

# Dependence of the Curie Temperature of tetrakis - (para-tetradecyloxy-phenyl) - porphyrinatomanganese (III) - tetracyanoethenide (Mn-OC<sub>14</sub>-TCNE) on Hydrostatic Pressure to 21 kbar

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## Abstract

The dependence of the Curie temperature on hydrostatic pressure has been determined to 21 kbar for the ferromagnetic molecular magnet [Mn(OC<sub>14</sub>H<sub>29</sub>)<sub>4</sub>[TCNE]], where Mn<sup>III</sup>-ions are situated in ferrimagnetic porphyrin chains separated by 31.2 Å. In the present experiments both He-gas and piston-cylinder pressure systems are used to 6 kbar and 21 kbar, respectively. Following an initial rapid decrease of the Curie temperature  $T_c$  with applied pressure from 20 K to 15 K at 1.5 kbar,  $T_c$  abruptly begins to increase with pressure at an equally rapid rate, ultimately reaching nearly 37 K at 21 kbar. The change in the sign in  $dT_c/dP$  at 1.5 kbar is likely the result of a phase transition in the spin and/or lattice system. The possible role of dipolar interactions in determining the magnetic state in a system of parallel ferrimagnetic chains is discussed.

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# 1 Introduction

Porphyrin-based molecular magnets  $[\text{Mn}(\text{R})_4\text{TPP}][\text{TCNE}] \times \text{solvent}$  are interesting materials which can show liquid crystalline as well as ferromagnetic properties [1]. Their molecular structure consists of porphyrin discs MnTPP (TTP = tetraphenylporphyrin) containing  $\text{Mn}^{\text{III}}$ -ions and substituents R at the peripheries, as seen in Fig. 1. These discs are coupled into long chains by the molecular TCNE (tetracyanoethylene) bridge located between two Mn ions. The magnetic moment of the  $\text{Mn}^{\text{III}}$ -ion, corresponding to the spin value  $S = 2$ , is strongly antiferromagnetically coupled with the delocalized spin  $s = \frac{1}{2}$  of the TCNE anion radical, yielding a ferrimagnetic chain. The spin density of TCNE was studied by polarized neutron diffraction by Zheludev *et al.* [2]. The substances of this family show a rich variety of magnetic behavior when different organic substituents R and various solvents are used. The substituents can change the magnetic interchain interactions; the solvent molecules, which intercalate between chains, can stabilize different crystal structures (i.e. different packing of chains). To date only a few substances have been structurally characterized (for  $\text{R} = \text{H}$  or  $\text{Cl}$ ) [3].

The magnetic properties of  $[\text{Mn}(\text{R})_4\text{TPP}][\text{TCNE}] \times \text{solvent}$  with  $\text{R} = \text{OC}_{12}\text{H}_{25}$ , F, CN have been extensively studied by Bałanda *et al.* [4] by means of dc and ac magnetic susceptibility techniques. The prominent ac susceptibility maximum observed at temperatures near 20 K was interpreted as signaling the transition to a magnetically ordered state. An alternate interpretation, whereby the susceptibility maximum comes from relaxation effects in a nanoparticle system [5], seems unlikely since electron microscope TEM and SEM studies show that the diameters of typical particles are quite large ( $\sim 1 \mu\text{m}$ ) and X-ray diffraction patterns show sharp reflexes [6].

An important outstanding problem in these quasi one-dimensional molecular magnets is the nature of the magnetic interactions between chains. There is no chemical bond between the chains and the interchain distances  $d$  are very large (for  $\text{R} = \text{H}$  or  $\text{Cl}$ ,  $d \approx 10 - 17.5 \text{ \AA}$  [3], even reaching  $30.8 \text{ \AA}$  for  $\text{R} = \text{OC}_{12}\text{H}_{25}$  [4]). It is natural to suspect, therefore, that long-range dipolar interactions might be responsible for the interchain coupling. It can be shown using the formula

$$T_c = 2S(S + 1)\sqrt{4J_{intra}J_{inter}} \quad (1)$$

from Ref. [7] that weak interchain interactions  $J_{inter}$  in the presence of strong intrachain coupling  $J_{intra}$  can give rise to a finite critical temperature  $T_c$ . Wynn *et al.*[8] suggested that for the appearance of ferromagnetism in this class of materials a spin canting is necessary; such canting might result from local changes in the anisotropy axes caused by solvent molecules.

Drillon and Panissod [9] considered layered (two-dimensional) substances in which ferromagnetic planes with anisotropy axes perpendicular to the planes are coupled through dipolar interactions. They showed that spontaneous magnetization can

appear below  $T_c \approx 20$  K and that  $T_c$  depended only very weakly on the distance between planes. In quasi one-dimensional systems, however, the conditions for the appearance of ferromagnetism originating from dipolar interchain interactions are less obvious.

