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# New antiferromagnetic Mn(II) pivalate polymer: synthesis and reactivity

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**Abstract**

An antiferromagnetic pivalate polymer complex $[Mn(OOCCMe_3)_2(EtOH)]_n$ (**1**) has been prepared by the reaction between $MnCl_2 \cdot 4H_2O$ and $KOOCCMe_3$ in EtOH. The reaction of **1** with 2,6-diaminopyridine (L) in MeCN resulted in an antiferromagnetic binuclear $L_2Mn_2(\mu\text{-}OOCCMe_3)_4$ (**2**) complex solvated with the four acetonitrile molecules. The oxidation of **1** was shown to give rise to a hexanuclear pivalate cluster $Mn_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(HOOCCMe_3)(HOEt)_3$ (**3**). Both the X-ray and the thermographic studies revealed low temperature phase transitions for **1** and **2**.


*Keywords:* Pivalate manganese(II) clusters; X-ray structures; Magnetic property; Thermographic study; Solid state phase transitions

Chemistry of transition metal carboxylate complexes is the subject of a considerable literature to a large measure because of their role in catalytic [1] and enzymatic processes [2–5]. Magnetic properties of polynuclear transition metal carboxylates with high spin metal ions and availability of intra and intermolecular spin–spin interactions are of great interest. In this paper, we report the synthesis, structure and magnetic properties of a new pivalate polymer with high spin Mn(II) ions ($S = 5/2$) and its reactions.

The interaction of $MnCl_2 \cdot 4H_2O$ with potassium pivalate (reagent ratio 1:2) in EtOH at 78 °C was found to result in the formation of new air sensitive coordination polymer $[Mn(OOCCMe_3)_2(HOEt)]_n$ (**1**) in a good yield (87%). According to the X-ray data [6] (Fig. 1), compound **1** contains the chains of the Mn(HOEt) fragments (Mn–Mn 3.892(1) Å, Mn–Mn–Mn angle 146.9°; Mn–O 2.176(3) Å) bridged by the pairs of carboxylate groups (Mn–O 2.078(2)–2.157(2) Å).

The polymer **1** exhibits antiferromagnetic properties with the $\mu_{eff}$ value 5.693 $\mu_B$ decreasing monotonically up to 1.807 $\mu_B$ (calculated for mononuclear unit) within the temperature range 300–2 K (Fig. 2(a)). However, thermographic study [7] revealed the polymer **1** to undergo a phase transition in the range 128–193 K (Fig. 2(b)).

The polymer **1** reacts with 2,6-diaminopyridine (L) in MeCN solution giving rise to a binuclear complex $L_2Mn_2(\mu\text{-}OOCCMe_3)_4$ (**2**) with the "China lantern" structure that was isolated as a solvate with four MeCN molecules. The X-ray study [8] shows that the Mn–Mn

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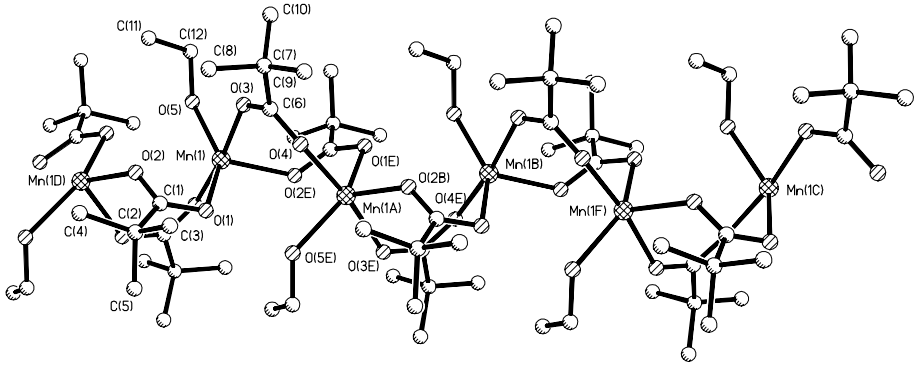


Fig. 1. Fragment of the polymeric compound $[Mn(OOCCMe_3)_2(EtOH)]_n$ (**1**).

