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FULL PAPER

Synthesis and characterization of two manganese phosphonocarboxylates: $Mn_3(O_3PCH_2COO)_2$ and $Mn_3(O_3PCH_2CH_2COO)_2$

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The hydrothermal synthesis and single crystal XRD characterization have been performed for two manganese phosphonocarboxylates, $Mn_3(O_3PCH_2COO)_2$ **1** and $Mn_3(O_3PCH_2CH_2COO)_2$ **2**. Compound **2** forms a pillared structure related to that of the analogous zinc compound and **1** exhibits a three-dimensional network; MnO_5 and MnO_6 polyhedra are observed and all oxygens take part in coordination of the Mn^{2+} ions. Magnetization measurements of **1** and **2** indicate weak ferromagnetic and antiferromagnetic ordering, respectively, at low temperatures. Thermogravimetric analyses show the structure to be stable up to 430 and 400 °C for **1** and **2**, respectively.

Introduction

Open-framework hybrid materials with organic and inorganic moieties are an attractive field of research due to their composite properties and the possibility of tuning their chemistry.[1] The potential of these hybrid materials lies in their use as sorbents, ion exchangers, catalysts or charge storage materials. Striking examples are the metal oxide *meso*-structures, which are formed with the aid of organic surfactants.[2] The use of bifunctional anionic units in this field, *e.g.* diphosphonates ($[O_3P–R–PO_3]^{4-}$),[3] aminophosphonates ($[O_3P–R–NH_2]^{2-}$),[4] and phosphonocarboxylates ($[O_3P–R–COO]^{3-}$), has led to many new materials. These contain a $PO_3/NH_2/CO_2/M$ inorganic core separated by tunable organic units (R = alkyl or aryl) bound to the phosphonate, carboxylate or amino groups. Whereas the chemistry of metal phosphonates has been investigated in detail[5] and led to a large number of interesting architectures, only a few metal phosphonocarboxylates have been reported. Thus, phosphonocarboxylates of the following metals are known: Al,[6] Ga,[7] Pb,[8] Sn,[9] Bi,[10] Zn,[11] Cu,[12] Co,[13] V,[14] Fe,[15] Zr,[16] Pr.[17] Their structural variety ranges from three-dimensional open-frameworks (*e.g.* $Pb_3(O_3PCH_2CH_2COO)_2$ and $Co_3(O_3PCH_2CH_2COO)_2·6H_2O$), to pillared (*e.g.* $Zn_3(O_3PCH_2CH_2COO)_2$ and $Pr(O_3PCH_2COO)$) and layered materials (*e.g.* $Al(O_3PCH_2COO)·3H_2O$ and $Zr(O_3PCH_2COOH)_2$). With $MnZn_2(O_3PCH_2CH_2COO)_2$ a material with two different metal atoms that is isostructural to the all Zn containing compound has also been described.[18] The all Mn containing compound was mentioned to be isostructural, based on the X-ray powder pattern, but no conclusive proof was given. In this paper we describe the hydrothermal synthesis and structural elucidation, as well as the thermal and magnetic properties, of the two phosphonocarboxylates $Mn_3(O_3PCH_2COO)_2$ **1** and $Mn_3(O_3PCH_2CH_2COO)_2$ **2**.

Experimental

Synthesis

The compounds $Mn_3(O_3PCH_2COO)_2$ **1** and $Mn_3(O_3PCH_2CH_2COO)_2$ **2** were synthesized by hydrothermal reactions of $MnCl_2·4H_2O$ and $H_2O_3PCH_2COOH$ or $H_2O_3PCH_2CH_2COOH$, respectively. In a typical experiment, 396 mg (2 mmol) of $MnCl_2·4H_2O$ and 154 mg (1 mmol) of phosphonopropionic acid were mixed in 10 g water. After the pH value was adjusted to 4 using 4 M NaOH, the reaction mixture was stirred to obtain homogeneity, transferred to a 23 ml PTFE (polytetrafluoroethylene) bottle and sealed in a stainless steel autoclave (Parr, USA). The reaction was carried out at 150 °C for 48 h under autogenous pressure. The resulting single phase product, which contained plate-like cystals, was filtered off and washed thoroughly with deionized water. Compound **1** was similarly prepared from 396 mg (2 mmol) $MnCl_2·4H_2O$ and 140 mg (1 mmol) phosphonoacetic acid, adjusting the H^+ concentration to pH 5 using 4 M NaOH.

