



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

Magnetic Properties of a [Co(II)Cu(II)] Bimetallic Chain Incorporating the obp = Oxamidobis(N,N'-Propionato) Ligand

A. K. Sra^{a b}, Olivier Kahn^a & J. V. Yakhmi^b

^a Laboratoire des Sciences Moleculaires, ICMCB, UPR 9048, 33608, PESSAC, Cedex, France

^b Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

Version of record first published: 24 Sep 2006

To cite this article: A. K. Sra, Olivier Kahn & J. V. Yakhmi (1999): Magnetic Properties of a [Co(II)Cu(II)] Bimetallic Chain Incorporating the obp = Oxamidobis(N,N'-Propionato) Ligand, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 335:1, 1-9

To link to this article: <http://dx.doi.org/10.1080/10587259908028846>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Magnetic Properties of a [Co(II)Cu(II)] Bimetallic Chain Incorporating the obp = Oxamidobis(*N,N'*-Propionato) Ligand

A.K. SRA^{ab}, OLIVIER KAHN^a and J.V. YAKHMI^b

^a*Laboratoire des Sciences Moléculaires, ICMCB, UPR 9048, 33608 PESSAC Cedex France and* ^b*Chemistry Division, Bhabha Atomic Research Centre, Mumbai – 400 085, India*

Dehydration of single crystals of the non-magnetic molecular compound $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ yields a compound $\text{CoCu}(\text{obp})$ which exhibits long range magnetic order. However, the magnetic transition temperature is rather low (viz. 7 K) and its $M(H)$ plot shows no hysteresis width, which is unusual for a compound derived from Co(II)Cu(II) bimetallic chains. The origin of this magnetic behaviour appears to lie in the absence of the first-order angular momentum of the parent compound $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$.

Keywords: Co(II)Cu(II) bimetallic chains; long range magnetic order

INTRODUCTION

Ever since the first reports on the synthesis of molecular magnets exhibiting spontaneous magnetization below a critical temperature in 1986^[1,2], a large variety of them have been synthesized all of which essentially deal with molecular assemblies containing open-shell units^[3-8]. The spin carriers in these materials could be either the organic radicals themselves, where the unpaired spins reside in the p orbitals, or they could be the transition-metal ions having their unpaired spins in the d orbitals, or, even their hybrids, in which case the unpaired spins exist both in p and d orbitals. These spin carriers need to be incorporated into molecules which are functionalized so that when these molecules assemble in a two-dimensional, or preferably a three-dimensional network, a ferromagnetic interaction may arise between the constituent molecules. A very successful and convenient strategy to synthesize molecular magnets, deals with designing quasi-one-dimensional ferrimagnetic chains (or planar units) and positioning them in a crystal lattice in such

a way as to provide a net ferromagnetic alignment of spins which becomes possible only when the interchain separation is shortest between the opposing unequal spins S_A and S_B ^[6]. Heterobimetallic species, in which two different metal ions are bridged by extended bisbidentate ligands such as oxamato^[9-14], oxamido^[15, 16], oxalato^[17], dithiooxalato^[18] or oximato^[19], in particular allow a variety of spin topologies. These ligands are known to transmit antiferromagnetic spin-spin interactions quite effectively. The first alternating bimetallic chain compound of this type was $MnCu(obp)(H_2O)_3 \cdot H_2O$, where obp stands for oxamidobis(*N,N'*-propionato), which was obtained by the reaction of copper(II) precursor $[Cu(obp)]^{2-}$ with the manganese(II) ion^[20]. Its structure consists of chains with alternation of both the spin carriers, Mn(II) and Cu(II), with the oxamido and carboxylato bridges linking them, and it behaved as a typical one-dimensional ferrimagnet. Subsequently, the synthesis of an isostructural analogue, namely $Co(II)Cu(II)(obp)(H_2O)_3 \cdot H_2O$ was also reported and its structural and magnetic behaviour investigated in detail^[21]. In spite of its typical chain structure, $CoCu(obp)(H_2O)_3 \cdot H_2O$ did not show one-dimensional ferrimagnetic behaviour. The system has been described as consisting of oxamido-bridged $Co(II)Cu(II)$ units which are ferromagnetically coupled through the carboxylato bridge, with the ratio $J(\text{carboxylato})/J(\text{oxamido})$ being very small. In this paper, we report the magnetic behaviour of the dehydrated compound, $CoCu(obp)$, and relate its rather low magnetic transition temperature and absence of magnetic hysteresis width to the peculiar magnetic state of the parent $CoCu(obp)(H_2O)_3 \cdot H_2O$.

