

Title of the Project: PHYSICO CHEMICAL PROPERTIES OF 1<sup>ST</sup> ROW TRANSITION METAL COMPLEXES: EMPHASIS ON MOLECULAR MAGNETISM  
Cost 2,00,000/- ( UGC: MRP(S)-0592/13-14/KLCA009/UGC-SWRO 28<sup>th</sup> March 2014)  
Principal Investigator Dr. Padmakumar K, Dept. of Chemistry, Govt. Victoria College, Palakkad

### Summary of the Project

Quite a few ferricenium systems are studied using Mossbauer spectroscopy. Most of them are those containing decamethylferrocenium cations with paramagnetic anions like tetracyanoethylene (TCNE<sup>-</sup>), tetracyanoquinodimethane (TCNQ<sup>-</sup>) etc. These anions provide an internal dipolar field leading to slow paramagnetic relaxation along with three dimensional ordering process which gives rise to the Zeeman split pattern in the Mossbauer spectrum.

In the above cases, the anions provide internal magnetic field and produces the split pattern, but they themselves are Mossbauer inactive. In our study, we present a case where both the cation and the anions are Mossbauer active which makes our study unique.

Our first system, [FeCp<sub>2</sub>]<sup>+</sup>[FeBr<sub>4</sub>]<sup>-</sup>, the anion is a S=5/2 system which itself is Mossbauer active center. The temperature dependent <sup>57</sup>Fe Mossbauer spectrum of [FeCp<sub>2</sub>]<sup>+</sup>[FeBr<sub>4</sub>]<sup>-</sup> in the region 80K to 1.7K. The room temperature spectrum exhibits slightly broadened line which can be resolved to two absorption lines corresponding to two centers. This situation continues up to 13K. ; at which there is a clear cut six line pattern formed from one of the centers. Further cooling down to 2.9K broadens the second singlet line which resolves into a six line pattern at 1.7K.

The complete analysis of Mossbauer spectrum of [FeCp<sub>2</sub>]<sup>+</sup>[FeBr<sub>4</sub>]<sup>-</sup> is shown in table.1. By comparing the isomer shift values with that of already recorded data of ferricenium cation and tetrabromoferrate anion, it is inferred that, the first singlet which resolves to six line pattern at 13K corresponds to [FeBr<sub>4</sub>]<sup>-</sup> (indicated as site 1) and the singlet resolving at 1.9K corresponds to [FeCp<sub>2</sub>]<sup>+</sup> (indicated as site 2). Site 1 contains Fe atom tetrahedrally surrounded by bromine atoms. The isomer shift values ranges from 0.32mm/s to 0.36mm/s in the temperature region 80K to 1.7K. There is a charge transfer from the ferricenium cation to the anion (D<sup>+</sup> to A<sup>-</sup> charge transfer) producing large dipolar field which produces the spectral resolution. The site 2 shows isomer shift values from 0.542 to 0.56mm/s.

The temperature dependence of the internal hyperfine field is attributed to slow paramagnetic relaxation broadening and three dimensional ferromagnetic ordering, a necessary condition for molecular ferromagnetism.

There is yet another explanation for the appearance of the Zeeman split six line pattern at the two different centers at two different temperatures from the point of view of electronic relaxation rates for the two centers.

- A. For  $[\text{FeBr}_4]^-$ , D, the zero field splitting parameter is negative. So  $S=\pm 5/2$  state is lowest with  $S=\pm 3/2$  and  $S=\pm 1/2$  as excited states. At room temperature, all these states are populated leading to fast electronic relaxation. But at lower temperatures, only  $S=5/2$  state is populated. The electronic transitions among these are forbidden (the selection rule being  $\Delta S=0, \pm 1$ ) leading to paramagnetic relaxation and the nucleus is able to feel the magnetic field. This leads to the six line pattern at temperatures below 14K.
- B. For  $[\text{FeCp}_2]^+$ , the net spin is  $S=1/2$ . So  $S=\pm 1/2$  is the only electronic state. Relaxation among these two is much faster leading to the appearance of six line pattern only at very low temperatures of the order of 1.7K.

These support the fact that both the sub lattices undergo a cooperative interaction which is ferromagnetic in nature.

For the second system studied  $[\text{FeCp}_2]^+[\text{FeI}_4]^-$ , we didn't see any magnetic hyperfine interaction down to 1.7K. This could be due to the dipolar broadening caused by the heavy Iodine atom, which completely mask the magnetic field. May be, if the temperature is lowered below 1K, there is a possibility of resolution to a six line pattern. The spectrum and Mossbauer parameters of  $[\text{FeCp}_2]^+[\text{FeI}_4]^-$  are shown in the report.

The  $[\text{FeCp}_2]^+[\text{FeI}_4]^-$  exhibits magnetism at very low temperature and  $[\text{FeCp}_2]^+[\text{FeBr}_4]^-$ , at temperature fairly greater than the former. So it is reasonable to expect that, the chloro and fluoro derivatives if prepared, may present even more interesting cases. They may exhibit this ferromagnetic ordering at even higher temperature than these.

From comparative study of the IR spectrum of these compounds with that of ferrocene it can be concluded that the ferrocenium part is remaining intact. This is indicated by the close similarity of the spectra. The major peaks obtained for the compound  $[\text{FeCp}_2]^+[\text{FeBr}_4]^-$  are at around  $3090\text{cm}^{-1}$  ( $\alpha$  C-H stretching),  $1420\text{cm}^{-1}$  (C-C stretching),  $1010\text{cm}^{-1}$  ( $\beta$  C-H stretching) and  $855\text{cm}^{-1}$  ( $\gamma$  C-H stretching). For the iodo compound,  $[\text{FeCp}_2]^+[\text{FeI}_4]^-$  there is only slight variation in the position of the peaks. The major peaks obtained are  $3078\text{cm}^{-1}$  ( $\alpha$  C-H stretching),  $1420\text{cm}^{-1}$  (C-C stretching),  $1115\text{cm}^{-1}$  ( $\beta$  C-H stretching) and  $1011\text{cm}^{-1}$  ( $\gamma$  C-H stretching). These values are very close to that of ferrocene. So it can be concluded that there is no any structural changes to the ferricenium part in these compounds. That is, ferrocene retains its structural identity. The IR spectrum of ferrocene,  $[\text{FeCp}_2]^+[\text{FeBr}_4]^-$  and  $[\text{FeCp}_2]^+[\text{FeI}_4]^-$  are shown in fig(4), (5) and (6) respectively.

The low temperature magnetic ordering if made to happen at room temperature, it will be a giant leap in this field. For this, research based on ferricenium systems may help a lot. Proper substitution on the cyclopentadienyl ring and incorporation of suitable anionic complex may further improve their performance. This project work and results are just a beginning but truly an inspiration for further research in this field