Characterization

Powder X-ray diffraction patterns were recorded on a Scintag X2 instrument using Cu-Kα radiation. Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851 instrument coupled to a Balzer ThermoStar Mass Spectrometer, GSD 300 T, for identification of the volatile products. The samples were heated under nitrogen from room temperature to 1000 °C at a rate of 5 °C min^{-1}. IR spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer in the spectral range 4000–400 cm^{-1} using the KBr disk method. The magnetic susceptibility data were recorded over the temperature range 5–300 K using a SQUID magnetometer, Quantum Design Model 1802. The microcrystalline samples were zero-field cooled (z.f.c.) to 5 K and the magnetization measured on heating to 300 K in an applied field of 5000 G.

Single crystal X-ray diffraction analyses

Suitable single crystals of compounds **1** and **2** were carefully selected under a polarizing microscope. Single crystal structure determinations by X-ray diffraction were performed at room temperature on a Siemens Smart-CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å). Crystal data for **1**, $Mn_3(O_3PCH_2COO)_2$: triclinic, space group $P\bar{1}$, $a = 6.3922(6)$, $b = 8.4863(8)$, $c = 10.0086(9)$ Å, $\alpha = 106.187(1)$, $\beta = 96.428(2)$, $\gamma = 101.436(2)°$, $V = 502.92(8)$ Å^3, $Z = 2$, $M = 438.38$, $\mu = 4.078$ mm^{-1}, total data 5198 reflections, observed data 2260 reflections (1978 with $I > 2\sigma(I)$), $R(\text{int}) = 0.0525$, $R1 = 0.0381$, $wR2 = 0.0795$ (all data). Crystal data for **2**, $Mn_3(O_3PCH_2CH_2COO)_2$: monoclinic,

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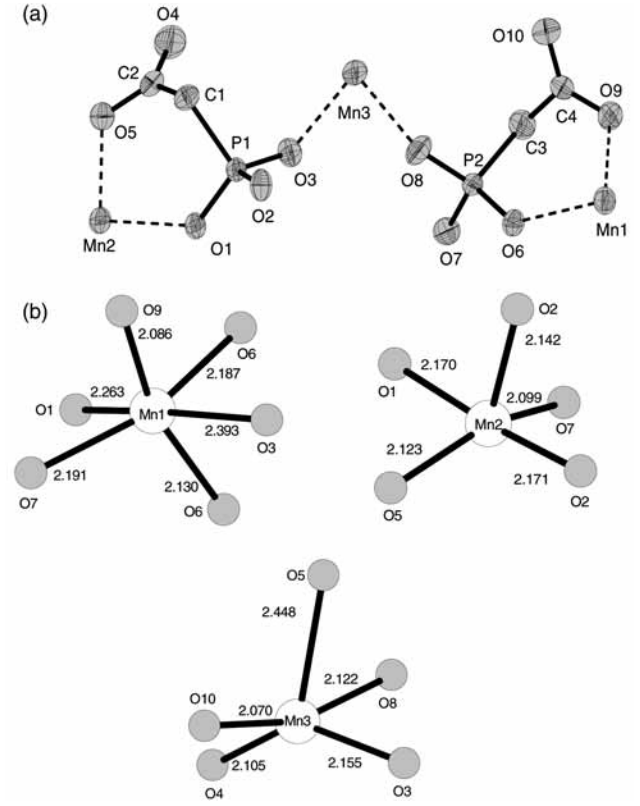

Fig. 1 (a) Asymmetric unit of $Mn_3(O_3PCH_2COO)_2$. Thermal ellipsoids are shown at 75% probability. (b) MnO polyhedra in $Mn_3(O_3PCH_2COO)_2$.

space group $P2_1/c$, $a = 8.207(3)$, $b = 9.340(3)$, $c = 9.188(3)$ Å, $\beta = 104.91(1)°$, $V = 680.5(4)$ Å^3, $Z = 2$, $M = 466.88$, $\mu = 3.021$ mm^{-1}, total data 4102 reflections, observed data 1561 reflections (1124 with $I > 2\sigma(I)$), $R(\mathrm{int}) = 0.0878$, $R1 = 0.0889$, $wR2 = 0.2329$ ($I > 2\sigma(I)$).