EXPERIMENTAL

Single crystals of $CoCu(obp)(H_2O)_3 \cdot H_2O$ were obtained by the method described earlier^[21], viz. slow evaporation at 50°C of a solution containing 2mmol of cobalt (II) perchlorate and 2 mmol of $Na_2[Cu(obp)] \cdot 3.5 H_2O$ dissolved in 40ml of water. C,H,N and elemental analysis was carried out for preliminary analysis of the crystals and it gave satisfactory results, in conformity with the previous data^[21].

Thermogravimetric measurements were carried out with a Setaram TAGDSC apparatus, in the range 20-250°C under a nitrogen atmosphere. Magnetic measurements were performed with a Quantum Design MPMS-5S SQUID

magnetometer, working in both the dc and ac modes, in the temperature range 2-300K. The temperature dependence of the dc magnetic susceptibility was recorded at a magnetic field of 100 Oe, and its field dependence with an applied field upto 50 kOe. The temperature dependence of the ac magnetic susceptibility were recorded at a field alteration frequency of 125 Hz and a drive amplitude of 1 Oe.

RESULTS and DISCUSSION

The crystal structure of $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ has been described in detail by Gulbrandsen et al.^[21]. It crystallizes in the triclinic system, space group $P\bar{1}$ and consists of bimetallic chains in which the Co(II) ion and Cu(II) ion are alternately bridged by oxamido and carboxylato groups. The Cu atom within one chain have long axial bonds to the carboxylato atoms in a centrosymmetrically related chain, thus leading to formation of double chains. The schematic of the structure of a single chain is shown in Fig.1. In particular, the Co atom has somewhat distorted octahedral surroundings with two oxamido oxygen atoms, one carboxylate oxygen atom and one water molecule in equatorial positions and two water molecules in axial positions. The Cu atom is in distorted square-pyramidal surroundings.

Fig. 2 shows the overlay of temperature and percentage change in weight versus time for a sample of $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$. The water loss starts at about 90°C and is fairly sharp initially upon heating upto about 110°C, but rather gradual upon warming further. At temperature of about 200°C, the sample loses all its 4.0 mol of water per CoCu unit. Heating the sample beyond 227°C results in the decomposition of the compound.

The magnetic behaviour of the dehydrated compound $\text{CoCu}(\text{obp})$ are presented in Fig. 3 in the form of a $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature (290 K), the value of $\chi_M T$ is equal to 2.60 emuKmol^{-1} at room temperature, it decreases as T is lowered, presenting a minimum of 1.95 $\text{cm}^3\text{Kmol}^{-1}$ at 60 K, and then increases very abruptly as T is lowered further till it reaches a maximum at 7K below which it falls down quickly.

This indicates the onset of a long range magnetic ordering at about 7 K,

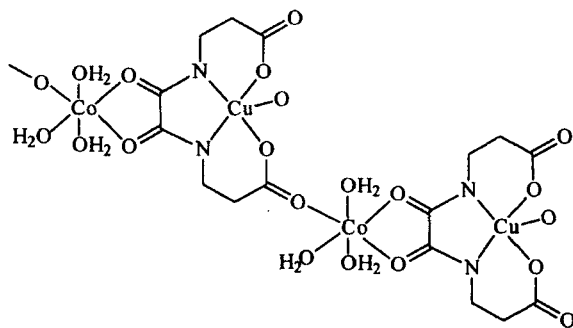


FIGURE 1. Section of single chain in $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$