To further our understanding of the nature of the magnetic interchain interactions in these molecular magnet systems, it would be useful to apply high hydrostatic pressure to the sample. Because there is no chemical bond between chains, the compressibility in directions perpendicular to the chains would be expected to be much larger than along the chains. The pressure dependence of  $T_c$  might thus be expected to depend mainly on changes in the distance between chains  $d$ . If dipolar interactions between chains were the sole interchain interaction determining the magnetic ordering temperature, then from Eq. (1) one would expect  $T_c$  to increase with applied pressure according to  $T_c \propto d^{-3/2}$ . In the present work we have determined  $T_c(P)$  to 21 kbar for the porphyrin-based molecular ferromagnet with  $R = OC_{14}H_{29}$  by measuring the ac magnetic susceptibility under hydrostatic high-pressure conditions.

## 2 Experiment

Metal-free porphyrin was synthesized according to Adler et al. [10]; the metallization and bridging reactions are described by Jones et al. [11] and Summerville et al. [12]. We then dissolved 0.1 mol para-tetradecyloxybenzaldehyde in 300 ml boiling propionic acid and slowly added 0.1 mol pyrrol to this mixture. After refluxing the solution for one hour, the precipitated violet product was filtered and washed with acetone and water. The reaction yielded 0.005 mol (21 %) of the crude tetra-(para-tetradecyloxyphenyl)-porphyrin. After drying, the porphyrin is dissolved in 300 ml hot DMF whereupon 0.05 mol manganese(II)acetate tetra hydrate is added to the mixture. After refluxing for one hour, the precipitating green product is filtered, washed with water, dried in air, and dissolved in 150 ml of hot methanol. The same volume of half-concentrated hydrochloric acid is added to this solution and the precipitating green product is filtered, washed with water, and dried in air. The reaction yielded 88 % of manganese(III)-tetra-(para-tetradecyloxyphenyl)-porphyrinato-chloride.

The bridging reaction with tetracyanoethylene (TCNE) is done in Schlenk-type glassware under an argon atmosphere. 0.5 mmol of the green manganese(III)chloride are dissolved in 20 ml methanol and 20 ml pyridine. 10 mmol sodium borohydride is then added and the stirred mixture is refluxed for one hour. After this procedure the purple product is filtered, washed with methanol, and dried in vacuum. A solution of 1.5 mmol TCNE in 15 ml toluene is then added to the compound. After stirring the mixture for one hour at room temperature, the precipitating dark green product is filtered, washed with toluene, and dried in vacuum for several hours. The overall yield for the bridging reaction is 82 %. The success of the bridging reaction with TCNE is proved via the typical shift of the  $\nu_{CN}$  wagging bands in the IR spectroscopy ( $\nu_{CN}$  (1)

= 2198 cm<sup>-1</sup>,  $\nu_{CN}(2) = 2144$  cm<sup>-1</sup>). The elemental analysis gives satisfying results with one molecule of methanol residing in the structure ( $C_{cal}$ : 76.58  $C_{exp}$ : 76.63,  $H_{cal}$ : 8.71  $H_{exp}$ : 8.70,  $N_{cal}$ : 6.68  $N_{exp}$ : 6.60).

Because of the high flexibility of the long alkoxy chains, we have not yet been able to grow single crystals and determine the detailed atomic positions for this complex. However, powder X-ray diffraction measurements at temperatures above  $\sim 110^\circ\text{C}$  point to an hexagonal columnar liquid crystalline phase with interchain distance 31.2 Å[13]. In this temperature region the tetragonal porphyrin molecules rotate freely. As the temperature decreases below 110°C, this rotation stops and the lattice symmetry would be expected to decrease to fit the reduced symmetry of the porphyrin molecule. X-ray diffraction experiments at room temperature show an asymmetrical broadening of the relevant peaks; the diffraction pattern revealed no reflexes characteristic for typical Mn impurity phases. The homogeneity of the substance was confirmed by SEM and TEM studies. X-band EPR spectra showed only a single peak attributed to the TCNE radical anion [6].

DC magnetic susceptibility measurements were performed using a Faraday balance. From a fit of the temperature dependence of the susceptibility to the formula given by Drillon et al. [14], the exchange coupling constant was determined to be  $J_{intra} \approx -102.8$  cm<sup>-1</sup> [6].

The He-gas compressor system (Harwood) used in these experiments is capable of generating hydrostatic pressures to 14 kbar; the pressure is determined by a calibrated manganin gauge in the compressor system at ambient temperature. The CuBe pressure cell (Unipress), which is connected to the compressor system by a 3 mm O.D.  $\times$  0.3 mm I.D. CuBe capillary tube, is 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.  $\sim 50$  K at 8 kbar). In the present experiments the pressure was only changed at ambient temperature.

The Curie temperature of the  $\sim 2$  mg powder sample of Mn-OC<sub>14</sub>-TCNE in the high pressure environment was detected by the ac susceptibility technique using a miniature primary/secondary coil system located inside the 7 mm I.D. bore of the pressure cell. In the present studies in the He-gas compressor system a magnetic field of 1.13 Oe (rms) at 507 Hz is applied. Further details of the He-gas experimental setup are given elsewhere [15].