For the data processing, structure solution and structure refinement the program package SHELXTL[22] was used. The structure of compound **1** could only be solved in the analog acentric space group $P1$. Using the program PLATON 98[19] the inversion center was found and the input file for refinement in the space group $P\bar{1}$ was generated. The graphic program DIAMOND[20] was used to draw the structures. For both compounds the positions of the H atoms could not be located from the Fourier difference maps. They were therefore calculated and refined using the riding model with fixed C–H distances.

CCDC reference number 186/2210.

See http://www.rsc.org/suppdata/dt/b0/b006411o/ for crystallographic files in .cif format.

Results and discussion

X-Ray diffraction and crystal structure

Both compounds **1** and **2** have been obtained as monophasic polycrystalline products as well as in the form of single crystals. This was established by comparing the measured and simulated powder patterns using the program POWDERCELL.[21] $Mn_3(O_3PCH_2COO)_2$, **1**, forms a three-dimensional framework structure. The asymmetric unit contains 19 non-hydrogen atoms and is shown in Fig. 1(a); selected bond lengths and angles are given in Table 1. Three crystallographically independent Mn^{2+} ions and two $O_3PCH_2COO^{3-}$ ions are observed. Whereas Mn1 forms MnO_6 octahedra, Mn2 and Mn3 are surrounded by five oxygen atoms with bond lengths up to 2.45 Å [Fig. 1(b)]. Mn2 and Mn3 are associated with a sixth oxygen (O8 and O4 from a phosphonate and a carboxylate group, respectively) at a distance of 2.71 Å, which is very long compared to Mn–O distances in other manganese phosphates. Taking all six oxygen atoms into account the bond valence sums change from 2.002, 1.942, and 1.846 to 2.002, 2.025, and 1.929 for Mn1, Mn2, and Mn3, leading only to a minor improvement. The MnO polyhedra are linked by corners and edges to form a complex three-dimensional framework. The phosphonoacetate ions act as chelating as well as bridging ligands. The first $O_3PCH_2COO^{3-}$ ion chelates Mn2 *via* O1 and O5, forming a six-membered P–C–C–O–Mn–O ring in an envelope conformation. All oxygens except O4 are bridging two Mn^{2+} ions. The second anion chelates Mn1 *via* O6 and O9 in the same way, forming a ring with a distorted chair conformation. Only O7 and O6 are bridging two Mn^{2+} ions. Thus a three-dimensional framework is formed with narrow channels along [100] (approximate dimensions: 380 × 1000 pm) into which the H atoms are pointing (Fig. 2). The structure can also be seen as made up of ribbons of $Mn(1)O_6$ and $Mn(2)O_5$ polyhedra which are connected *via* the $Mn(3)O_5$ units to form layers in the *a*,*b* plane (Fig. 3). These layers are connected by the carboxylate groups, thus forming the three-dimensional framework.

Table 1 Selected bond lengths (pm) and angles (°) for compound **1**

P1–O	152.8(2)–153.1(2)	Mn1–O7	219.1(2)
P1–C1	181.9(3)	Mn1–O9	208.6(2)
C1–C2	151.2(5)	Mn2–O1	217.0(3)
C2–O	124.4(4), 128.1(5)	Mn2–O2^{ii}	214.2(2)
P2–O	151.3(2)–153.4(2)	Mn2–O2^{i}	217.1(2)
P2–C3	180.6(3)	Mn2–O5	212.3(2)
C3–C4	153.0(5)	Mn2–O7	209.9(2)
C4–O	126.0(4), 125.5(5)	Mn3–O3	215.5(2)
Mn1–O1	226.3(2)	Mn3–O4	210.5(2)
Mn1–O3	239.3(2)	Mn3–O5	244.8(3)
Mn1–O6^{i}	213.0(2)	Mn3–O8	212.2(2)
Mn1–O6^{ii}	218.7(2)	Mn3–O10	207.0(3)
O–P1–O	109.9(2)–113.6(2)	O–P2–O	108.5(2)–113.3(2)
O–P1–C	106.7(2)–108.1(2)	O–P2–C	106.3(2)–110.2(2)
O–C2–C1	122.2(3), 117.5(3)	O–C4–C3	120.7(3), 117.6(3)
O4–C2–O5	120.2(3)	O10–C4–O9	121.7(3)

Symmetry codes: (i) $-1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 2 - y, 1 - z$.

