



Hydrostatic pressure dependence of the Curie temperature of $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ for $\text{R} = \text{OC}_{10}\text{H}_{21}$, $\text{OC}_{14}\text{H}_{29}$, and F (TPP, tetraphenylporphyrin; TCNE, tetracyanoethylene)

C.W. Looney^a, K. Falk^b, James J. Hamlin^c, Takahiro Tomita^c,
James S. Schilling^{c,*}, W. Haase^b, Z. Tomkowicz^d

^a Department of Physics, Merrimack College, 315 Turnpike St., North Andover, MA 01845, USA

^b Institut für Physikalische Chemie, Technische Universität Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

^c Department of Physics, Washington University, C.B. 1105, One Brookings Dr., St. Louis, MO 63130, USA

^d Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Krakow, Poland

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Abstract

The dependence of the Curie temperature T_c on hydrostatic pressure has been determined to 6 kbar for the ferromagnetic molecular magnets $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ for $\text{R} = \text{OC}_{10}\text{H}_{21}$, $\text{OC}_{14}\text{H}_{29}$ and F in which the magnetic moments of Mn^{III} -ions and TCNE molecules order ferrimagnetically along chains with the appreciable separations $d \approx 24.2$, 31.2, and 13.7 Å, respectively. In all three cases, T_c decreases initially with pressure but passes through a sharp minimum near 2 kbar. This anomalous behavior is likely caused by competing effects, including a possible pressure-induced lattice distortion which weakens the ferromagnetic dipolar interaction between chains.

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1. Introduction

Low-dimensional molecular magnetic systems are of great current interest not only because of their many potential applications but because of the unusual forms of magnetism they may display. Magnetic ordering in insulating molecular systems is normally the result of superexchange interactions between the structural elements harboring local magnetic moments, magnetic dipolar interactions playing an insignificant role. Falk et al. [1] have succeeded in synthesizing quasi-1D Mn-porphyrin based charge-transfer complexes $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ (TPP = tetraphenylporphyrin, TCNE = tetracyanoethylene, and R = various periphery substituents)

consisting of ferrimagnetic chains, which order ferromagnetically near 20 K (see Fig. 1 in [2] for the chemical structure). There is no chemical bond between the chains and the interchain distances d are very large (for $\text{R} = \text{H}$ or Cl , $d \approx 10$ – 17.5 Å [3,4] even reaching 30.8 Å for $\text{R} = \text{OC}_{12}\text{H}_{25}$ [5]), too large to support superexchange interactions. In such systems 3D magnetic ordering via the magnetic dipolar interaction is a viable possibility.

Richards [6] has shown that weak interchain interactions J_{inter} in the presence of strong intrachain exchange coupling J_{intra} can give rise to a finite critical temperature obeying the relation $T_c \propto \sqrt{J_{\text{intra}}J_{\text{inter}}}$. Under hydrostatic pressure both J_{inter} and J_{intra} (and thus T_c !) would be expected to increase since all interatomic separations r are reduced. In fact, the exchange interaction J_{exch} falls off much more rapidly with distance r than the dipolar interaction J_{dipolar} (for a dimer $J_{\text{exch}} \sim r^{-10}$ whereas $J_{\text{dipolar}} \sim r^{-3}$) [7]. High-pressure experiments can, therefore, be used to help identify the

* Corresponding author. Tel.: +1-314-935-6239; fax: +1-314-935-6219.

E-mail address: schill@wuphys.wustl.edu (J.S. Schilling).

dominant interaction leading to magnetic ordering in the above and comparable quasi-1D systems.

In recent hydrostatic high-pressure experiments in He-gas to 6 kbar on $[\text{Mn}(\text{OC}_{14}\text{H}_{29})_4\text{TPP}][\text{TCNE}]$, where $d \simeq 31.2 \text{ \AA}$, we observe that, in contrast to the above expectations, T_c initially *decreases* rapidly with pressure, only to abruptly begin increasing above the critical pressure $P_c \approx 1.5 \text{ kbar}$ (see Fig. 1) [1,2]. This anomalous behavior is reversible in pressure if the pressure is changed at room temperature (RT), i.e., the minimum in $T_c(P)$ occurs at the same critical pressure P_c whether the pressure is increased or decreased.