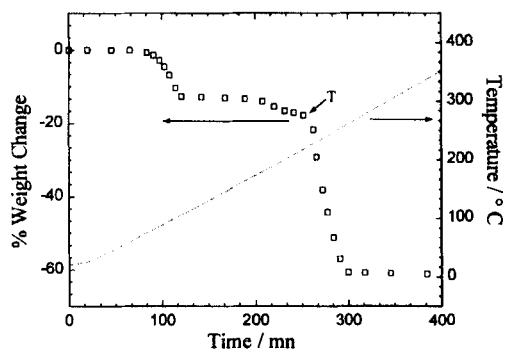


FIGURE 2. Overlay of temperature and percentage weight loss versus time, obtained by a thermogravimetric study of $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$

which is confirmed by the the temperature dependence of the in-phase, χ' , and out-of-phase, χ'' , components of ac magnetic susceptibilities shown in Fig. 4. Both present a peak at 7.5 and 6 K, respectively. A non-zero χ'' value indicated by the rounded peak in the region of the transition temperature, in particular, indicates the presence of net magnetic moments and a ferromagnetic behaviour.

In the paramagnetic state, the magnetic behaviour of the dehydrated compound $\text{CoCu}(\text{obp})$ is in sharp contrast to that of the parent $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$. At 290 K, the $\chi_{\text{M}}T$ for the latter had a value $2.93 \text{ cm}^3\text{Kmol}^{-1}$ which decreased rapidly as the temperature was lowered, tending to zero at absolute zero. This behaviour indicated that the compound $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ has no first-order angular momentum in its ground state, which was against the anticipated behaviour of a minimum in $\chi_{\text{M}}T$ versus T plot, characteristic of the underlying one-dimensional ferrimagnetic chains, as for instance, in the case of $\text{CoCu}(\text{pbaOH})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$, which showed a minimum in $\chi_{\text{M}}T$ versus T plot at 60 K.^[22] The non-magnetic behaviour of $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ was explained to be essentially due to the splitting of the 4T_1 state, caused by the rhombic distortion of the symmetry of the Co(II) ion (with respect to the ideal octahedral symmetry), into three spin-quartet orbital-singlet states, each of them being further split into two Kramers doublets by the spin-orbit coupling. Since only the ground Kramers doublet of Co(II) is thermally populated at low temperatures, the interaction of its effective spin ($=1/2$) with the $S_{\text{Cu}} = 1/2$ Kramers doublet of Cu(II) may give rise to a non-magnetic ($S = 0$) ground pair state.

Dehydration of the compound, resulting in the elimination of all water molecules, obviously leads to an increase in the inter-chain spin-spin interaction among the neighbouring double chains of the compound $\text{CoCu}(\text{obp})$, which is supposed to be through-space as against the intra-chain spin-spin interactions which are through-bond among hetero-bimetallic compounds of this nature^[6]. Removal of water molecules, particularly the three water molecules belonging to the coordination sphere of Co(II), presumably: (i) helps to remove the distortion of the octahedral symmetry of the Co(II) ion, at least partially; and (ii) brings the chains closer to each other in such a way that the shortest separation between metal atoms belonging to the neighbouring chains is Co-Cu, thus ensuring a long range ferromagnetic order at low temperatures.

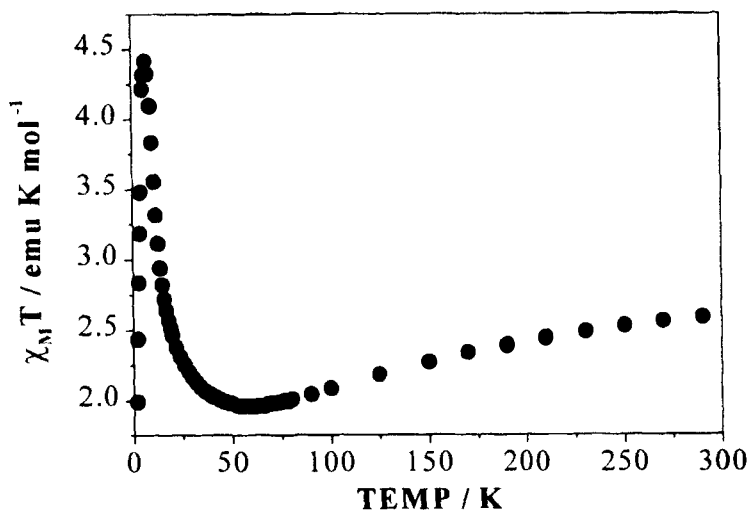


FIGURE 3. Temperature dependence of $\chi_M T$ for CoCu(obp)

