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Magnetic properties of a new 3D-cobalt phosphonate: $Co_3(O_3PC_2H_4CO_2)_2$

Pierre Rabu,*[a] **Pascal Janvier**[b] **and Bruno Bujoli***[b]

[a]*IPCMS, UMR CNRS 7406, Groupe des Matériaux Inorganiques, 23 rue du Loess, 67037 Strasbourg cedex, France*
[b]*Laboratoire de Synthèse Organique, UMR CNRS 6513, Faculté des Sciences et des Techniques, BP 92208, 2, rue de la Houssinière, 44322 Nantes cedex 03, France. E-mail: Bruno.Bujoli@chimie.univ-nantes.fr*

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The magnetic properties of a new cobalt(II) phosphonate have been investigated. The compound is isostructural with the pillared layered metal phosphonates $M_3(O_3PC_2H_4CO_2)_2$, M = Zn, Mn. In this structure, the magnetic transition metal ions are arranged within layers formed by the interconnection of CoO_4 tetrahedra and CoO_6 octahedra. The ac and dc magnetic susceptibilities and magnetization measurements show that $Co_3(O_3PC_2H_4CO_2)_2$ is a canted antiferromagnet at $T_N = 15.5$ K. Below T_N, the hysteresis cycles exhibit an S shape related to a spin flop effect. The specific heat measurements indicate that large short-range correlations are present above T_N in relation with the layered character of the structure.

Metal phosphonates are organic–inorganic hybrid materials in which the nature of the organic moiety, covalently bonded to the inorganic portion, can be designed to confer specific properties to this class of solids. For this reason, there has been an exponential growth of research in the exploration of their chemistry, and the use of phosphonates as ion exchangers, sensors, proton conductors, nonlinear optical materials, catalysts, photochemically active materials and hosts for intercalation is now well documented in the literature.[1]

One attractive feature is the 2D character of most phosphonate compounds, in which the metal-containing layers are separated by organic sheets, thus offering the possibility of magnetic studies in confined 2D systems. In the literature, detailed experiments have been performed on the isostructural $M^{II}(O_3PR)\cdot H_2O$ compounds (M^{II} = Mn, Fe, Co, Ni, Cr; R = alkyl, phenyl),[2] a new family of 2D antiferromagnets. Field-induced weak ferromagnetism below 25 K was observed in the iron series, due to spin canting.

The magnetic behaviour of other structural types has also been reported, mainly based on copper[3] and vanadium[4] phosphonates. On the other hand, interesting magnetic properties could also be expected in the cobalt phosphonate series but, until now, the reported magnetic susceptibility measurements only show paramagnetic behaviour because of the presence of isolated cobalt pairs or trimers.[5]

After looking carefully at the structural features of various divalent zinc phosphonates that we had previously prepared, we paid particular attention to $Zn_3(O_3PC_2H_4CO_2)_2$,[6] in which the zinc atoms are found in two types of environments (Fig. 1). One type is coordinated by three oxygen atoms from the phosphonate groups and one oxygen atom from a carboxyl group. These ZnO_4 tetrahedra are arranged in edge-sharing pairs, resulting in Zn–O–Zn–O parallelograms [intermetallic distance: 3.058(1) Å]. The other type of Zn centre is coordinated by two oxygen atoms from two carboxyl groups and four phosphonate oxygen atoms. Each oxygen of the PO_3 groups is bonded to a metal atom, ensuring the connection of the ZnO_4 and ZnO_6 polyhedra within layers in the (*b*,*c*) plane. The organic groups extend roughly perpendicular to these layers, which are linked together *via* the carboxyl moieties, thus leading to a three-dimensional network, with the two oxygen atoms of the CO_2 units bonded to zinc atoms. An interesting feature of this compound lies in the presence of chains (parallel to the *c*-axis) formed by pairs of ZnO_4 tetrahedra interconnected by ZnO_6 octahedra *via* corner-sharing (Fig. 1). For this reason, attempts to prepare a cobalt structural analogue of this compound were made and we describe in this paper the magnetic properties of the resulting solid, $Co_3(O_3PC_2H_4CO_2)_2$.

