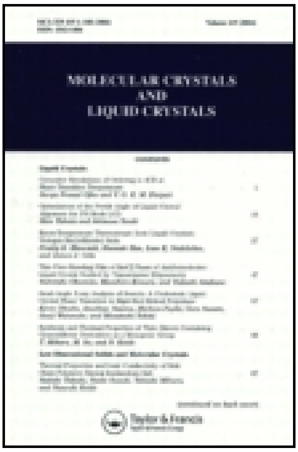

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Magnetism in Binuclear Compounds MCu[(obbz).nH_2O with M = Mn or Co

S. A. Chavan [a] , J. V. Yakhmi [a] & I. K. Gopalakrishnan [a]

[a] Chemistry Division, Bhabha Atomic Research Centre, Bombay, 400 085, India

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MAGNETISM IN BINUCLEAR COMPOUNDS MCu[(obbz)].nH_2O with M = Mn or Co

S.A. CHAVAN, J.V. YAKHMI and I.K. GOPALAKRISHNAN
Chemistry Division, Bhabha Atomic Research Centre
Bombay 400 085, India

Abstract The antiferromagnetic (T_N = 2.3 K) compound MnCu(obbz).5H_2O [obbz=oxamido- bisbenzoato] was synthesized by Nakatani et al[1]. It was reported to yield, upon dehydration, a ferromagnetic compound MnCu(obbz).1H_2O with T_c = 14 K. The exact crystal structure of both these MnCu-based compounds is not known. The ferromagnetic ordering, however, is suggested to occur when four non-coordinated water molecules leave causing a re-adjustment of the relative positions of 1D ferrimagnetic chains comprising Mn(II) and Cu(II) ions. We report on the ac-susceptibility (χ_{ac}), dc magnetization (VSM) and TG data on MCu(obbz).nH_2O (M=Mn or Co). For vacuum dehydrated MnCu-compound, a large divergence in χ_{ac}(T) data is observed. FC and ZFC magnetization data and M(H) loops confirm the ferromagnetism with a saturation magnetization of 480 G at 4.5 K. TG data taken on the precursor MnCu(obbz).nH_2O between R.T. and 130° C, however, indicates that 'n' cannot be specified unequivocally for the ferromagnetic compound. A sharp peak is obtained in χ_{ac} at 27 K for one of the CoCu(obbz).nH_2O samples indicating magnetic ordering.

INTRODUCTION

With a view to design novel molecular magnets, Kahn's group has, during the past few years, devised an approach to synthesize ordered 1D ferrimagnetic bimetallic chains and arrange them in a 3D crystallographic lattice so as to achieve net ferromagnetic behaviour[1-7]. A typical example of such a bimetallic chain is MnCu(obbz).nH_2O with an antiferromagnetic interaction between the adjacent local spins S_{Mn} = 5/2 and S_{Cu} = 1/2 separated by oxamido and carboxylato bridging groups which transmit the magnetic effects. When these ferrimagnetic chains are assembled within the crystal lattice, interchain interactions take place, giving rise to the onset of magnetic order. The compound MnCu(obbz).5H_2O was shown to exhibit the typical behaviour of a 1D ferrimagnet with a minimum in the $\chi_M T$ vs T plot at 44 K and a sharp maximum at 2.3 K indicating a three-dimensional antiferromagnetic ordering. Vacuum dehydration of this compound at room temperature yielded a ferromagnetic compound MnCu(obbz).1H_2O. The $\chi_M T$ vs T plot showed a sudden divergence in the region of the critical temperature T_C = 14 K, and a spontaneous magnetization below T_C[1].

The crystal structures of MnCu(obbz).5H_2O and MnCu(obbz).1H_2O have not been determined so far due to lack of single cyrstals. The related compound NiCu(obbz).6H_2O crystallizes in the monoclinic system (with space group $P2_1/n$) and consists of isolated heterodinuclear units with Ni(II) and Cu(II) ions bridged by an oxamido group[1]. However, NiCu(obbz).6H_2O is not isomorphous to either of the two MnCu-based compounds. The XANES and EXAFS spectra at both Mn and Cu edges in the case of MnCu-based compounds were suggestive of a basic structure of alternating bimetallic Mn(II) and Cu(II) spin carriers with oxamido and carboxylato groups providing the interaction pathways[1]. In particular, the geometry around Mn(II) ion was shown to be octahedral in both the cases. In the case of the monohydrate MnCu(obbz).1H_2O it was assumed that the chains were linked to each other, forming a two- or three-dimensional network. Both, the Mn(II) and Cu(II) coordination spheres remained virtually unchanged upon dehydration and it was proposed that the four water molecules that are lost upon dehydration are not coordinated to the metal ions[1].