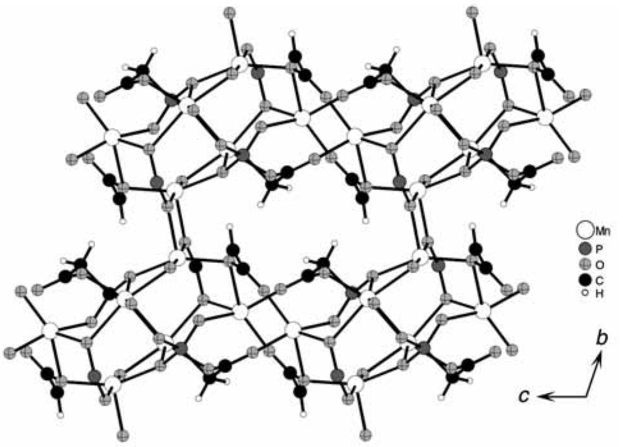

Fig. 2 Three-dimensional structure of $Mn_3(O_3PCH_2COO)_2$ showing H atoms extending into narrow channels along [100].

$Mn_3(O_3PCH_2CH_2COO)_2$ **2** forms a pillared structure related, but not isotypic, to that of $Zn_2Mn(O_3PCH_2CH_2COO)_2$ and $Zn_3(O_3PCH_2CH_2COO)_2$.[18] The asymmetric unit contains 11 non-hydrogen atoms and is shown in Fig. 4(a); selected bond lengths and angles are given in Table 2. Fig. 4(b) shows the coordination environment of the two crystallographically independent Mn atoms. Mn1 is octahedrally surrounded by four oxygens of the phosphonate group and two carboxylate oxygens. The other manganese (Mn2) is five-coordinated by

Table 2 Selected bond lengths (pm) and angles (°) for compound **2**

P1–O1	152.8(7)	C1–C2	148.0(14)
P1–O2	155.7(7)	C2–C3	152.9(15)
P1–O3	153.1(7)	C3–O4	125.8(12)
P1–C1	180.8(10)	C3–O5	126.7(14)
Mn1–O (6×)	213.9(7)–217.0(6)	Mn2–O (5×)	203.2(8)–225.3(7)
O5–C3–O6	118.3(9)	O1–P1–O3	112.9(4)
O5–C3–C2	117.1(10)	O1–P1–O2	104.2(4)
O6–C3–C2	118.3(9)	O3–P1–O2	111.0(4)
C2–C1–P1	112.4(7)	O1–P1–C1	109.8(4)
C1–C2–C3	114.3(9)	O3–P1–C1	109.4(5)

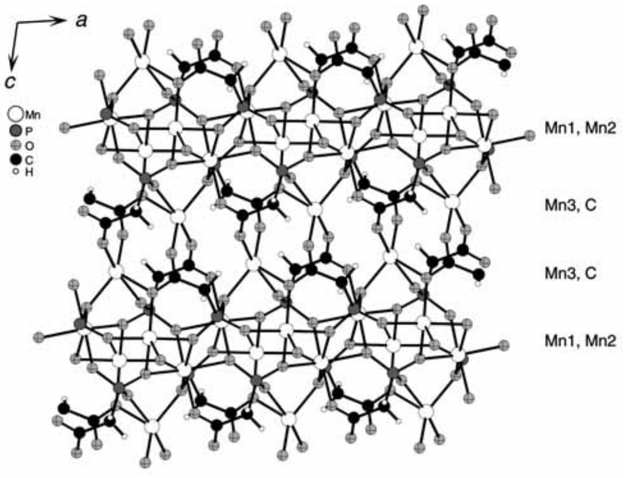

Fig. 3 Three-dimensional structure of $Mn_3(O_3PCH_2COO)_2$ made up of ribbons of $Mn(1)O_6$ and $Mn(2)O_5$ polyhedra which are connected *via* the $Mn(3)O_5$ units to form layers in the *a*,*b* plane. These layers are connected by the carboxylate groups.

