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# Solid State Displacement Reactions of Transition Metal Polymers. A Calorimetry Study of Some Bispyridyl Transition Metal Chlorides

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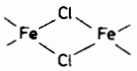
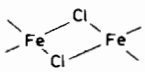
## Introduction

The series $M(py)_2Cl_2$, where py is pyridine and M is Mn, Fe, Co, Ni, and Cu, has been extensively studied because of its interesting structural, electronic, and magnetic properties. The compounds are polymeric linear chains with *trans*-axial pyridine molecules and chlorine atoms bridging between the metal atoms [1]. At very low temperatures (<10 K) it has been shown that some members of this series exhibit intrachain antiferromagnetism (Mn, Cu) [2, 3] and others (Fe, Ni, Co) [2, 4, 5] intrachain ferromagnetism as well as metamagnetic behavior [6]. Long *et al.* [4] have studied the temperature dependence of the iron-57 Mössbauer spectra of $Fe(py)_2Cl_2$ and suggest the presence of two structural phases for this compound, with a transition temperature of 235 K. In the same work, X-ray powder results show that the high temperature form of $Fe(py)_2Cl_2$ is isomorphous to $\alpha$-$Co(py)_2Cl_2$, the high temperature polymeric phase of $Co(py)_2Cl_2$. Both these Fe and $\alpha$-Co compounds are characterized by symmetric




bridging units, local symmetry $D_{4h}$ for the $MN_2Cl_4$ chromophore. Long postulated that at low temperatures (<235 K) the symmetric bridge undergoes a molecular displacement to give an asymmetric bridging framework similar to that found in $Cu(py)_2Cl_2$ at room temperature in an X-ray study by Dunitz [1]. The local symmetry of the ligand metal chromophore in the asymmetric phase is $D_{2h}$. In subsequent Fe-57 Mössbauer dilution studies on $Mn(py)_2Cl_2$ and $Ni(py)_2Cl_2$.




Yoshihashi [7] suggests that the Mn analogue undergoes a structural phase transitiou at 230 K, while for Ni it occurs at 5 K.

In a recent definitive single crystal X-ray study [8], $Co(py)_2Cl_2$ has been shown to undergo the phase transition from a symmetric bridge, $\alpha$-$Co(py)_2Cl_2$(C2/b), to $\gamma$-$Co(py)_2Cl_2$(P21/n) with an asymmetric bridge at 150 K.

Reiff *et al.* [9] have applied high field Mössbauer spectroscopy to $Fe(py)_2Cl_2$ to determine the sign of the electric field gradient tensor of the two structural forms. In both cases the sign is positive indicating the same $d_{xy}$ orbital ground state. Finally, Sanchez *et al.* [10] determined the temperature dependence of the absorption and emission Mössbauer spectra of $Fe(py)_2Cl_2$ and $^{57}Co(py)_2Cl_2$ respectively and found the $\alpha$ to $\gamma$ transition to be hysteretic.

From a review of the literature, it appears that the only thermal analyses of this series were done by Takeda [2] and Klaaijsen [5]. In both cases the heat capacity was studied in the temperature region of magnetic orrdering, <10 K. A similar calorimetric study can potentially yield additional useful information on the nature of the structural phase change discussed herein. In this letter we report the results of thermal analysis using differential scanning calorimetry on the above series.

## Experimental

The compounds were prepared by essentially the literature methods through reaction of stoichiometric amounts of $MCl_2 \cdot XH_2O$ in 100% ethanol with degassed pyridine. In all cases crystals formed immediately. The resulting precipitates were collected, washed with ethanol, and dried.

The thermal measurements were carried out using a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. The temperature scans were done in two phases, heating from 123 to 300 K and 300 to 700 K. A helium atmosphere was used in the low temperature region whereas nitrogen was used in the higher temperature scans. The heating rate was 40°/min. The sample was prepared by first grinding the material to a fine powder and then encapsulating ~10 mg in an aluminium sample holder. The calorimeter was temperature calibrated with ice, nonane, ether, and 1-octene. The areas of the endotherms were measured using a planimeter and referenced to the heat content of a given area and to the heat of fusion of indium metal. The enthalpy change for the $\gamma \rightarrow \alpha$ transition for $Co(py)_2Cl_2$ was further determined on a Dupont 990 thermal