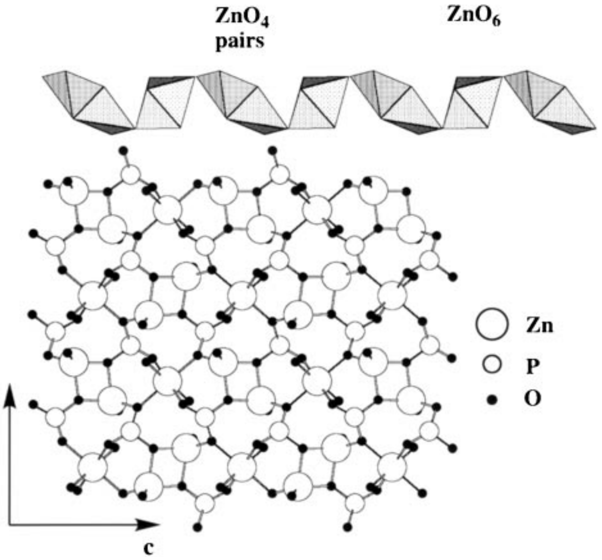

Fig. 1 Schematic representation of a $Zn_3(O_3PC_2H_4CO_2)_2$ layer as seen perpendicular to the *a*-axis. The carbon atoms that are not bound to phosphorus have been omitted for clarity. A chain formed by pairs of ZnO_4 tetrahedra interconnected by ZnO_6 octahedra (along the *c*-axis) is shown.

Experimental

Synthesis and characterization

$Co_3(O_3PC_2H_4CO_2)_2$ was prepared by mixing 2 mmol of cobalt nitrate, 2 mmol of 2-carboxyethylphosphonic acid, 6 mmol of DABCO and 4 ml of water in the PTFE cell (20 ml capacity) of an autoclave. This was then sealed and placed in a drying oven at 180 °C for 7 days. The purple compound, obtained as a powder, was filtered off under suction, washed with water and dried at room temperature (95% yield). Anal. Calc.: P, 12.93; C, 15.05; H, 1.68. Found: P, 12.82; C, 14.95; H, 1.70%. TGA room temperature to 300 °C, 0%. IR (KBr): ν(CO) 1593vs, ν(PO_3) 1075s, 1021s, 985s.

The magnetic measurements were carried out using Vibrating Magnetic Sample equipment (Foner) for magnetization at low temperature (in the range 0–1.6 T), and a MPMS-XL Quantum Design SQUID magnetometer (in the temperature and field ranges 2 K–300 K and 0–4 T, respectively). The latter was also used for ac susceptibility measurements in the frequency range 0–1 kHz. Magnetization measurements have been performed at low temperature by including the sample in a poly(ethyleneglycol) (PEG) matrix in order to avoid the crystallites turning with the applied field. The magnetization values were then scaled with the signal of the pure compound and corrected for the diamagnetic contribution of the PEG. Specific heat measurements were carried out using a quasi-adiabatic setup.[7]

Results

We have recently shown that pillared layered zinc phosphonates can be prepared using functionalized phosphonic acids.[6,8] One of them, $Zn_3(O_3PC_2H_4CO_2)_2$, can easily be prepared starting from 2-carboxyethylphosphonic acid. Later a manganese structural analogue of this product $Mn_3(O_3PC_2H_4CO_2)_2$ was obtained.[9] When the metal source is cobalt nitrate, $Co_3(O_3PC_2H_4CO_2)_2$ is isolated in good yield. We then checked that the cell parameters of this compound [$a=8.168(4)$, $b=9.209(2)$, $c=8.686(5)$ Å, $\beta=105.90(4)°$] were comparable to those reported for $Zn_3(O_3PC_2H_4CO_2)_2$ [$a=8.126(1)$, $b=9.237(1)$, $c=8.587(2)$ Å, $\beta=106.26(3)°$] and $Mn_3(O_3PC_2H_4CO_2)_2$ [$a=8.23(1)$, $b=9.32(2)$, $c=8.25(2)$ Å, $\beta=104.7(2)°$]. Moreover, as FTIR spectroscopy is very sensitive to the metal–O_3P arrangement in metal phosphonates, the strong similarities observed in the IR data collected for the cobalt, manganese and zinc compounds (for the CO, PO_3 and CH_2 absorptions) gives clear evidence that the structural features in these products are entirely similar.