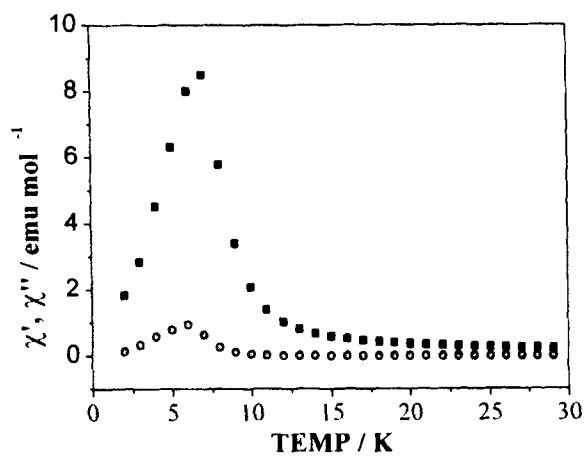


FIGURE 4. Temperature dependence of the in-phase (■) and out-of-phase (○) ac susceptibilities for CoCu(obp).

Field-dependence of the magnetization recorded at 2 K is shown in Fig. 5. The sample did not show any measurable hysteresis width. An applied field of 5 T was not found adequate to obtain saturation magnetization at 2 K, which is expected to be $g_{\text{Co}}S_{\text{Co}} + g_{\text{Cu}}S_{\text{Cu}} = 2 N\beta$, where g_{M} and S_{M} are the local Zeeman factors and local spin, respectively. The magnetization at 50 kOe, however, is only about $1.1 N\beta$ due obviously to the strong anisotropy of the Co(II) ion not allowing it to align along the direction of the applied field.

In contrast with the bimetallic molecular magnets based on Mn(II)Cu(II) ferrimagnetic chains, containing the magnetically isotropic Mn(II) ions, one hopes in principle, to obtain improved values of the magnetic transition temperatures and much higher values of coercivity in the case of Co(II)Cu(II)-based chain compounds in view of the magnetic anisotropy of the Co(II) ion in octahedral surroundings. We have, in fact, recently reported that the Co(II)Cu(II)-based bimetallic chain compounds based on ligands like 'pbaOH'^[22], 'obbz' and 'obze'^[23], and 'pba'^[24], denoting hydroxy-propylenebisoxamato, oxamido-bisbenzoato, oxamido-benzoato-ethanoato and propylenebisoxamato, respectively, do indeed show these features. For instance, the antiferromagnetic compound $\text{CoCu}(\text{pbaOH})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ transforms upon dehydration to a ferromagnetic state with record values of T_{c} (= 38 K) and H_{c} (= 5.66 kOe at 2 K)^[23]. We termed these abovementioned Co(II)Cu(II) molecular magnets as *magnetic molecular sponges* because they show a reversible cross-over: a transition to a long-range magnetically ordered state with spontaneous magnetization under dehydration, and a transformation back to their initial non-magnetic/antiferromagnetic state upon rehydration, and some of them, exhibiting even a colour change reversibly at the transition temperature. It was with this aim in mind that the magnetic behaviour of the dehydrated compound $\text{CoCu}(\text{obp})$ was analysed. It, however, shows a rather low value of T_{c} , and no measurable H_{c} , which is surprising. The answer lies in the unusual magnetic behaviour of the parent hydrated system $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$, which showed that it had no first-order angular momentum in its ground state^[21], as discussed above.

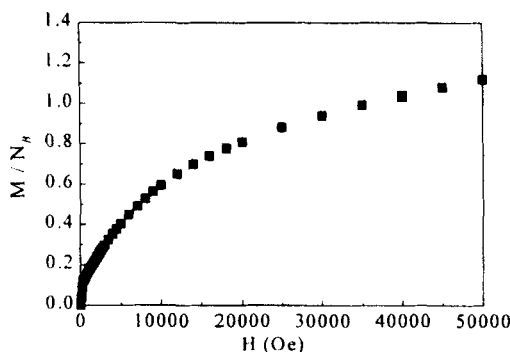


FIGURE 5. Field dependence of magnetization at 2 K for CoCu(obp).

