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MAGNETIC SUSCEPTIBILITY OF $(IPA)_2FeCl_4$, $(IBuA)_2FeCl_4$ AND $(IPA)_2CuCl_4$ *

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ABSTRACT

The magnetic susceptibility of $(IPA)_2FeCl_4$, $(IBuA)_2FeCl_4$ and $(IPA)_2CuCl_4$, where $IPA = (CH_3)_2CHNH_3^+$ and $IBuA = (CH_3)_2CHCH_2NH_3^+$, were measured in the temperature range from 80 K up to a temperature near the melting points of the samples. The results obtained were interpreted in terms of a canted two-dimensional antiferromagnet. The variation of the magnetic susceptibility with the change in the composition was also discussed.

INTRODUCTION

The study of magnetic properties in quasi-two-dimensional systems has recently been a subject of great interest [1–5]. This interest grew out of the study of low dimensional materials. Frequently, the theoretical models used to describe three-dimensional systems are intractable but are solvable in lower dimensions. The study of low dimensional materials will lead to a greater understanding of many phenomena such as the physics of magnetism, conductivity, etc.

Investigations by several workers of the two-dimensional-sheet C_2MCl_4 compounds reveal several interesting properties. C equals a monovalent cation such as the alkylammonium ion and M can be Cu(II), Fe(II) or Mn(II). These compounds exhibit interesting electrical and magnetic properties which are dependent upon the space between the sheets. This space increases with increasing length of the cation.

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* IPA, isopropylammonium ion; IBuA, isobutylammonium ion.

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The purpose of this paper is to report the magnetic study of $(IPA)_2FeCl_4$, $(IBuA)_2FeCl_4$ and $(IPA)_2CuCl_4$, where IPA = isopropylammonium ion and IBuA = isobutylammonium ion. The study of the effect of the change of the composition on the magnetic properties is one of the aims of the research.

The structure of these compounds is composed of MCl_6 octahedra (M = Cu or Fe) extending in an infinite two-dimensional network, the alkylammonium groups bonding these layers together via van der Waal's forces.

EXPERIMENTAL

The complexes were prepared by mixing stoichiometric amounts of the appropriate amine hydrochloride and either $CuCl_2 \cdot 2H_2O$ or $FeCl_2 \cdot 4H_2O$ in aqueous alcoholic solution [6], in a nitrogen atmosphere. The precipitated plate-like crystals were obtained upon cooling. The samples were washed with a mixture of ethanol and ether, and then dried under vacuum.

The grinding and mounting of the samples were carried out in a dry glove box under purified nitrogen gas. The sample tubes were completely sealed after mounting. The magnetic susceptibility of the powderd samples was measured using the conventional Gouy method. Diamagnetic correction was carried out by measuring the magnetic susceptibility of the isomorphous cadmium compounds.

RESULTS AND DISCUSSION

Figure 1 shows the relation between the corrected molar magnetic susceptibility, χ_M, and the temperature for $(IPA)_2FeCl_4$ and $(IBuA)_2FeCl_4$. From the figure, it is clear that the χ_M value of $(IPA)_2FeCl_4$ is about four times that of $(IBuA)_2FeCl_4$ at liquid nitrogen temperature. Both compounds were found to obey the Curie–Weiss law. The magnetic constants were calculated from the plots of $1/\chi_M$ versus T and are given in Table 1. The plot of χ_M versus T for $(IPA)_2FeCl_4$, Fig. 1, shows a broad peak ranging from 170 to 220 K. This deviation from the Curie–Weiss law has also been observed in the same temperature range by plotting $\chi_M T$ versus T, Fig. 2. A deviation from the Curie–Weiss law is also observed for $(IBuA)_2FeCl_4$ in the plot of χ_M T versus T at a temperature of 170 K, Fig. 2. Generally, the negative θ values obtained for $(IPA)_2FeCl_4$ and $(IBuA)_2FeCl_4$ indicate that both can be considered as antiferromagnetic compounds.

