

# Magnetic susceptibility of (para-Br-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub> and (meta-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>2</sub>Br<sub>2</sub>

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# Magnetic susceptibility of (*para*-Br-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub> and (*meta*-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>2</sub>Br<sub>2</sub>

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**Abstract.** The magnetic susceptibility of the two compounds (*para*-Br-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub> and (*meta*-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>2</sub>Br<sub>2</sub> is measured in the temperature range of 77–300 K. The compounds have the layered structure of K<sub>2</sub>NiF<sub>4</sub> type. The compounds show transition to weak ferromagnetic ordering at 94 K and 98 K respectively. Short range ordering is observed at ≈140 K and 190 K for the two compounds respectively. This short range ordering indicates the two-dimensional antiferromagnetic character of these compounds.

## Introduction

Recently, increased theoretical and experimental attention has been paid to the study of low dimensional magnetic systems. Two series of compounds of the general formula (C<sub>n</sub>H<sub>2n+1</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub> and (C<sub>n</sub>H<sub>2n</sub>)(NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub> where  $n = 1, 2, 3, \dots$  in the first series and  $n = 2, 3, 4, \dots$  in the second series, have been studied in our laboratory [1–7]. The compounds of the two series are members of the family of compounds having K<sub>2</sub>NiF<sub>4</sub> structure.

In the previous work [8] we have prepared and studied the compounds (*para*-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4-y</sub>Br<sub>y</sub>, where  $y = 0, 2$  and  $3$ . The compounds (*para*-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>MCl<sub>4</sub>, where  $M = \text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  were first prepared and studied by Blake [9, 10]. It is very interesting to study the effect of replacement of Cl by Br in the *para* position and also the effect of changing Cl from *para* to *meta* position in the benzene ring. This is the object of the present work.

## Experimental

The compounds were prepared by using the analar salts of aniline ((*para*-Br-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>Cl) and (*meta*-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>Br)) with FeCl<sub>2</sub>·4H<sub>2</sub>O in a molar ratio of 2:1 for each compound. All preparations were performed in a dry nitrogen filled glove box and the ethanol used as solvent was refluxed under nitrogen gas. The hot solutions of FeCl<sub>2</sub>·4H<sub>2</sub>O and of the aniliniumchloride or anilinium bromide in ethanol were mixed and the resulting solution is evaporated and allowed to cool to obtain the compound in the powder form. The samples were finally ground under nitrogen atmosphere. The magnetic susceptibility measurements were carried out using the conventional Gouy method for powdered samples.

The diamagnetic correction was carried out by measuring the magnetic susceptibility of the isomorphous zinc compounds. Chemical analysis of compounds have been carried out before collecting the data and reported in Table 1.

Table 1  
Chemical analysis

Compound	C%		H%		N%	
	found	cal.	found	cal.	found	cal.
( <i>para</i> -Br-C <sub>6</sub> H <sub>4</sub> NH <sub>3</sub> ) <sub>2</sub> FeCl <sub>4</sub>	26.60	26.49	2.81	2.58	5.20	5.15
( <i>meta</i> -Cl-C <sub>6</sub> H <sub>4</sub> NH <sub>3</sub> ) <sub>2</sub> FeCl <sub>2</sub> Br <sub>2</sub>	26.52	26.49	2.69	2.58	5.28	5.15
	Cl%		Br%		Fe%	
	found	cal.	found	cal.	found	cal.
	26.05	26.12	29.42	29.39	10.25	10.27
	26.09	26.12	29.45	29.39	10.30	10.27

## Results and Discussion:

Figure 1(a) shows the variation of the corrected molar magnetic susceptibility with temperature for the compound (*para*-Br-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub>. Variation of the peak height with the magnetic field strength is observed as in Fig. 1(b). Such behaviour reflects the presence of ferromagnetic moments that tend to saturate