Acknowledgements

All the three authors are thankful to the Indo-French Centre (I.F.C.P.A.R.), New Delhi, for financial support under the project # 1308-4.

References

- [1] J.S. Miller, J.C. Calabrese, A.J. Epstein, R.W. Bigelow, J.H. Zhang, and W. M. Reiff, *J. Chem. Soc., Chem. Commun.*, 1026 (1986).
- [2] Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, and J.P. Renard, *J. Am. Chem. Soc.*, **108**, 7428 (1986).
- [3] Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa, *Phys. Rev. B*, **46**, 8906 (1992).
- [4] R. Chiarelli, M.A. Nowak, A. Rassat, and J.L. Tholence, *Nature*, **363**, 147, (1993).
- [5] D. Gatteschi, *Adv. Mater.*, **6**, 635 (1994).
- [6] O. Kahn, *Molecular Magnetism*. (New York: VCH) 1994.
- [7] O. Kahn, *Advances in Inorganic Chemistry*, **43**, 79 (1996).
- [8] J.S. Miller and A.J. Epstein, *Angew. Chem., Int. Edn. Eng.*, **33**, 385 (1994).
- [9] O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard, and J. Sletten, *J. Am. Chem. Soc.* **110**, 782 (1988).
- [10] K. Nakatani, J. Bergerat, E. Codjovi, C. Mathoniere, Y. Pei and O. Kahn, *Inorg. Chem.*, **30**, 3978 (1991).
- [11] H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, and O. Kahn, *Science*, **261**, 447 (1993).
- [12] H.O. Stumpf, Y. Pei, O. Kahn, J. Sletten, and J.P. Renard, *J. Am. Chem. Soc.*, **115**, 6738 (1993).
- [13] H.O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat, and O. Kahn, *J. Am. Chem. Soc.*, **116**, 3866 (1994).
- [14] H.O. Stumpf, Y. Pei, C. Michaut, O. Kahn, J.P. Renard, and L. Ouahab, *Chem. Mater.*, **6**, 257 (1994).
- [15] K. Nakatani, J.Y. Carriat, Y. Journax, O. Kahn, F. Lloret, J.P. Renard, Y. Pei, J. Sletten, and M. Verdaguer, *J. Am. Chem. Soc.*, **111**, 5739 (1989).
- [16] Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathoniere, and J. Sletten, *J. Am. Chem. Soc.*, **113**, 6558 (1991).

- [17] H. Okawa, M. Mitsumi, M. Ohba, M. Kodera, and N. Matsumoto, *Bull. Chem. Soc. Japan*, **67**, 2139 (1994).
- [18] H. Tamaki, M. Mitsumi, M. Nakamura, N. Matsumoto, S. Kida, H. Okawa, and S. Iijima, *Chem. Lett.* 1975 (1992).
- [19] F. Lloret, R. Ruiz, M. Julve, J. Faus, Y. Journaux, I. Castro, and M. Verdaguer, *Chem. Mater.*, **4**, 1 150 (1992).
- [20] Y. Pei, O. Kahn, J. Sletten, J.P. Renard, R. Georges, J.C. Gianduzzo, J. Curely, and Q. Xu, *Inorg. Chem.*, **27**, 41 (1988).
- [21] A. Gulbrandsen, J. Sletten, K. Nakatani, Y. Pei, and O. Kahn *Inorg. Chimica Acta*, **212**, 271, (1993).
- [22] S. Turner, O. Kahn, and L. Rabardel, *J. Am. Chem. Soc.*, **118**, 6428 (1991).
- [23] J. Larionova, S.A. Chavan, J.V. Yakhmi, A. Gulbrandsen, J. Sletten, C. Sourisseau, and O. Kahn, *Inorg. Chem.*, **36**, 6374 (1987).
- [24] S.A. Chavan, J. Larionova, O. Kahn, and J.V. Yakhmi, *Philos. Mag. B*, **77**, 1657 (1998).