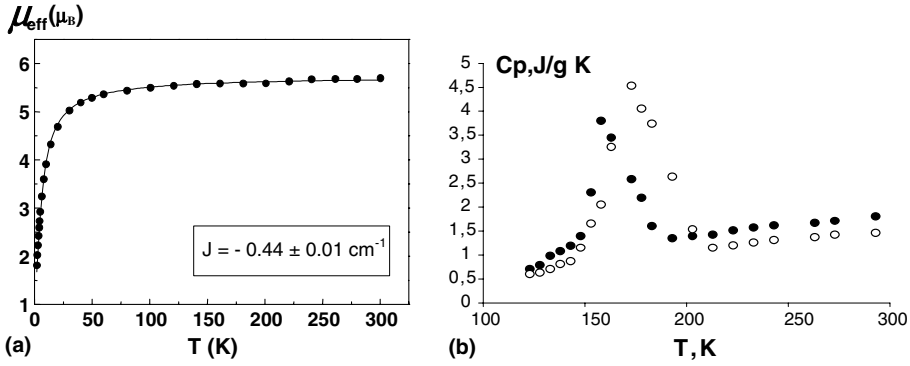


Fig. 2. The magnetic properties of **1** (a) and low temperature phase transitions (b) for the polymer **1** and the binuclear complex **2**.

distance in the metal carboxylate core of **2** is non-bonding (3.084(2) Å) as well as in similar Mn(II) complexes $L_2Mn_2(\mu\text{-}OOCR)_4$ with L = quinoline (3.131(2) Å, R = $Ph_2CH$; 3.168(4) Å, R = $Ph_2MeC$ [9]). The amino group protons of axial ligands L in **2** are bound via hydrogen bonds with the solvating MeCN molecules forming the supramolecular unit **2** · 4MeCN (Fig. 3).

The magnetic behavior of complex **2** (Fig. 4) within the framework of HDVV model corresponds to the antiferromagnetic spin–spin interactions ($-2J = 18.06(2)$ $cm^{-1}$, $g = 2.00$, MSE = 0.078) [10], similarly to the known Mn(II) carboxylates with the "China lantern" structure [9–11]. In spite of the monotonical changes of magnetic moment or susceptibility vs temperature, the first-order phase transition for **2** was also observed ($T = 138$–$213$ K). Monoclinic crystal of **2** (measured at 200 K) transforms into triclinic ones (measured at 120 K). However, the molecular structure did not change significantly (Mn–Mn 3.119(4) Å at 120 °C for **2**).

The polymer **1** was found to react with air in EtOH at 80 °C with the formation of the hexanuclear cluster $Mn_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(HOOCCMe_3)(HOEt)_3$ (**3**) with the Mn(II) and Mn(III) atoms. According to the X-ray study [12], cluster **3** was isolated as a solvate with three EtOH molecules (**3** · 3EtOH). The metal carboxylate $Mn_6(O)_2(OOCCMe_3)_{10}$ core in **3** revealed a geometry (Mn-$\mu_4$-O 2.030(9) Å, Mn–O(OOCR) 2.060(11) Å) (Fig. 5), which was observed early for the similar compounds [13].

All operations including the synthesis of the Mn(II) complexes were carried out in argon atmosphere using standard Schlenk techniques. Infrared spectra were obtained from a Specord M82 spectrometer in KBr pellets. The temperature dependence of the magnetic susceptibility ($\chi_m$) was determined from SQUID-magnetometer MPMS-5S Quantum Design in the temperature range 300–2 K. Details of the calculation of the magnetic moment ($\mu_{eff} \approx (8\chi_m T)^{0.5}$) were described elsewhere [10]. The compounds **1**–**3** were prepared as follows.

Reaction mixture of 0.5 g (2.53 mmol) of $MnCl_2 \cdot 4H_2O$ and 0.71 g (5.06 mmol), $KOOCCMe_3$ was refluxed in 15 ml of EtOH at 78 °C for 10 min. When the $MnCl_2 \cdot 4H_2O$ crystals were dissolved and the residue of KCl formed was filtered off, the colorless solution was cooled to ~20 °C. The white crystals formed (suitable for the X-ray investigation) were separated from the solution by decantation, washed with cold EtOH (−15 °C) and dried in vacuo. Yield of $[Mn(\mu\text{-}OOCCMe_3)_2(EtOH)]_n$ (**1**) is equal to 0.67 g (87%). Found (%): C, 47.3; H, 7.7. $C_{12}H_{24}MnO_5$ (%): C, 47.53; H,