It is well-known that on replacing one transition metal ion by another in the same chelated compounds, the magnetic interaction and the symmetry of the crystal can each be changed. Accordingly, the magnetic properties of

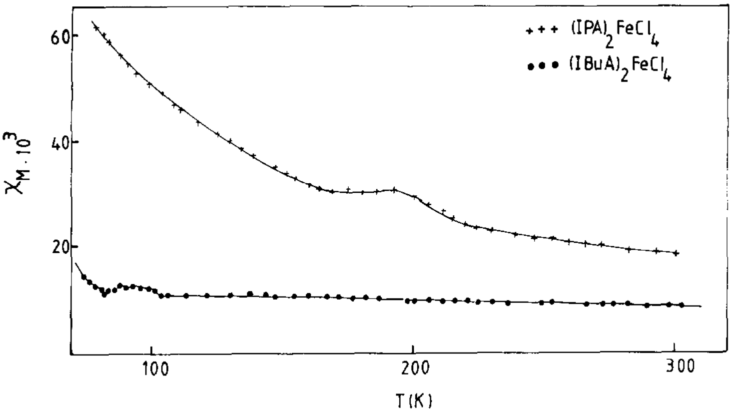

Fig. 1. Relation between the corrected molar magnetic susceptibility χ_M and the temperature for $(IPA)_2FeCl_4$ and $(IBuA)_2FeCl_4$.

TABLE 1

Magnetic constants of $(IPA)_2FeCl_4$, $(IBuA)_2FeCl_4$ and $(IPA)_2CuCl_4$

Compound	Curie–Weiss constant, θ (K)	Curie constant, C	Eff. mag. moment, μ (B.M.)
$(IPA)_2FeCl_4$	−14	4.6	6.06
$(IBuA)_2FeCl_4$	−30	4.1	5.77
$(IPA)_2CuCl_4$	20	0.47	1.95

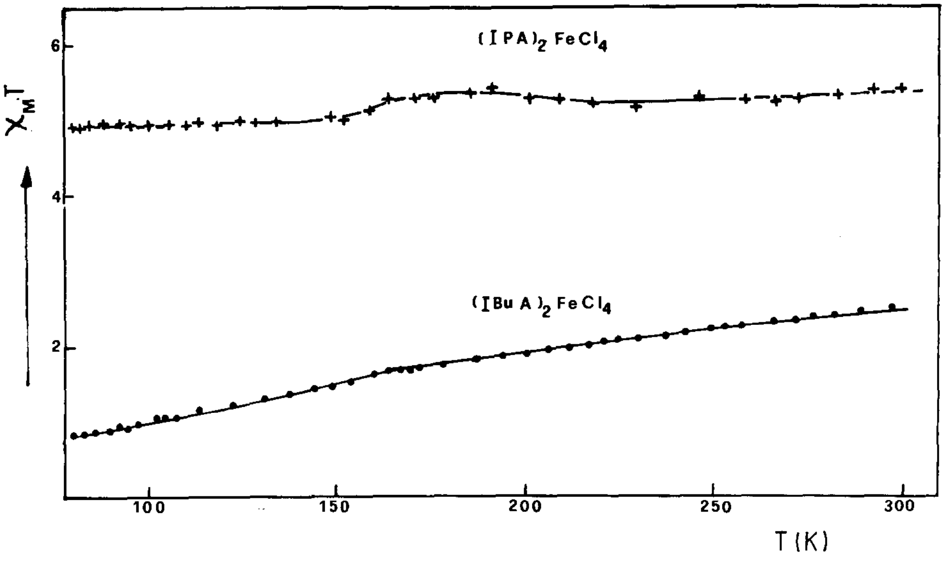

Fig. 2. Relation between $\chi_M T$ and the temperature for $(IPA)_2FeCl_4$ and $(IBuA)_2FeCl_4$.

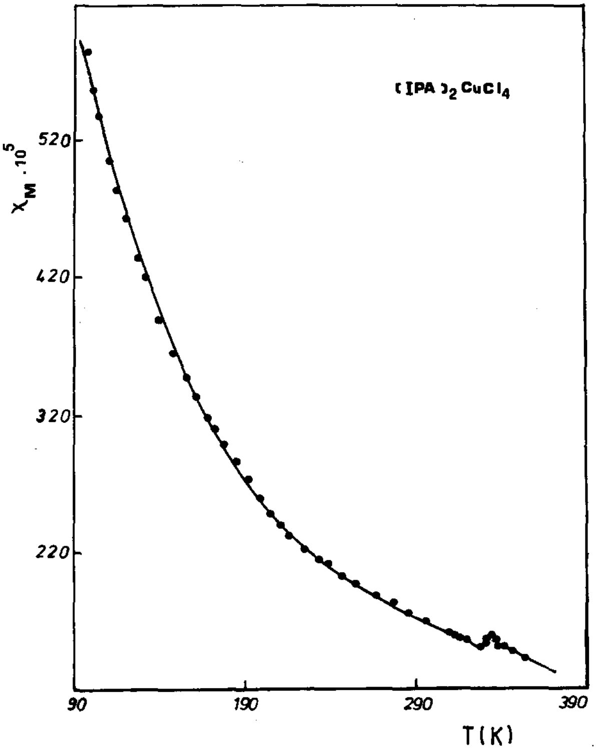

Fig. 3. Relation between the corrected molar magnetic susceptibility χ_M and the temperature for $(IPA)_2CuCl_4$.