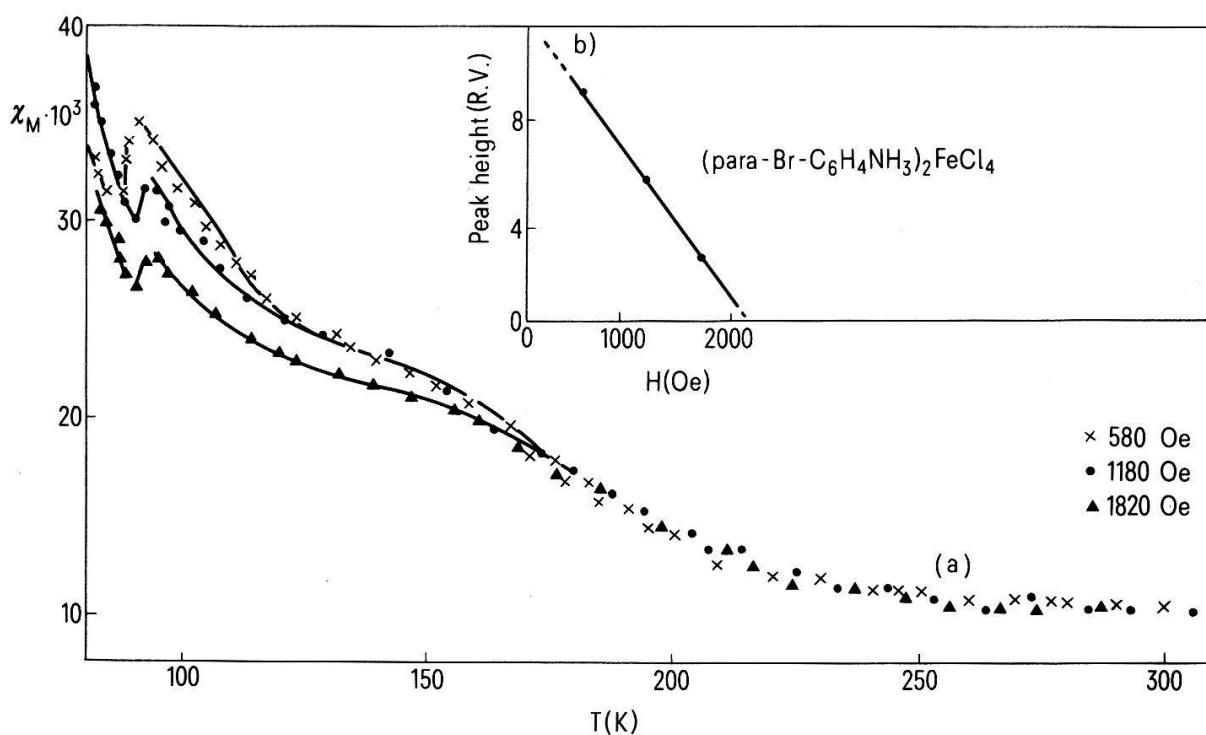


Figure 1  
(a) The variation of the corrected molar magnetic susceptibility with temperature. (b) The variation of the peak height (in relative values) with magnetic field strength, for the compound (*para*-Br-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>FeCl<sub>4</sub>.