High-pressure studies were also carried out utilizing a CuBe piston-cylinder pressure clamp. The sample ( $\sim 30$  mg) was loaded into a 5 mm I.D. teflon capsule with a 1:1 mixture of n-pentane and isoamyl alcohol as pressure fluid. The teflon capsule was then placed inside a hardened CuBe cylinder with CuBe anti-extrusion disks at both ends of the capsule. Tungsten carbide pistons were used to transmit the pressure force to the cylinder and the force is then retained by locking the pressure clamp. The ac susceptibility coils are located around the outside of the pressure cylinder directly over the sample. Additional details of the piston-cylinder self-clamp technique

can be found in Ref. [16].

### 3 Results of Experiment and Discussion

The temperature  $T_c$  at which the ferromagnetic transition occurs can be readily determined by measuring the ac susceptibility  $\chi$ . As seen in Fig. 2, the real part of the ac susceptibility  $\chi$  of Mn-OC<sub>14</sub>-TCNE at ambient pressure passes through a well-defined maximum at  $T_c \simeq 20$  K which we use here as a measure of the Curie temperature; the maximum in the imaginary part of the susceptibility occurs at a slightly lower temperature [17]. The data shown were taken at 1.13 Oe excitation field; lowering the field to 0.11 Oe results in no measurable change in  $\chi(T)$ .

The dependence of the real part of the ac susceptibility on temperature  $\chi(T)$  at various applied pressures is shown in Fig. 3. It is seen that  $T_c$  decreases from 20 K to nearly 17 K at 0.7 kbar pressure at the rate  $dT_c/dP \simeq -3.7$  K/kbar, with  $\chi_{\max}$  also decreasing. As the pressure is further increased to 2.7, 3.3, 4.1, 5.2 and 6.0 kbar, however, both  $T_c$  and  $\chi_{\max}$  are observed to *increase* rapidly ( $dT_c/dP \simeq +3.4$  K/kbar). The results of the complete set of experimental data for  $T_c(P)$  and  $\chi_{\max}(P)$  to 6 kbar are shown in Figs. 4(a) and 4(b), respectively, for both increasing and decreasing pressure; both dependences are seen to be reversible in pressure. The critical pressure separating negative and positive pressure dependences for  $T_c(P)$  and  $\chi_{\max}(P)$  is  $P_c \approx 1.5$  kbar.

Unfortunately, the melting curve for the <sup>4</sup>He pressure medium lies near 18 K at 1.5 kbar, the same temperature as the ferromagnetic transition at this pressure. This means that at 18 K the sample is in fluid <sup>4</sup>He for  $P < 1.5$  kbar, but in solid <sup>4</sup>He for  $P > 1.5$  kbar. The question thus arises whether the abrupt change in slope  $dT_c/dP$  at 1.5 kbar is an intrinsic property of the sample or perhaps the result of the <sup>4</sup>He pressure medium being in a fluid or solid state. The latter scenario would not seem likely since helium is the softest of all solids; in addition, the pressure cell is cooled slowly through the melting curve of <sup>4</sup>He using a well-established temperature-gradient procedure developed by Schirber [18] which essentially eliminates shear stresses on the sample. There is also the possibility that He atoms are small enough to be able to intercalate into spaces between the porphyrin chains. Further experiments using an entirely different pressure medium would be useful to resolve these issues.

To establish whether or not the abrupt slope reversal in  $dT_c/dP$  at 1.5 kbar is an intrinsic property of the sample, parallel high-pressure studies were carried out in a standard piston-cylinder cell using as pressure medium 1:1 n-pentane isoamyl-alcohol, which is solid at temperatures near  $T_c$  for *all* pressures. The results of the piston-cylinder experiments to 21 kbar are shown in Fig. 5 and compared with the He-gas data to 6 kbar from Fig. 4(a). The abrupt change in slope  $dT_c/dP$  at 1.5 kbar is indeed seen in the piston-cylinder data, confirming that this feature is an intrinsic property of the sample. The extended pressure range of the piston-cylinder experiments reveals that  $T_c$  increases under 21 kbar pressure to nearly 37 K.

The maximum in the ac susceptibility  $\chi_{\max}$  increases monotonically with pressure for pressures above 1.5 kbar, reaching a value of  $\sim 26$  emu/mol at 21 kbar.

The aim of the present work is to shed light on the nature of the interchain magnetic interactions in Mn-OC<sub>14</sub>-TCNE. As pointed out in the Introduction, the magnetic phase transition occurs at  $T_c \approx 20$  K to a state with a net magnetic moment. If dipolar interactions between the chains were to determine the value of  $T_c$ , then one would expect  $T_c$  to *increase* with pressure. The fact that in the present experiments  $T_c$  initially *decreases* with pressure would appear to be inconsistent with dominant dipolar interactions. Pressure-induced changes in the Mn-Mn separation along the chains or in the local anisotropy of the Mn<sup>III</sup>-ions may play a role.