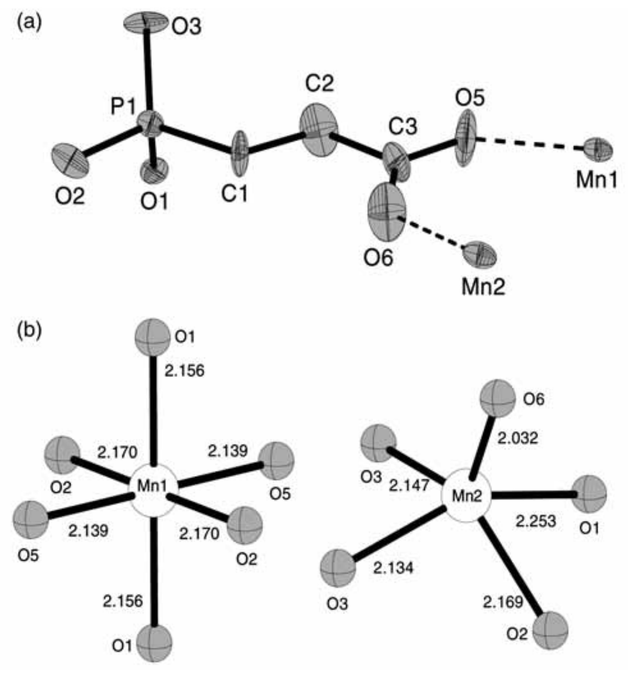

Fig. 4 (a) Asymmetric unit of $Mn_3(O_3PCH_2CH_2COO)_2$. Thermal ellipsoids are shown at 75% probability. (b) MnO polyhedra in $Mn_3(O_3PCH_2CH_2COO)_2$.

four oxygens of the phosphonate group and one of the carboxylate group. The five-coordinated polyhedra form edge-sharing pairs (Fig. 5a). These pairs are corner linked to the MnO_6 octahedra forming layers in the *b*,*c* plane. The phosphonopropionate ions act as bridging as well as chelating ligands. In contrast to compound **1**, the chelation involves only the oxygens (O1, O2) of the O_3PC group, thereby forming a four membered ring (P1, O1, Mn2, O2). Whereas the carboxylate oxygens coordinate only one manganese ion, all phosphonate oxygens are three-coordinated, thus connecting two manganese ions at the same time. Fig. 5(b) shows the connection of the O_3P group holding the MnO_5 and MnO_6 polyhedra together. Comparison of these layers with those formed in $Zn_2Mn(O_3PCH_2CH_2COO)_2$ and $Zn_3(O_3PCH_2CH_2COO)_2$ shows that fivefold coordination of the Mn2 is accomplished by rotation of the O_3PC group leading to the fifth bond which is shown as a dashed line. As found in the zinc compounds, the organic groups are approximately perpendicular to the layers. Thus the coordination of the carboxyl oxygens to the manganese ions leads to formation of a three-dimensional framework with a pillared structure (Fig. 6).