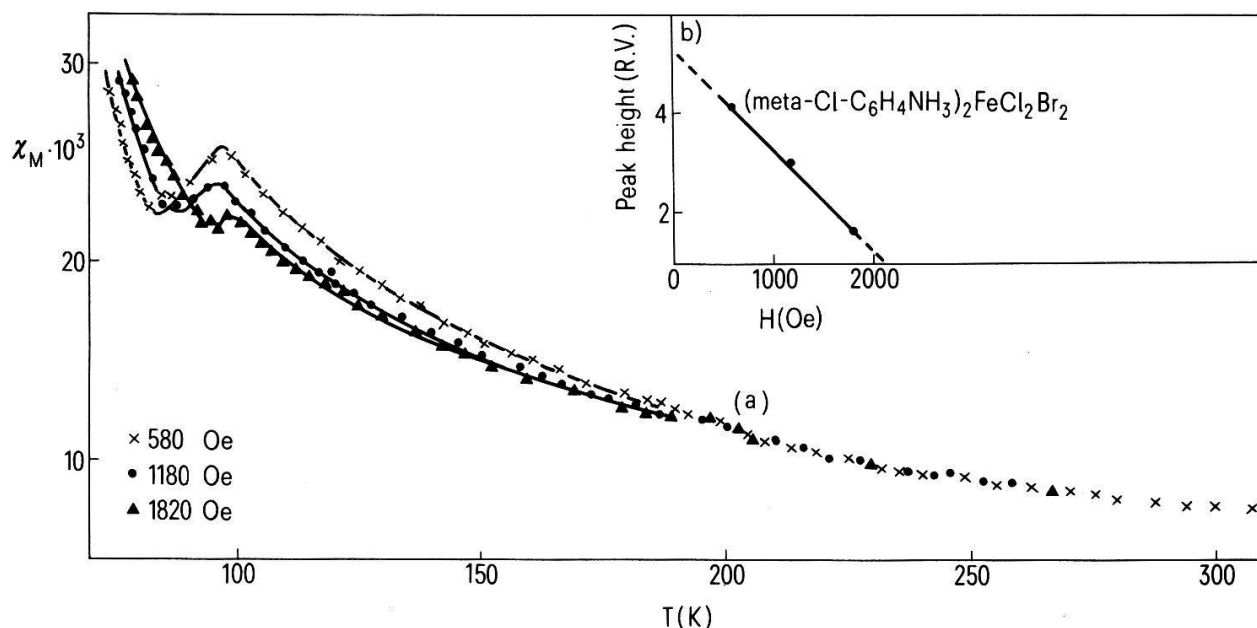


Figure 2

(a) The variation of the corrected molar magnetic susceptibility with temperature. (b) The variation of the peak height (in relative values) with the magnetic field strength, for the compound  $(\text{meta-Cl-C}_6\text{H}_4\text{NH}_3)_2\text{FeCl}_2\text{Br}_2$ .

with increasing magnetic field. From the figure it is clear that decreasing temperature results in an increase in the magnetic susceptibility. At a temperature of  $\approx 94$  K a sharp peak has appeared which is accompanied by a magnetic transition to long range order, characterizing to this type of spin canting antiferromagnet [4].

Figure (2) shows the dependence of molar magnetic susceptibility on temperature for the compound  $(\text{meta-Cl-C}_6\text{H}_4\text{NH}_3)_2\text{FeCl}_2\text{Br}_2$ . The behaviour of this compound is quite similar to that of  $(\text{para-Br-C}_6\text{H}_4\text{NH}_3)_2\text{FeCl}_4$ , except a little shift of about 4 degrees in the transition temperature to higher value ( $T_N \approx 98$  K). Both compounds obey the Curie-Weiss law with magnetic constant as reported in Table 2.

Table 2

The reported are the Curie-Weiss constant  $\theta$ , the Curie constant  $C$  and the effective magnetic moment  $\mu_{\text{eff}}$

Compound	$\theta$	$C$	$\mu_{\text{eff}}$
$(\text{para-Br-C}_6\text{H}_4\text{NH}_3)_2\text{FeCl}_4$	-190	4.42	5.94
$(\text{meta-Cl-C}_6\text{H}_4\text{NH}_3)_2\text{FeCl}_2\text{Br}_2$	-40	3.06	4.95

From the two figures 1 and 2 and at still lower temperatures than the transition point, weak ferromagnetism appears, causing the susceptibility to increase sharply and becomes field dependent [10].

To account for the behaviour of the magnetic susceptibility of the compounds under investigation, it is better to discuss the general feature of the anilinium

compounds. It was found by Blake [10] that the compounds of the general formula  $A_2MCl_4$ , where  $A^+$  is a para-substituted anilinium ion  $(x-C_6H_4NH_3)^+$  and  $M$  is the divalent metal ions  $Mn^{2+}$  or  $Fe^{2+}$ , have the layer structure of the  $K_2NiF_4$  type. The layer separation  $C/2$  of these compounds varying from 15.8 to 23.5 Å depending upon the substituent  $x$  (F, Br or  $n$ -butyl).

The general behaviour of the magnetic susceptibility of the two compounds (*para*-Br- $C_6H_4NH_3$ ) $_2FeCl_4$  and (*meta*-Cl- $C_6H_4NH_3$ ) $_2FeCl_2Br_2$  is quite similar to the two compounds (*para*-Cl- $C_6H_4NH_3$ ) $_2FeCl_4$  and (*para*-Cl- $C_6H_4NH_3$ ) $_2FeCl_2Br_2$  except a reduction of the peaks height as shown in Fig. 3. Furthermore the values of  $T_N$  are not changed by varying the magnetic field strength as it is clear from figures 1 and 2.

It seems to us that the reduction of the peak height on replacing Br instead of Cl in the para position may be due to the larger size of Br which will take the out of plane position. This results in a smaller canting than the case of Cl, which in turn leads to the observable reduction in the peak height. It is clear that this reduction in the peak height is more pronounced as the number of  $Br^-$  ions increases. This may also be due to the change in the crystal field upon replacing  $Cl^-$  by  $Br^-$  ions as well as the different electronic configuration. In other words,