In a subsequent experiment to 21 kbar we found that the $T_c(P)$ anomaly near 1.5 kbar is also observed using a standard piston-cylinder pressure cell with *n*-pentane/isoamyl alcohol as pressure medium instead of helium [1,2]. We conclude, therefore, that the minimum in $T_c(P)$ is an intrinsic property of the sample and does not depend on the pressure transmitting medium used, at least not in our experiments. Several mechanisms were suggested for the sharp minimum in $T_c(P)$ [1,2]; further experiments are required to clarify this matter. It would be important, for example, to establish whether or not a minimum in $T_c(P)$ occurs for other members of the porphyrin-TCNE family. Such studies should help further our understanding of the role of dipolar interactions in the formation of the ferromagnetic state.

In this paper we present the results of recent experiments under hydrostatic He-gas pressure to 6 kbar on two further $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ compounds with widely differing interchain separations ($d \simeq 24.2 \text{ \AA}$ for

$\text{R} = \text{OC}_{10}\text{H}_{21}$ and $d \simeq 13.7 \text{ \AA}$ for $\text{R} = \text{F}$). We find minima in $T_c(P)$ at the critical pressures $P_c \approx 2.3$ and 1.7 kbar, respectively, which depend somewhat on the temperature at which the pressure is changed.

2. Experimental methods

The sample preparation procedures for the $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ family of molecular magnets have been published elsewhere [1].

The He-gas compressor system (Harwood) used in these experiments is capable of generating hydrostatic pressures to $\sim 10 \text{ kbar}$; the pressure is determined by a calibrated manganin gauge in the compressor system at ambient temperature. The CuBe pressure cell (Unipress) is connected to the compressor system by a 3 mm O.D. \times 0.3 mm I.D. CuBe capillary tube and inserted into a two-stage closed-cycle refrigerator (Leybold) operating in the temperature range 2–320 K. The pressure in the cell can be changed at any temperature above the melting curve of the He pressure medium (e.g., $\sim 39 \text{ K}$ at 5 kbar).

The Curie temperature of the $\sim 2 \text{ mg}$ powder samples in the high-pressure environment was detected by the ac susceptibility technique (ac field 1.13 Oe at 507 Hz) using a miniature primary/secondary coil system located inside the 7 mm I.D. bore of the pressure cell. As seen in Fig. 2, the real part of the ac susceptibility χ' of $[\text{Mn}(\text{OC}_{10}\text{H}_{21})_4\text{TPP}][\text{TCNE}]$ and $[\text{MnF}_4\text{TPP}][\text{TCNE}]$ at ambient pressure passes through a well-defined