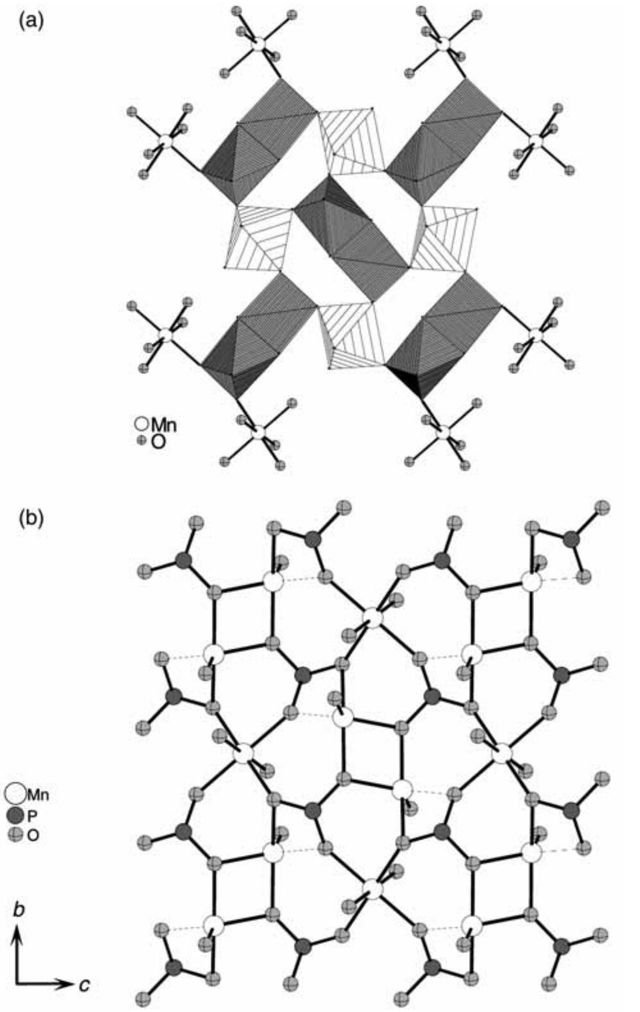

Fig. 5 Layered Mn–O arrangement in $Mn_3(O_3PCH_2CH_2COO)_2$. (a) The five-coordinated polyhedra forming edge-sharing Mn_2O_{10} pairs. These pairs are corner linked to the MnO_6 octahedra forming layers in the *b*,*c* plane. (b) Connection of the O_3PC, MnO_5 and MnO_6 groups. In comparison to the layers in $Zn_2Mn(O_3PCH_2CH_2COO)_2$ a fivefold coordination of Mn2 is accomplished by rotation of the O_3PC group leading to the fifth bond which is shown as a dashed line.

TG/MS measurements showed that the compounds are stable in an inert atmosphere up to 430 and 400 °C for **1** and **2**, respectively. As volatile decomposition products at higher temperatures only H_2O and CO_2 have been identified.

Magnetic measurement

Fig. 7 shows the inverse magnetic susceptibility of $Mn_3(O_3PCH_2COO)_2$ (top) and $Mn_3(O_3PCH_2CH_2COO)_2$ (bottom) plotted as a function of temperature. At higher temperatures both compounds exhibit Curie–Weiss behavior and the data were least-squares fitted by a Curie–Weiss equation $\chi_m = C/(T - \theta)$ where $C = 4.16$ emu K mol^{-1} and $\theta = -43.03$ K for **1**

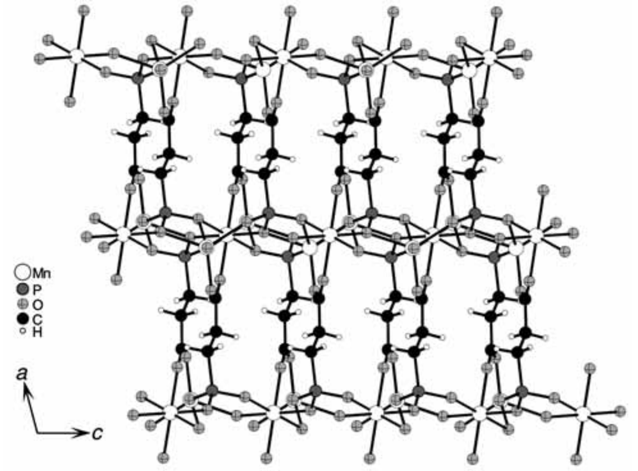

Fig. 6 Pillared structure of $Mn_3(O_3PCH_2CH_2COO)_2$ with the organic groups approximately perpendicular to the layers.

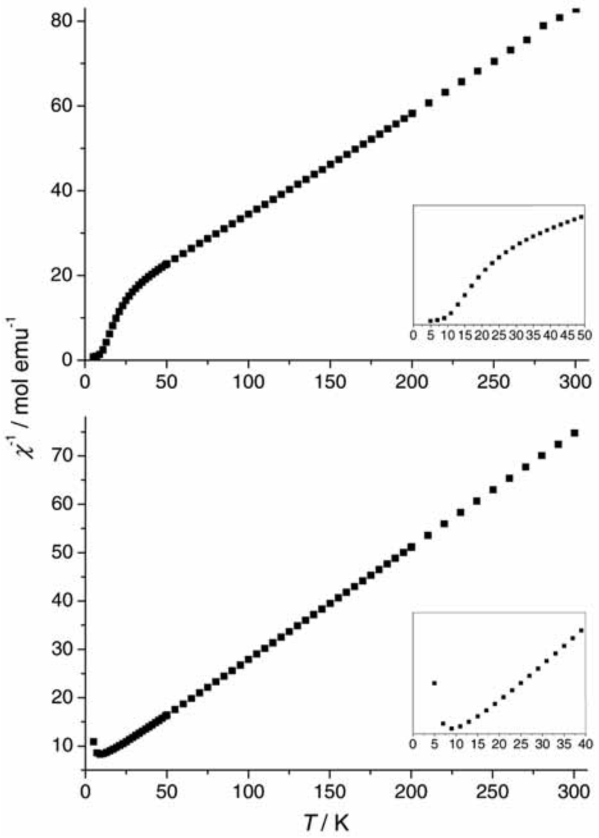

Fig. 7 The inverse molar magnetic susceptibility of polycrystalline $Mn_3(O_3PCH_2CH_2COO)_2$ (bottom) and $Mn_3(O_3PCH_2COO)_2$ (top) plotted as a function of the temperature (5–300 K).