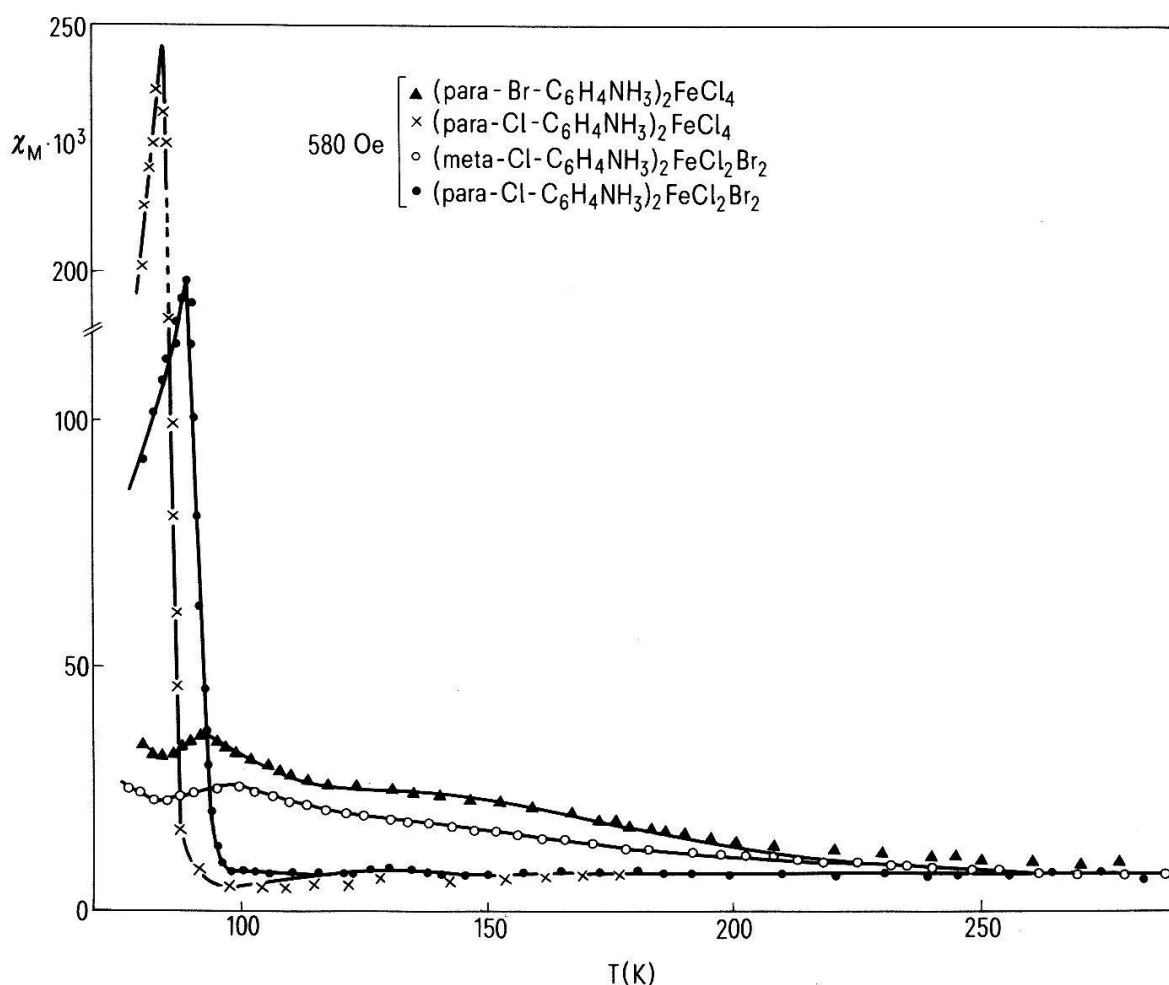


Figure 3

Comparison of the molar magnetic susceptibility of the two compounds ((*para*-Br- $C_6H_4NH_3$ ) $_2FeCl_4$  and (*meta*-Cl- $C_6H_4NH_3$ ) $_2FeCl_2Br_2$ ) with the two compounds ((*para*-Cl- $C_6H_4NH_3$ ) $_2FeCl_4$  and (*para*-Cl- $C_6H_4NH_3$ ) $_2FeCl_2Br_2$ ).

the  $\text{Br}^-$  will affect the geometry around  $\text{Fe}^{2+}$  such that the  $\text{FeCl}_4\text{Br}_2$  are less tilted than  $\text{FeCl}_6$  octahedra.

In conclusion, one can say that in the anilinium compounds containing  $\text{Fe}^{2+}$  ions the peak height is greatly affected and also the geometry around  $\text{Fe}^{2+}$  whether the  $\text{Br}^-$  ions are inserted in the  $x$ -substituent or replaced in the  $\text{Cl}_4$  position.

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