Single crystals of one of the precursors of MnCu(obbz).1H_2O, namely MnCu(obbz)$(H_2O)_3$.DMF were grown recently and its structure determined to be orthorhombic, consisting of alternating bimetallic chains running along the 'c' axis, the Mn(II) and Cu(II) ions being alternately bridged by oxamido and carboxylato groups. Following this, Lloret et al[7] proposed a scheme describing the irreversible transformation of this DMF' precursor to the molecular ferromagnet MnCu(obbz).1H_2O, according to which the Mn(II) ion in MnCu(obbz).1H_2O is bound to two free carboxylato oxygen atoms belonging to the adjacent chains just above and below the 'a' axis producing the 2D network. In view of the fact that X-ray powder patterns of MnCu(obbz).5H_2O and MnCu(obbz).1H_2O are almost identical, the dramatic change in the magnetic characteristics of the former compound upon dehydration is intriguing and the role of exact number of water molecules and their location appears to be a crucial factor in this transformation. A schematic representation of the 2D structure of MnCu(obbz).H_2O was proposed presuming that upon dehydration not only the noncoordinated DMF molecule but also two of the three water molecules bound to the Mn(II) ions in MnCu(obbz)$(H_2O)_3$.DMF were lost.

In order to look into the role of water molecules in the structure, we have synthesized MnCu(obbz).nH_2O by the reaction of Mn(II) with the Cu(II) precursor $[Cu(obbz)]^{2-}$ and report our results on ac-susceptibility, dc magnetization (VSM) and TG measurements. An attempt has been made to synthesize CoCu(obbz).nH_2O and the data on it is also reported.

EXPERIMENTAL

MnCu(obbz).nH_2O was synthesized following the procedure described by Nakatani et al[1]. Briefly, the ligand H_4obbz was prepared first by adding 1.3 g of oxalyl chloride to 3.0 g of anthranilic acid dropwise in 150 mL of THF. The precipitate was filtered, washed with THF and dried. The yield was 85%. Next, the mononuclear complex Na_2[Cu(obbz)].4H_2O was prepared by reacting H_4obbz with $Cu(NO_3)_2.H_2O$ in aqueous solution containing NaOH (double-distilled, demineralized water was used in all steps). The yield was 57%. The compound MnCu(obbz).nH_2O was prepared by adding dropwise 20 mL of aqueous solution containing 0.18 g of $Mn(ClO_4)_2.6H_2O$ to 250 mL aqueous solution of Na_2[Cu(obbz)].4H_2O. A pale green precipitate was obtained by filteration and dried over silica gel. Ac-susceptibility data was obtained using an APD close cycle refrigerator in conjunction with a lock-in amplifier. DC magnetization data were taken as a function of temperature and applied field using an E.G. & G, P.A.R. model 4500 Vibrating Sample Magnetometer. A microbalance was used for TG analysis. The Co-analogue was synthesized by reacting cobalt(II) perchlorate hexahydrate with the mononuclear complex Na_2[Cu(obbz)].4H_2O. The compound was subjected to varying conditions of dehydration and magnetic data of the dehydrated phases were taken.

RESULTS AND DISCUSSION

About 100 mg of the precursor MnCu(obbz).5H_2O was dehydrated by evacuation at room temperature. The dehydrated product showed a large divergence in $X_{ac}(T)$ data at ~15 K (Fig 1). Field cooled and zero-field cooled magnetization data as a function of temperature are shown in Fig 2 and are consistent with ferromagnetic behavior below 15 K (T_C). M(H) hysteresis loops were recorded at 4.5 K and 7.0 K. At 4.5 K, the values of saturation magnetization, coercive field (H_C) and remanence were 480 G, 105 G and 7 emu/g, respectively, (Fig 3), which is in agreement with Nakatani et al[1]. However, TG data taken on a number of samples of MnCu(obbz).nH_2O is not consistent with the loss of exactly four water molecules of water, as proposed earlier[1]. For instance, TG data taken on samples from three different lots of MnCu(obbz).nH_2O yielded different values for the percentage weight loss between room temperature and 130° C. Three different samples A, B, C weighing 50 mg each when heated in static air environment from R.T. up to 130° C showed losses in weight equivalent to 8.5, 4.4 and 8.5 mg, respectively, which corresponds to a loss of nearly 5.9, 3.0 and 5.9 H_2O molecules. The weight loss continued to occur gradually upon heating until 120° - 130° C, with no steps in TG data. Above 130° C, however, only very small amount of water was lost and the compound began to decompose at 280° C.