It is an interesting question, in fact, whether a ferromagnetic state is possible at all for a system of ferrimagnetic chains mutually coupled by dipolar interactions. To this end we have searched for the low temperature equilibrium magnetic state for a cluster of chains in an hexagonal or slightly orthorhombically distorted lattice by simulated annealing using a Monte Carlo program based on Metropolis algorithm [19]. In these simulations easy axis anisotropy was taken into account; the energy of this anisotropy was assumed to be much greater than that of dipolar interactions. No ferromagnetic state was obtained by assuming single-axis anisotropy. However, with two-axis anisotropy the ferromagnetic state is possible; here two-axis anisotropy means that half the Mn spins have a different easy axis direction than the other half. The optimal conditions for ferromagnetism exist when both anisotropy axes are perpendicular to each other and to the chain axis [20]. The reason for the two-axis anisotropy can be the presence of solvent molecules and/or lattice distortion which is anticipated at low temperatures.

Another important question is whether dipolar interactions are strong enough to give  $T_c$  values near 20 K. Calculations similar to those in Ref. [9] give the estimate  $T_c \approx 14$  K [21]. The observed minimum in  $T_c$  versus pressure thus has a number of potential origins: (1) variation in the angle between the anisotropy axes, (2) competition between Mn-Mn interactions along each chain and interactions between chains, or (3) the occurrence of a phase transition in the spin and/or lattice system. Neutron diffraction experiments under high pressure conditions, which are able to probe both the spin and lattice structure, should shed light on these questions. We also plan to study a second member of this family to ascertain whether the observed minimum in  $T_c(P)$  is a general property of the Mn(R)<sub>4</sub>[TTP][TCNE] compounds or only a property of the particular substance studied here.

In summary, the pressure dependence of the critical temperature  $T_c$  of the transition to the ferromagnetic state was obtained for the porphyrin-based molecular magnet Mn-OC<sub>14</sub>-TCNE composed of ferrimagnetic chains. This dependence  $T_c(P)$  shows a sharp minimum at 1.5 kbar which would appear to be inconsistent with a dominant magnetic dipolar interaction between chains. Numerical simulations show that the relatively high-temperature ferromagnetism characteristic for this class of materials can be accounted for in terms of dipolar interchain interactions if two-axis

anisotropy is included. Further experiments, particularly neutron diffraction studies under high pressure, should help resolve the important outstanding questions.

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## References

- [1] K. Griesar, M.A. Athanassopoulou, Z. Tomkowicz, and M. Bałanda, *Mol. Cryst. Liq. Cryst.* 306 (1997) 57; K. Griesar, M.A. Athanassopoulou, A. Soto Bustamante, Z. Tomkowicz, A.J. Zaleski, and W. Haase, *Adv. Mater.* 9 (1997) 45.
- [2] A. Zheludev, A. Grand, E. Ressouche, J. Schweizer, B.G. Morin, A.J. Epstein, D.A. Dixon, and J.S. Miller, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1397.
- [3] J.S. Miller, J.C. Calabrese, R.S. McLean, and A.J. Epstein, *Adv. Mater.* 4 (1992) 498; E.J. Brandon, D.K. Rittenberg, A.M. Arif, and J.S. Miller, *Inorg. Chem.* 37 (1998) 3376.
- [4] M. Bałanda, K. Falk, K. Griesar, Z. Tomkowicz, and W. Haase, *J. Magn. Magn. Mater.* 205 (1999) 14.
- [5] See, for example, N.G. Takzei, *Acta, Phys. Polon.* A93 (1998) S65.
- [6] K. Falk (unpublished results)
- [7] P.M. Richards, *Phys. Rev. B* 10 (1974) 4687.
- [8] C.M. Wynn, M.A. Girtu, K-I. Sugiura, E.J. Brandon, J.L. Manson, J.S. Miller, and A.J. Epstein, *Synth. Met.* 85 (1997) 1695.
- [9] M. Drillon and P. Panissod, *J. Magn. Magn. Mater.* 188 (1998) 93.
- [10] A.D. Adler, F.R. Longo, R.D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Organ. Chem.* 32 (1967) 476.
- [11] R.D. Jones, D.A. Summerville, and F. Basolo, *J. Amer. Chem. Soc.* 100 (1978) 4416.



- [12] D.A. Summerville, T.W. Cape, E.D. Johnson, and F. Basolo, *Inorgan. Chem.* 17 (1978) 3297.
- [13] Poster presentation at the *6th International Conference on Molecular Based Magnets*, ICMM2000, San Antonio, Texas Sept. 16-21, 2000.
- [14] M. Drillon, E. Coronado, D. Beltran, R. Georges, *Chem. Phys.* 79 (1983) 449.
- [15] J. S. Schilling, J. Diederichs, S. Klotz, and R. Sieburger in: *Magnetic Susceptibility of Superconductors and Other Spin Systems*, eds. R. A. Hein, T. L. Francavilla and D. H. Liebenberg (Plenum, New York, 1991) p. 107.
- [16] T. F. Smith, *J. Low Temp. Phys.* 6 (1972) 171.
- [17] In Ref. 4,  $T_c$  is defined by either the temperature of the inflection point on the high temperature side of the maximum in the real part of  $\chi$  or the temperature of the sharp rise in the imaginary part of  $\chi$  upon cooling. These various definitions have no consequence for the change in  $T_c$  with pressure.
- [18] J. E. Schirber, *Cryogenics* 10 (1970) 418.
- [19] P. Lacorre and J. Pannetier, *J. Magn. Magn. Mater.* 71 (1987) 63.
- [20] Z. Tomkowicz (unpublished)
- [21] S. Ostrovsky (private communication).