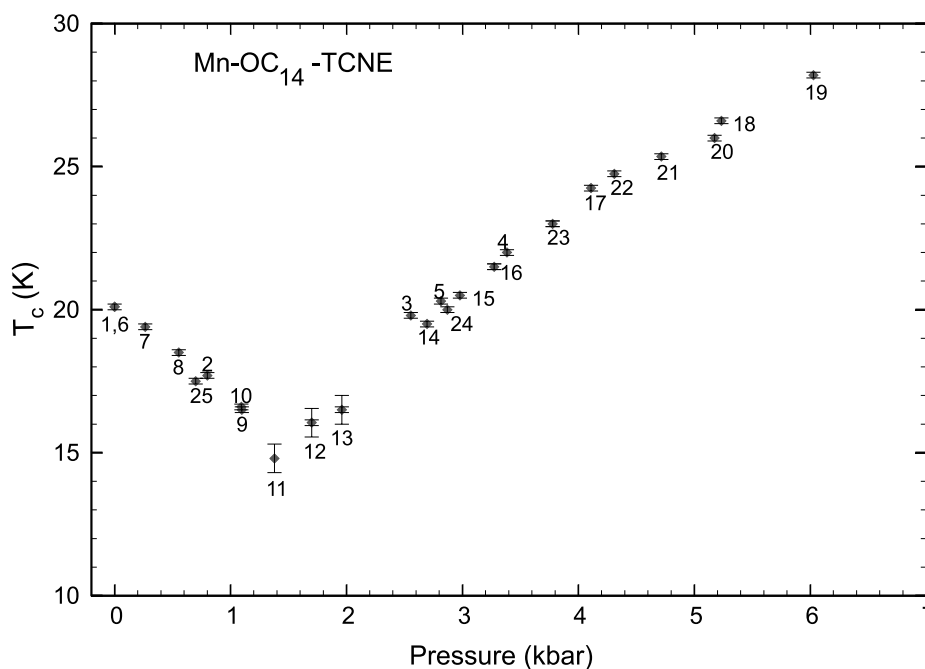


Fig. 1. Dependence of the Curie temperature T_c of $[\text{Mn}(\text{OC}_{14}\text{H}_{29})_4\text{TPP}][\text{TCNE}]$ on hydrostatic pressure. Pressure was changed at room temperature. Numbers give order of measurement.

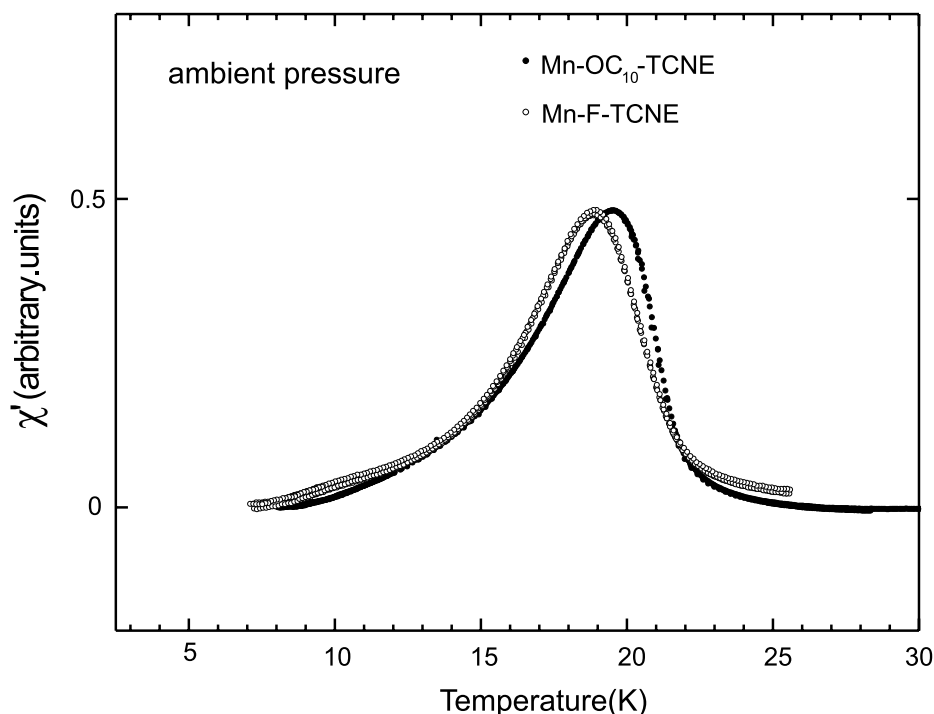


Fig. 2. Real component of the ac susceptibility vs. temperature at ambient pressure for (●) $[\text{Mn}(\text{OC}_{10}\text{H}_{21})_4\text{TPP}][\text{TCNE}]$ and (○) $[\text{MnF}_4\text{TPP}][\text{TCNE}]$.

maximum near $T_c \approx 20$ K which we use here as a measure of the Curie temperature [8]. Further details of the He-gas experimental setup are given elsewhere [9].

