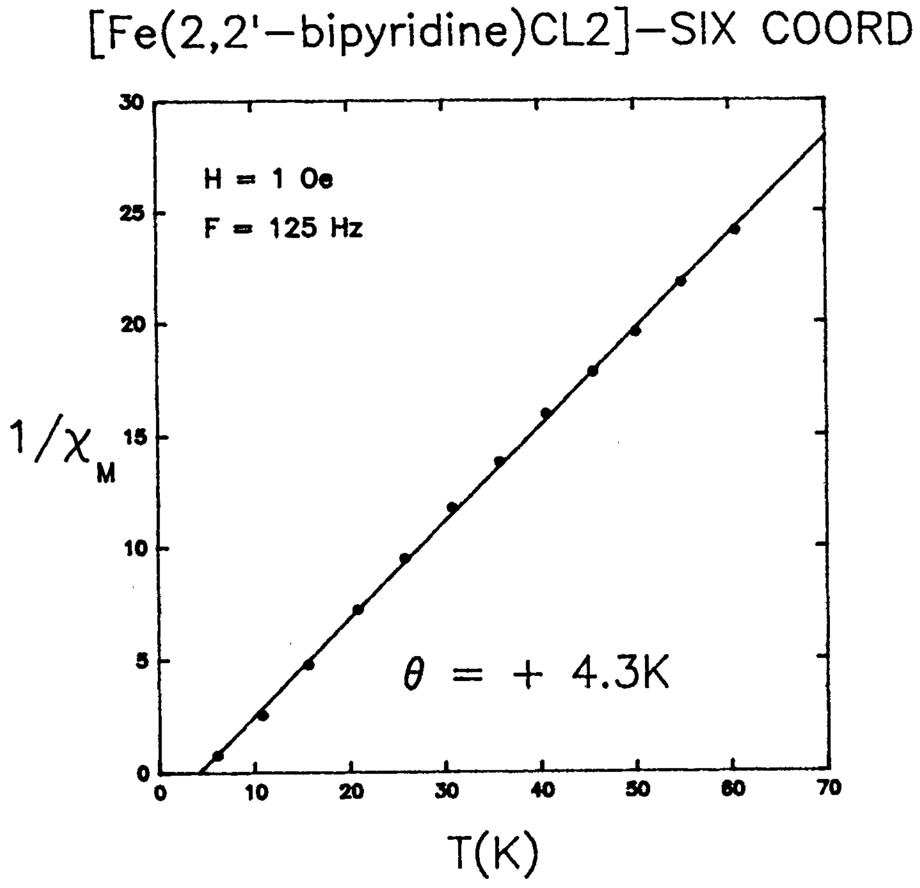


FIGURE 6 Reciprocal susceptibility versus temperature for six coordinate iron form [Fe(2,2′-bipyridine)Cl_2]

The magnetic susceptibilities of the related [Co(2,2',-bipyridine)Br_2] and [Co(2,2'-bipyridine)I_2] exhibit strong out of phase components at $T_{critical}$ suggesting either canted antiferro-magnetic or ferromagnetic 3D-ground states and overall, a rich variety of magnetic behavior in this series.

In closing, we point out that there is also a five coordinate iron isomer of [Fe(2,2'-bipyridine)Cl_2] that is obtained by simple thermal annealing of the six-coordinate form. The structure of the latter is that shown in Figure 1 for the cobaltous analogue where *two chlorine atom bridging is evident*. Previous (5) Mossbauer and far infra-red spectroscopy studies confirm five coordinate high-spin Fe^{II} and suggest a chain structure but with single chlorine atom bridging of ferrous centers. This leads to substantial reduction of magnetic exchange interaction such that the low temperature magnetic moment variation, Figure 7 vs Figure 5, is now entirely explicable in terms of single ion zero field splitting ($|D| \sim 10$ cm^{-1}) effects. The details for these and the related Mn, Ni and Cu analogues are the subject of further study and future publication elsewhere.

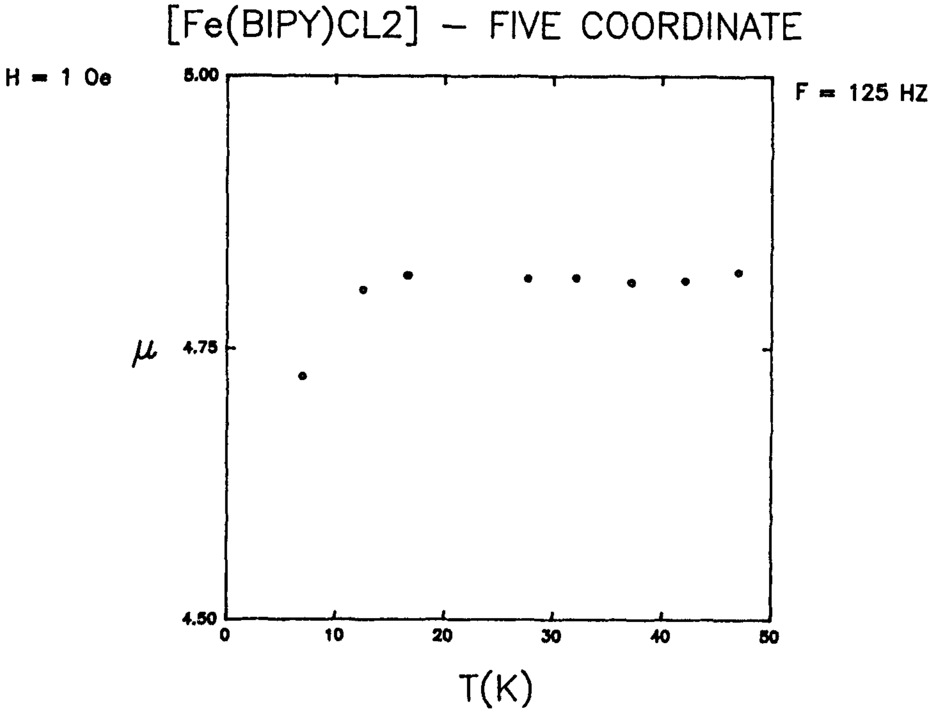


FIGURE 7 μ versus T for the five coordinate iron form of [Fe(2,2′-bipyridine)Cl_2]

*Supported by the NSF Div. of Mat. Res. † Current address, Xavier Univ., New Orleans, LA.

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