$(IPA)_2CuCl_4$ have been studied in order to investigate the change occurring in the magnetic properties by the replacement of Fe^{2+} ion with Cu^{2+} ion in the same chelated compound. A previous study on $(IPA)_2CuCl_4$ showed that the compound has a thermochromic behaviour [7] (a reversible colour change with temperature). Remy and Laves [7] reported that on cooling the greenish-yellow crystals of $(IPA)_2CuCl_4$ from room temperature, a first-order phase transition with a colour change was observed at about 210 K. The crystal structure of the greenish-yellow crystal (high temperature phase) was found to have [8] a triclinic space group P_1 with lattice constants $a = 7.245$ Å, $b = 14.588$ Å and $c = 21.738$ Å. The structure contains discrete $[CuCl_4]^{2-}$ ions which pack together to form a pair of crystallographically independent copper–chlorine ribbons extending parallel to the *a*-axis. These ribbons are held together by hydrogen bonds formed between $[CuCl_4]^{2-}$ ions and the isopropyl ammonium ions. Also, it has been reported [8] that one third of the $[CuCl_4]^{2-}$ ions has a square planar geometry, a second third has a slight tetrahedral distortion, while the last third has a larger tetrahedral distortion.

Figure 3 shows the relation between χ_M and T for $(IPA)_2CuCl_4$. The magnetic constants of the compound were calculated and are given in Table

1. The positive θ value obtained indicates the ferromagnetic character of $(IPA)_2CuCl_4$. This result shows that the replacement of Fe^{2+} in $(IPA)_2CuCl_4$ by Cu^{2+} led to a change in the magnetic character in the layers of the chelated compound from antiferromagnetic to ferromagnetic. However, these two compounds of Fe^{2+} and Cu^{2+} have almost similar features in that there are $[MCl_4]^{2-}$ ions ($M = Cu^{2+}$ or Fe^{2+}) and hydrogen bonding between the $[MCl_4]^{2-}$ ions and the isopropylammonium ions. The ferromagnetic character has disappeared from the Fe^{2+} compounds because the spins are aligned antiferromagnetically in the planes, while the planes are coupled ferromagnetically. Using this simple fact, the three-dimensional antiferromagnetic lattice obtained becomes an approximately magnetic layer with increasing space between the layers of the compounds. In other words, the antiferromagnetic character of the Fe^{2+} compound can be explained by the shift in the neighbouring planes by the values of $a/2$ and $b/2$ with respect to each other. Therefore, in the antiferromagnetic planes of the Fe^{2+} compound, the metal ions in the centre of the square layers, which have an equal number of neighbours with spin up as well as spin down, will not interact with each other in the neighbouring planes. Thus, the magnetic interactions between the central metal ions in the third direction (c) take place between the next-neighbouring layers. An interplanar super-exchange interaction also occurs via the four intervening anions, and it may be expected to be $\sim 10^{-6}$ of the intralayer exchange interaction. Finally, one can consider that the weak ferromagnetic moment may be due to canting of the antiferromagnetic sublattices occurring along the c-axis.

REFERENCES

1 G.F. Needham, R.D. Willett and H.F. Franzen, J. Phys. Chem., 88 (1984) 674.
2 K. Gesi, J. Phys. Soc. Jpn. 51 (1982) 203.
3 C. Socías, M.A. Arriandiaga, M.J. Tello, J. Fernândez and P. Gili, Phys. Status Solidi A: 57 (1980) 405.
4 V. Busico and M. Vacatello, Gazz. Chim. Ital., 111 (1981) 13.
5 G.F. Needham and R.D. Willett, J. Phys. Chem., 85 (1981) 3385.
6 R.D. Willett and C. Chow, Acta Crystallogr., B30 (1974) 207.
7 H. Remy and G. Laves, Ber. Dtsch. Chem. Ges., B66 (1933) 401.
8 N.D. Anderson and R.D. Willett, Inorg. Chim. Acta, 8 (1974) 167.