3. Results of experiment and discussion

In Fig. 3 we show the hydrostatic pressure dependence of the Curie temperature T_c of $[\text{Mn}(\text{OC}_{10}\text{H}_{21})_4\text{TPP}][\text{TCNE}]$. Following the measurement at ambient pressure (pt 1), 0.8 kbar pressure was applied at 190 K which is seen to lead to a decrease in T_c (pt 2), similar to that found previously for $[\text{Mn}(\text{OC}_{14}\text{H}_{29})_4\text{TPP}][\text{TCNE}]$ [1,2]. The pressure was then further increased to 5.3 kbar at RT, whereupon T_c increased to nearly 25 K (pt 3). The pressure was then bled off at low temperature in successive steps, resulting in data points 4–15; $T_c(P)$ is seen to pass through a minimum near 1 kbar. T_c does not return to its initial ambient-pressure value after the pressure is released at low temperature (pt 15). A markedly different behavior is obtained if the pressure is changed at room temperature (RT); here $T_c(P)$ is seen to (reversibly) pass through a sharp minimum at $P_c \approx 2.3$ kbar. The critical pressure P_c for the anomalous minimum in $T_c(P)$ thus depends on whether the pressure is changed at RT or low temperature. Note that, in contrast to the low-temperature experiment, T_c returns to its initial ambient-pressure value if the pressure is released at RT (pt 31).

The high-pressure experiment on $[\text{MnF}_4\text{TPP}][\text{TCNE}]$ was carried out in a somewhat different manner (see Fig. 4). The pressure was first increased at RT in nine steps to 5.5 kbar (pts 1–10), revealing a sharp minimum in $T_c(P)$ near $P_c \approx 1.7$ kbar. The reversibility of $T_c(P)$ was then checked by reducing the pressure from 5.5 to 1.7 kbar at RT (pt 11). Further pressure reductions were carried out at temperatures below 30 K (pts 12–15), where T_c is seen to increase somewhat less rapidly than for points 4–1, reaching an ambient-pressure value (pt 15) suppressed by ~ 1 K below the initial value (pt 1). Annealing the sample at RT for 17 h prompted T_c to increase back up to its initial value (pt 16).

For both $[\text{MnF}_4\text{TPP}][\text{TCNE}]$ and $[\text{Mn}(\text{OC}_{10}\text{H}_{21})_4\text{TPP}][\text{TCNE}]$ the change in T_c with pressure is less rapid if the pressure is changed at low temperatures compared to changes at RT. Similar behavior has been observed in high-temperature oxide superconductors due to oxygen-ordering effects [10,11]. Since pressure-induced changes appear to be inhibited if the pressure is changed at low temperatures (see Figs. 3 and 4), it seems likely that the critical pressure P_c will shift to *higher*(*lower*) values if the pressure is applied(released) at temperatures below RT. The anticipated decrease in P_c if the pressure is released at low temperatures is, in fact, seen in Fig. 3 for points 4–15.

The present experiments have thus established that the sharp minimum in $T_c(P)$ at $P_c \approx 1.5$ kbar for $[\text{Mn}(\text{OC}_{14}\text{H}_{29})_4\text{TPP}][\text{TCNE}]$ is not restricted to this compound, but is also observed for the related