and $C = 4.30$ emu K mol^{-1} and $\theta = -20.40$ K for **2**. From the relation $C = (N\mu_{\mathrm{eff}})/(2k_{\mathrm{B}})$ one obtains the effective magnetic moments μ_{eff} per metal atom 5.77 and 5.87 μ_{B} for **1** and **2**, respectively, which are slightly smaller than the ideal value of 5.92 μ_{B} for a high-spin d^5 system. $Mn_3(O_3PCH_2COO)_2$ undergoes a gradual transition below 25 K to a state that appears to be very weakly ferromagnetic (see insert); in the light of the negative Weiss constant θ, it is perhaps a canted antiferromagnet. $Mn_3(O_3PCH_2CH_2COO)_2$ undergoes an antiferromagnetic ordering transition at 9 K (see insert) which is consistent with its negative Weiss constant.

IR spectroscopic study

The two manganese phosphonocarboxylates display similar characteristics in their IR spectra, which are shown in Fig. 8. Furthermore, the spectrum of **1** is similar to the one reported.[18] The spectra confirm the absence of water in the crystal structure and show the presence of CH_2 groups (2930, 3000 cm^{-1}). The coordination of the carboxylate function is seen by a shift from the expected value for the uncoordinated carboxylic acid (ν(C–O) typically around 1725–1700 cm^{-1}) to values of 1583 and 1405 cm^{-1} for **1** as well as 1621/1550 and 1427/1379 cm^{-1} for **2**; these arise from the symmetric and asymmetric stretching modes of the C–O bonds of the carboxylate group. The set of intense bands from 940 to 1200 cm^{-1} are due to the stretching vibrations of the tetrahedral CPO_3 group.

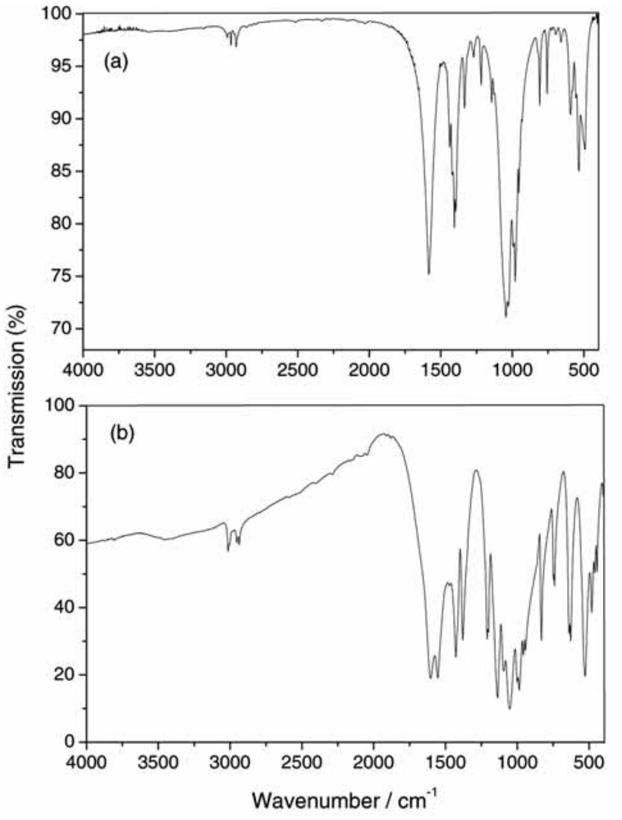

Fig. 8 IR spectra of $Mn_3(O_3PCH_2CH_2COO)_2$ (bottom) and $Mn_3(O_3PCH_2COO)_2$ (top).

Conclusion

Two manganese phosphonocarboxylates, $Mn_3(O_3PCH_2COO)_2$ **1** and $Mn_3(O_3PCH_2CH_2COO)_2$ **2**, have been described. The extension of the organic moiety from CH_2 to CH_2CH_2 leads to an extensive change in the crystal structure. It was shown unambiguously that **2** is not isostructural to $Zn_3(O_3PCH_2CH_2COO)_2$. Magnetic measurements showed a Curie–Weiss behavior at higher temperatures and weak ferromagnetic and antiferromagnetic ordering for **1** and **2**, respectively, at low temperatures.

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