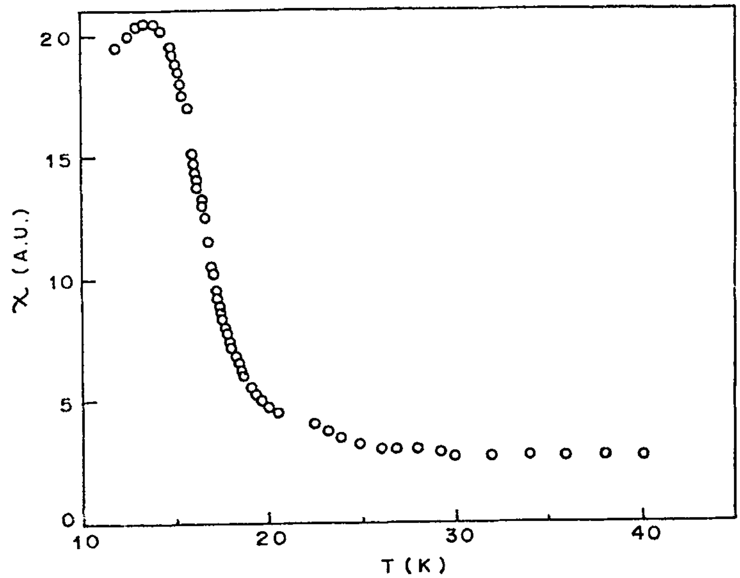

Fig 1 Ac susceptibility data on MnCu(obbz).nH_2O after dehydration

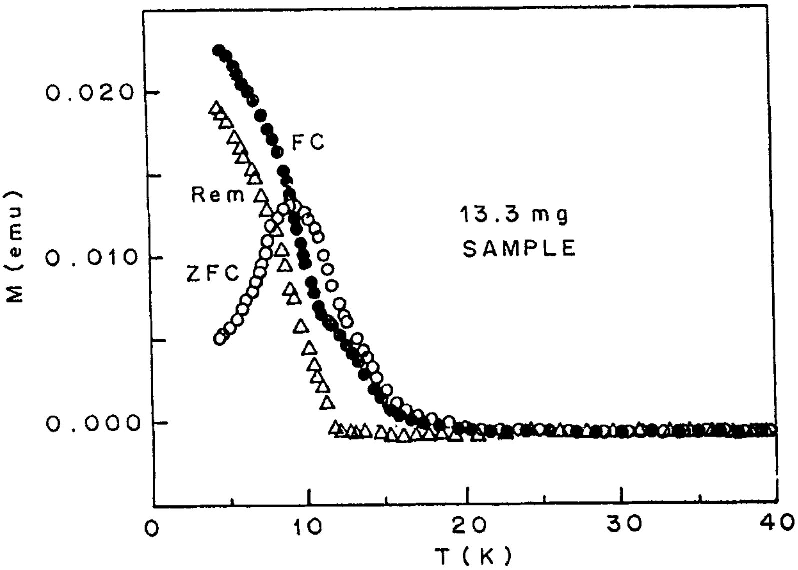

Fig 2 DC magnetization (VSM) data on 13.3 mg sample of MnCu(obbz).nH_2O after dehydration