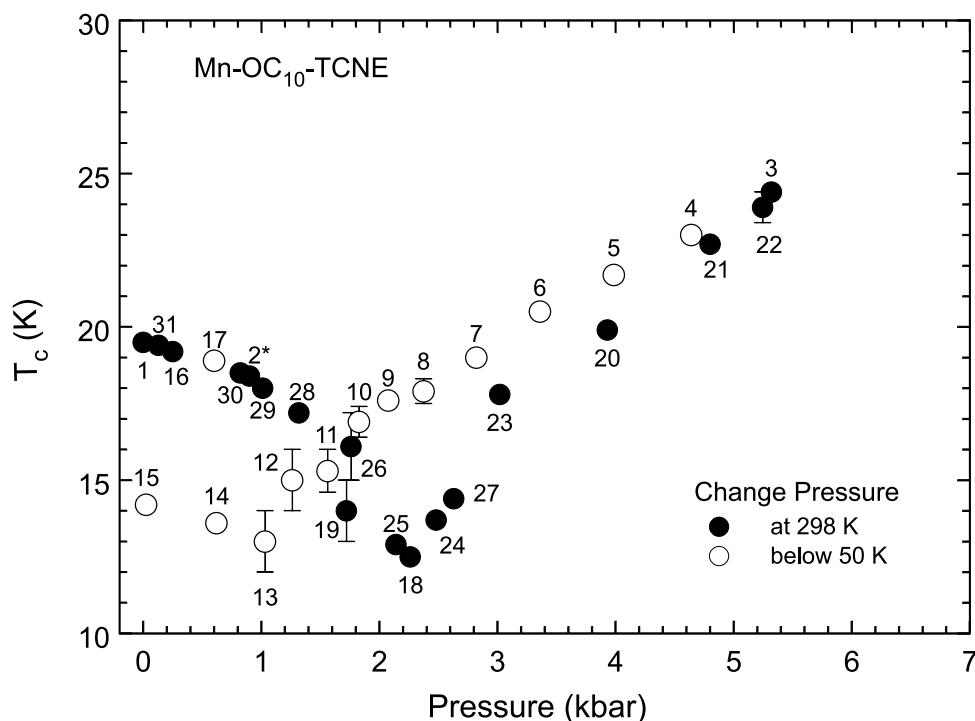


Fig. 3. Dependence of the Curie temperature T_c of $[\text{Mn}(\text{OC}_{10}\text{H}_{21})_4\text{TPP}][\text{TCNE}]$ on hydrostatic pressure. Pressure was changed at room temperature (\bullet) and low temperatures (\circ). Numbers give order of measurement. The asterisk (*) on pt 2 indicates that the pressure was changed at 190 K instead of 298 K.

compounds $[\text{Mn}(\text{OC}_{10}\text{H}_{21})_4\text{TPP}][\text{TCNE}]$ ($P_c \approx 2.3$ kbar) and $[\text{MnF}_4\text{TPP}][\text{TCNE}]$ ($P_c \approx 1.7$ kbar). We thus conclude that this $T_c(P)$ anomaly is a general feature of the $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ family of compounds. Since both intrachain and interchain interactions are believed to increase with pressure [7], the initial negative sign of dT_c/dP indicates that further factors are likely important.

In very recent work, Ostrovsky et al. [12] applied a modified mean-field model to show that exchange coupling along the chains and dipolar interactions between the chains can together account for the large magnitude (~ 20 K) of the Curie temperature in the $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ compound system if, and only if, single-ion anisotropy is present.¹ Without anisotropy the predicted value of T_c would lie near 2–3 K, an order of magnitude lower than the experimental values. Single-ion anisotropy also leads to an exponential divergence of the spin correlation length along the chains with decreasing temperature. The correlation length along an isolated chain is mainly determined by the strength of

the in-chain exchange coupling. Although the ferromagnetic structure is established by the interchain dipolar interactions, the magnitude of T_c is mainly determined by the in-chain exchange coupling. This model thus readily explains why the values of T_c are comparable in the $[\text{MnR}_4\text{TPP}][\text{TCNE}]$ compound family, even though the interchain separations differ widely.

Similar results were obtained for the two-dimensional case by Drillon and Panissod [13] who observed only small differences in T_c (21–19 K) for a family of substances with significant differences in the distance between ferromagnetic Cu(II) layers (29–40 Å). In the second paper of this group [14], the $T_c(P)$ dependence is presented for two substances in this family. The authors show that the distance between the Cu(II) layers is not significantly reduced by pressure (the organic distancing chains are quite stiff); however, T_c decreases with pressure by about 3 K up to the maximum applied pressure of 10 kbar. This result was explained by the weakening of the in-plane superexchange coupling as a result of the change of Cu–O–Cu angle under pressure, i.e., a buckling of the plane. In our one-dimensional case, a strengthening of the intrachain exchange coupling would be expected under pressure, as discussed above, unless the chains themselves buckle.