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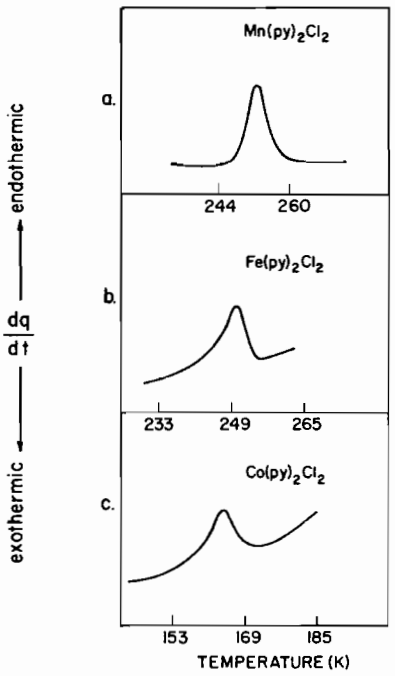


Fig. 1. Endotherms of (a) $MN(py)_2Cl_2$, (b) $Fe(py)_2Cl_2$, and (c) $Co(py)_2Cl_2$.

analyser and gave excellent agreement with the DSC-1B results.

## Results and Discussion

The endotherms of the transitions for Fe, Co and $Mn(py)_2Cl_2$ are displayed in Fig. 1. As can be seen, all show a broad transition. Listed in Table I are the compounds which exhibited transitions in the temperature range 130–300 K, their transition temperatures, and their respective enthalpy values. The latent heats are significantly different, although for the present we see no obvious correlation with metal configuration or orbital and spin ground state. It is not surprising that the $\gamma$ to $\alpha$-transition was not observed in the increasing temperature range 130 → 300 K for $Cu(py)_2Cl_2$ as this compound is essentially the $\gamma$ form at ambient temperatures. Unfortunately, the high temperature scan, 300 → 700 K, for $Cu(py)_2Cl_2$ did not show a transition which could be unequivocably assigned to the $\gamma$ to $\alpha$ structural transformation. In all cases the high temperature scans were difficult to analyze due to the presence of a combination of complex thermal transitions attributable to depolymerization, melting and subsequent removal of the pyridines, and high temperature structural phase transitions.

TABLE I. Thermal Data.

| Compound | Transition Temperature (K) | ΔH (cal/mol) |
|---|---|---|
| $Mn(py)_2Cl_2$ | 245 | 78 |
| $Fe(py)_2Cl_2$ | 236 | 54 |
| $Co(py)_2Cl_2$ | 154 | 14 |

The phase transitions are hysteretic, approximately 17 for $Co(py)_2Cl_2$, 12 for $Fe(py)_2Cl_2$, and 4 K for $Mn(py)_2Cl_2$. The observation of latent heats clearly indicates that these transitions are first order in nature.

The results obtained in this work agree well with previous studies, *i.e.*, the temperature dependence of the transition for $Fe(py)_2Cl_2$ using Mössbauer ($Fe^{57}$-absorbance) spectroscopy [4, 10] and for $Co(py)_2Cl_2$ using X-ray crystallographic [6], susceptibility studies and Mössbauer spectroscopy ($Co^{57}$-emission) [10]. In the case of $Mn(py)_2Cl_2$, we observed a transition temperature of 245 K, whereas Yoshihashi [7] reports 230 K using Mössbauer spectroscopy.

The structural phase changes observed in this study are reversible and have relatively low enthalpies. The perovskite-like layer compounds, $(C_nH_{2n+1}NH_3)_2MnCl_4$, as shown by Depmeier [12] using calorimetric and x-ray results are similar to the $M(py)_2Cl_2$ compounds in that they also undergo structural phase changes. It is interesting to note that in the perovskite-like compounds, the structural transformations involves a tilting of $MCl_6$ octahedra throughout an entire layer, whereas in $M(py)_2Cl_2$ it is a molecular displacement of $MCl_4N_2$ octahedra along polymeric linear chains, yet the enthalpy values for both systems are of similar magnitude.

We [13] have initiated an iron-57 Mössbauer spectroscopy study of $(CH_3NH_3)_2FeCl_4$ and find that one of its tilting transitions begins at ~270 K, although it does not go to completion for temperatures as low as 100 K even after long (several days) periods of thermal equilibration. Unlike the pyridine complexes of the present study, sample pulverization apparently introduced defects such that no transition is observed for a finely ground polycrystalline specimen of methylammonium complex.

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