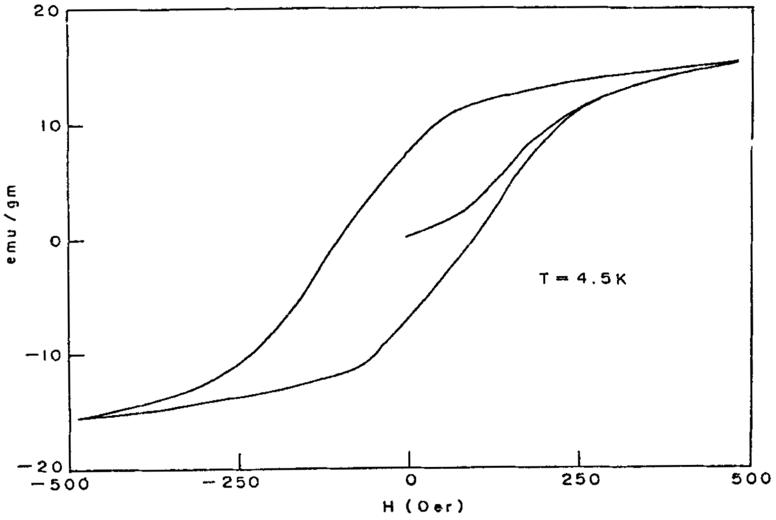

Fig 3 M(H) data on 13.0 mg sample of MnCu(obbz).nH_2O after dehydration

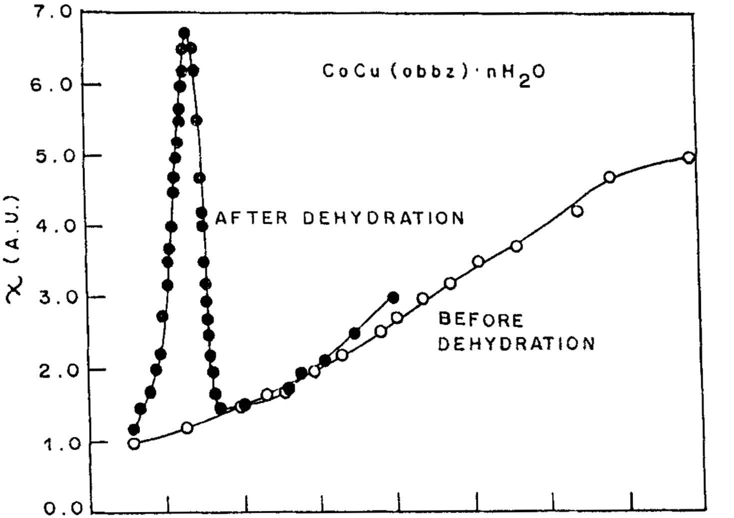

Fig 4 AC susceptibility data on CoCu(obbz).nH_2O

Interestingly, all the three samples A, B and C after dehydration in TG balance by heating at 1° C/min up to 130° C yielded identical χ_{ac} divergence (similar to Fig 1), which suggests that the exact number of water molecules in the ferromagnetically ordered state is not certain. Further studies made on sample B, do indicate, however, that the number of water molecules (or the amount of water in the material) has to be minimal to obtain good magnetic signals. For instance, dc magnetization data M(T) did not show any indication of magnetic ordering in sample B (the sensitivity of our χ_{ac} data is about two orders of magnitude higher than the dc magnetization data) but upon heating it further at 150° C for 1.5 hours, it gave M(H) amd M(T) results identical to samples A or C . As has already been suggested, the non-coordinated water molecules prevent the through-space interaction in the hydrated phase which, therefore, exhibits pronounced 1D character. This happens in spite of the fact that Mn(II) and CuII) ions pack in such a way so as to afford a 3D network. In the dehydrated phase, in the absence of the water molecules, through-space interactions become possible and the system shows deviations from the 1D character.

One of the CoCu(obbz).nH_2O samples when dehydrated at 65° C for six hours yielded a χ_{ac} peak at 27 K (Fig 4). However, the data was not reproducible. χ_{ac} and VSM data taken on samples dehydrated at 150° C/1 h in air do not show any evidence of magnetic ordering. In another case, a few mg of CoCu(obbz).nH_2O was subjected to dehydration for 1 h by giving thermal treatment at 150° C. The VSM data recorded for this sample was featureless. TG measurements were made at 1° C/min on a 10.0 mg sample of CoCu(obbz).nH_2O from room temperature to 160° C. The results show a loss of ~3.6 mg up to 160° C with a step at ~90° C. The question of bulk magnetic ordering in CoCu(obbz).nH_2O, and its nature, can be answered only after further detailed experiments.

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