As pointed out in our previous paper [2], a Monte Carlo simulation on a hexagonal system of ferrimagnetic chains mutually coupled by dipolar interactions

¹ Single-ion anisotropy is attributed here to the Jahn–Teller $\text{Mn}(\text{III})$ ions. The anisotropy direction is expected to deviate from that of the chain axis since the porphyrin planes are usually declined relative to the chain axis for this class of compounds [3,4]. The magnitude of the anisotropy is unknown, but can be obtained from magnetization measurements on single crystals.

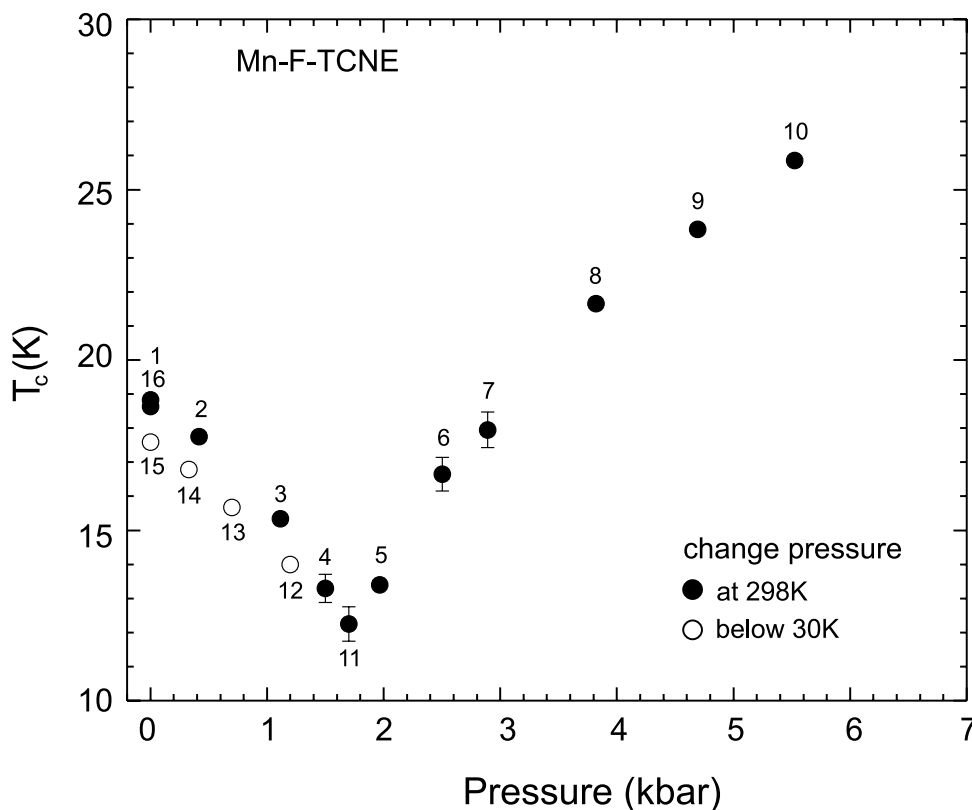


Fig. 4. Dependence of the Curie temperature T_c of $[\text{MnF}_4\text{TPP}][\text{TCNE}]$ on hydrostatic pressure. Pressure was changed at room temperature (\bullet) and low temperatures (\circ). Numbers give order of measurement.

only yields a ferromagnetic state if two-axis anisotropy is invoked; in such an anisotropy half of the Mn spins has a different easy-axis direction than the other half. The most favorable condition for ferromagnetism is obtained when the two easy-axis directions are perpendicular both to each other and to the chain axis. One might, therefore, speculate that the initial decrease in T_c under pressure is due to lattice distortions which spoil the geometrical conditions favorable for dipolar ferromagnetism. Were this lattice distortion to gradually saturate at higher pressures, T_c would then pass through a minimum and begin to increase with pressure as the interchain and intrachain exchange interactions begin to dominate. Alternatively, one might propose a first-order phase transition at P_c in the spin and/or lattice system as a possible mechanism for the sharp minimum in $T_c(P)$. High-pressure neutron diffraction experiments, which are able to probe both spin and lattice structures, should help provide answers to these open questions.

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