## 4 Figure Captions

**Fig. 1.** Chemical structure of the Mn-OC<sub>14</sub>-TCNE complex.

**Fig. 2.** Temperature dependence of the real (●) and imaginary (o) parts of the ac susceptibility  $\chi$  (ac field 1.13 Oe at 507 Hz) at ambient pressure for Mn-OC<sub>14</sub>-TCNE.

**Fig. 3.** Real part of the ac susceptibility (ac field 1.13 Oe at 507 Hz) of Mn-OC<sub>14</sub>-TCNE versus temperature at seven different values of the applied pressure in the He-gas system. Initially both the Curie temperature  $T_c$  and the maximum value of the susceptibility  $\chi_{\max}$  decrease with pressure; above 1.5 kbar both quantities increase.

**Fig. 4.** Dependence of the (a) Curie temperature  $T_c$  and the (b) maximum value of the real part of the ac susceptibility  $\chi_{\max}$  on pressure to 6 kbar. Numbers give the order of measurement.

**Fig. 5.** Dependence of the Curie temperature  $T_c$  on pressure to 21 kbar using data from both the piston-cylinder (●) and He-gas (+) high-pressure experiments. Numbers give the order of measurement for the piston-cylinder data.

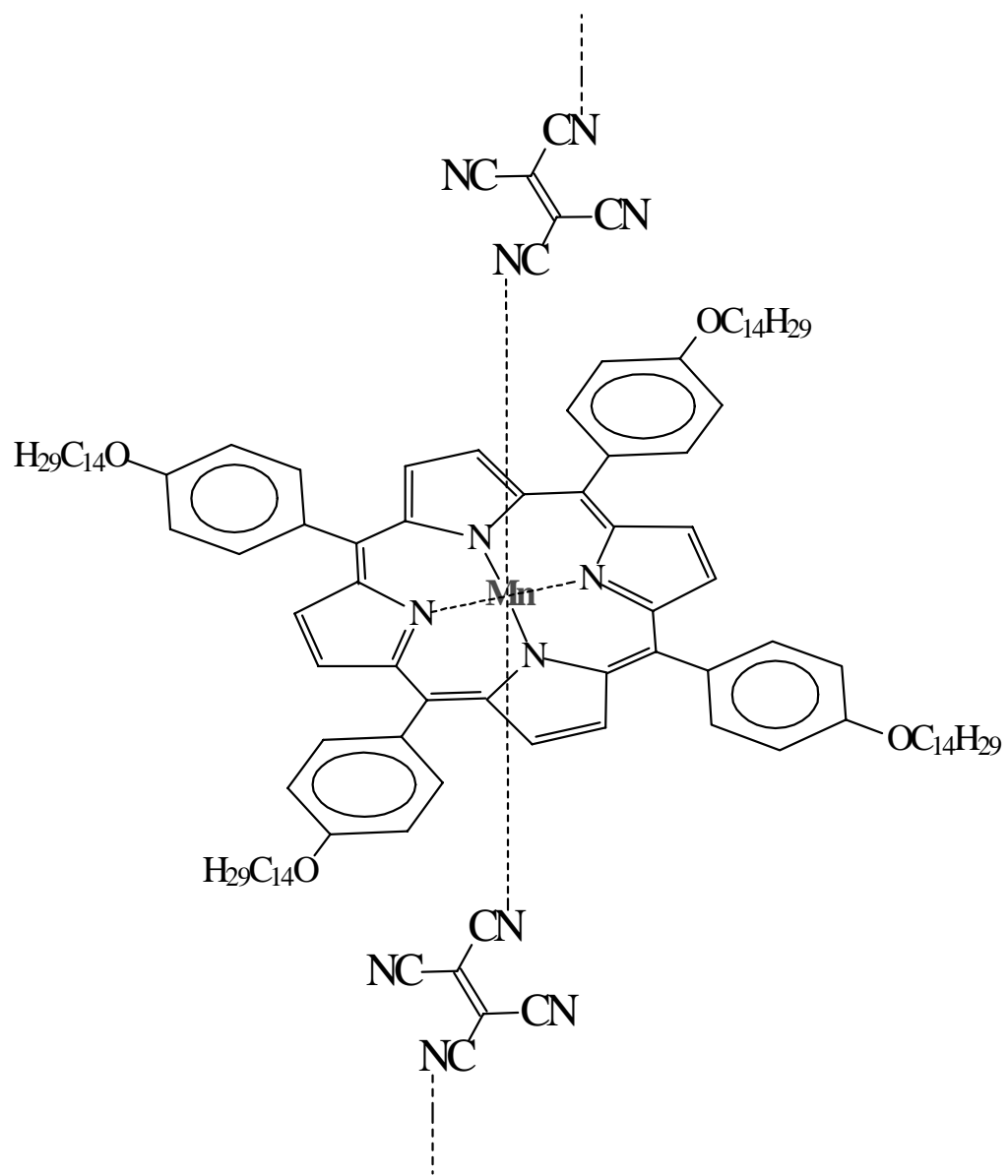


Fig. 1

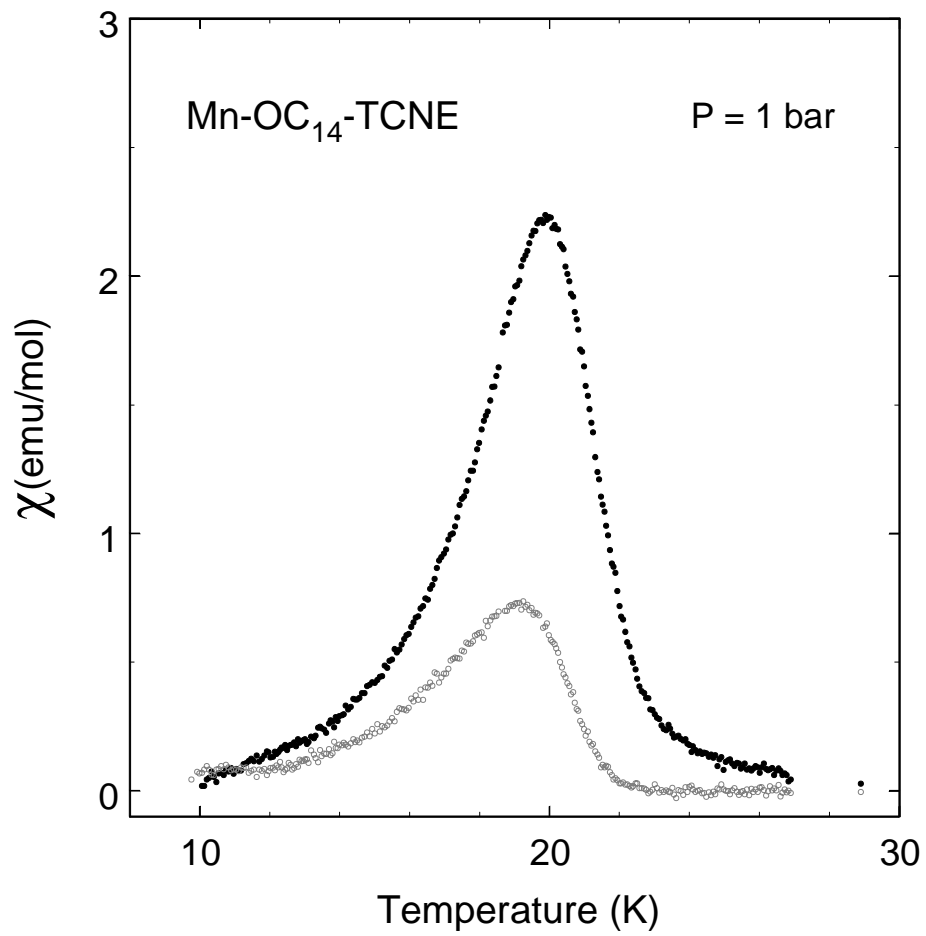


Fig. 2

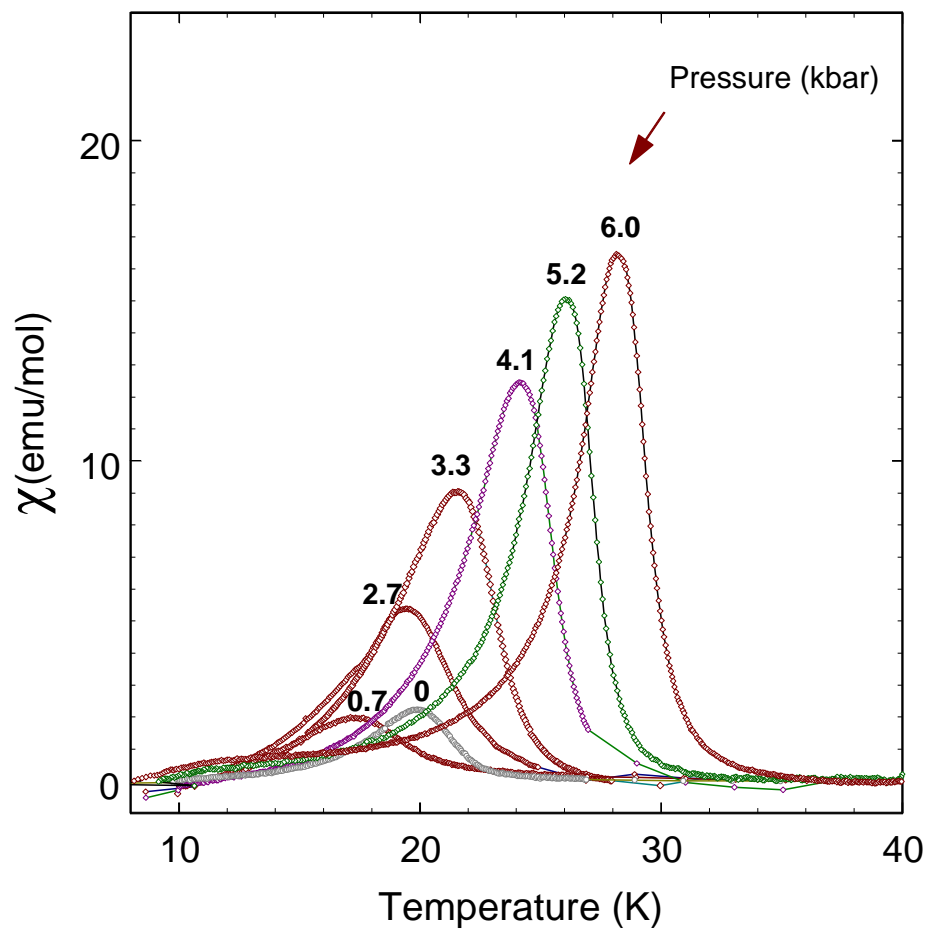


Fig. 3

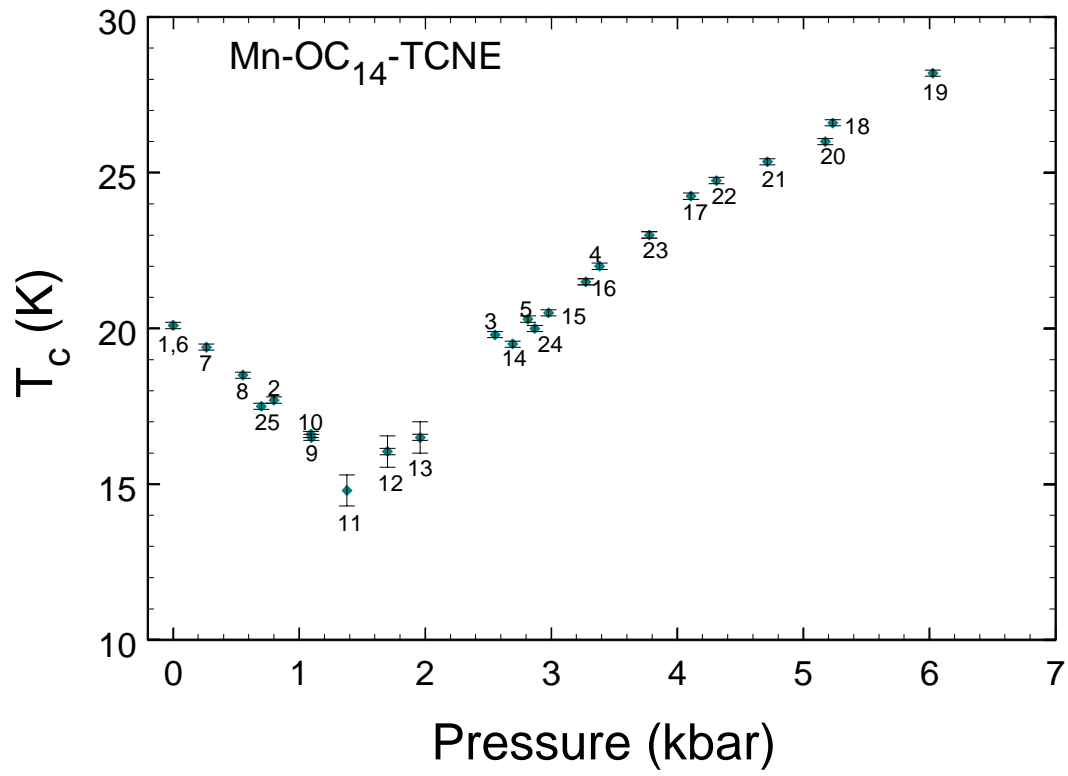


Fig. 4a

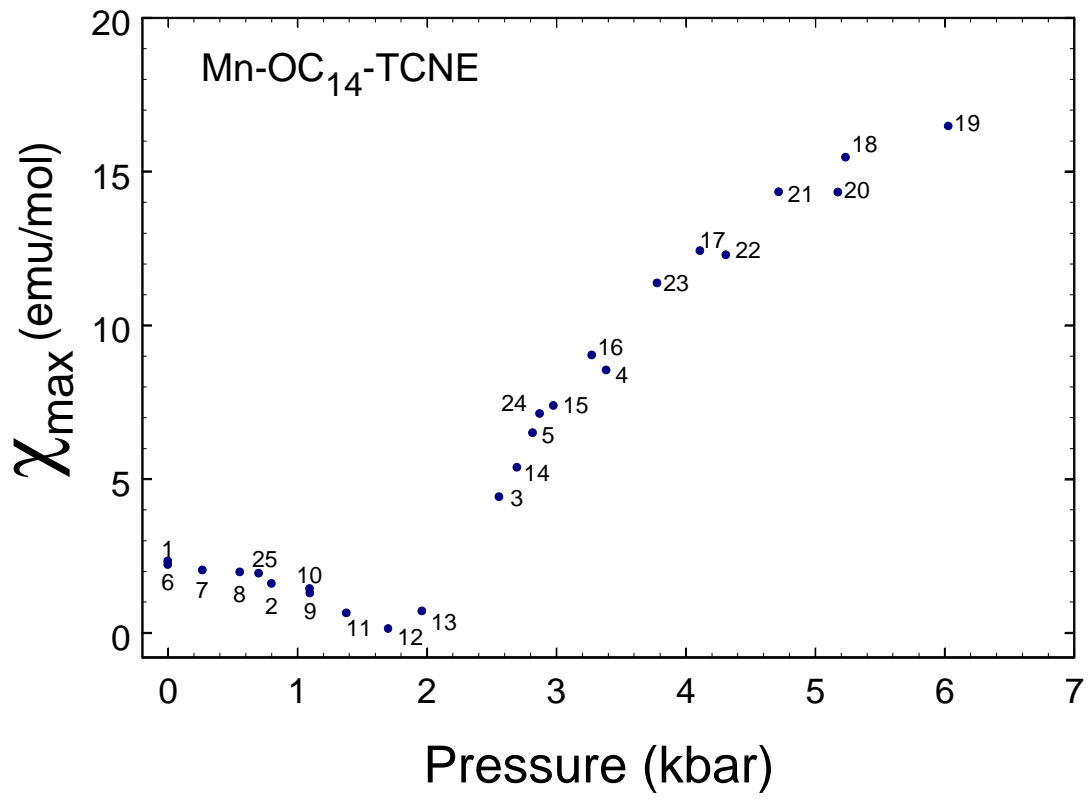


Fig. 4b

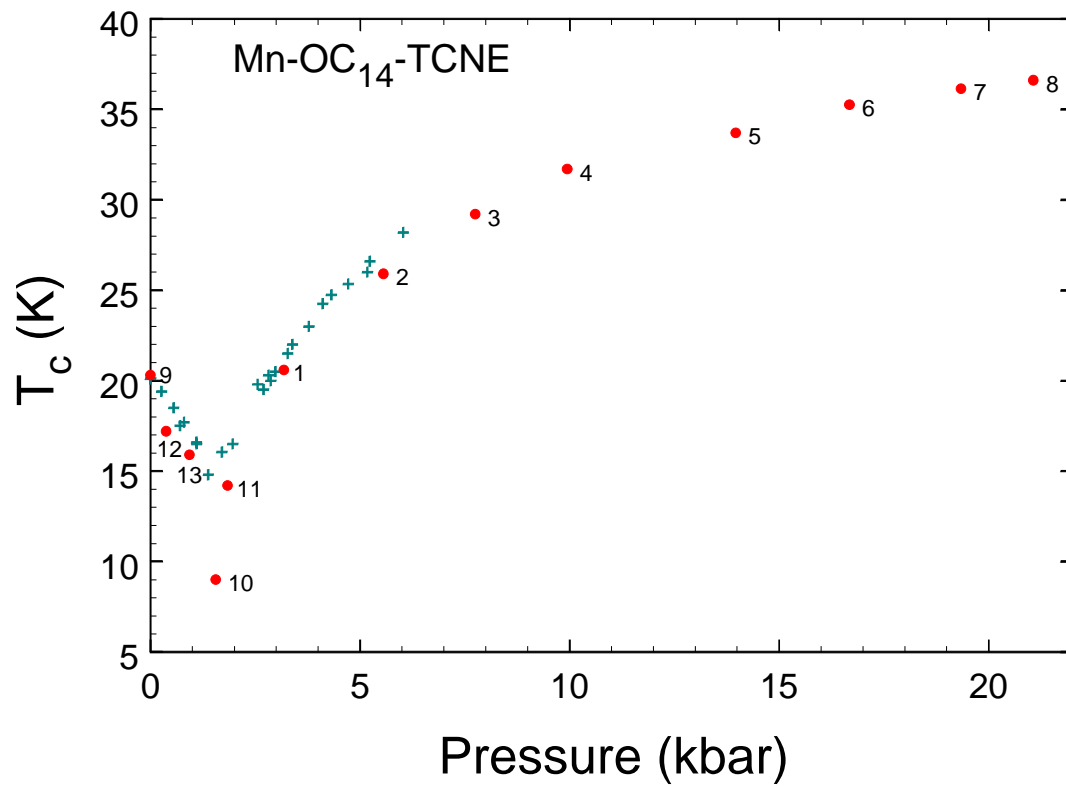


Fig. 5