The low field (20 Oe) magnetic susceptibility of $Co_3(O_3PC_2H_4CO_2)_2$ as a function of temperature is displayed in Fig. 2. Two data sets are presented, corresponding to field cooled (FC) and zero-field-cooled (ZFC) measurements. In the inset of the figure, the ZFC χT product decreases with temperature from 7.23 cm^3 K mol^{-1} at 300 K down to an intermediate minimum of 4.00 cm^3 K mol^{-1} at 20 K. A sharp increase is then observed up to a maximum of 19.78 cm^3 K mol^{-1} at $T_C=15.5$ K, followed by a steep fall to zero upon cooling. Accordingly, the ZFC susceptibility shows a sharp maximum at T_C, but the FC susceptibility measured under 20 Oe exhibits a continuous increase and a saturation up to 2.37 cm^3 mol^{-1} at 2 K, indicating a strong field dependence of the magnetic moment. In the high temperature range ($T>200$ K), the inverse susceptibility can be well fitted with a Curie–Weiss law ($C=7.65$ K cm^3 mol^{-1} and $\theta=-13.5$ K). The deduced Curie constant is in agreement with the expected value for one octahedral and two tetrahedral cobalt(II) ions; the Weiss constant is negative, which may be related to both antiferromagnetic interactions and spin–orbit coupling effects for cobalt(II).[10,11]

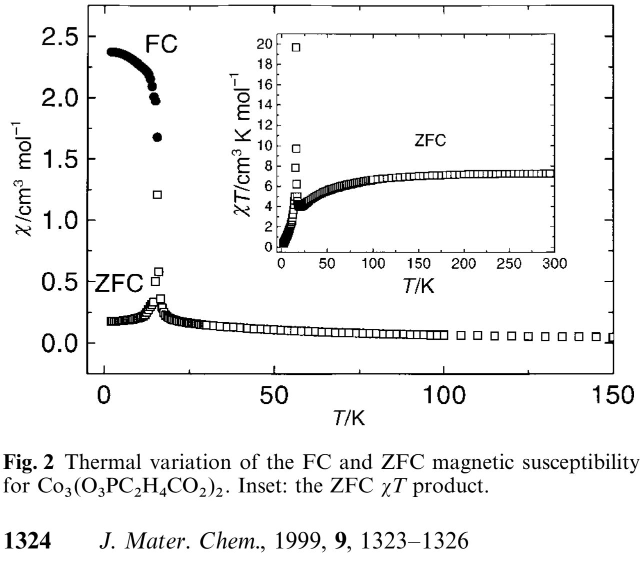

Fig. 2 Thermal variation of the FC and ZFC magnetic susceptibility for $Co_3(O_3PC_2H_4CO_2)_2$. Inset: the ZFC χT product.

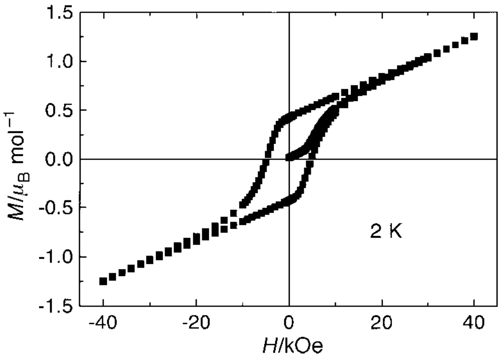

Fig. 3 Initial magnetization and hysteresis cycle for $Co_3(O_3PC_2H_4CO_2)_2$ at 2 K.

The magnetization measurements at 2 K are given in Fig. 3. The initial magnetization increases linearly with the applied field H up to 0.068 μ_B for $H=2400$ Oe, then it grows more rapidly with H. No saturation is observed up to $H=4$ T but a linear variation according to the relation $M=0.43+1.437\times10^{-5}\,H$ (with M in μ_B and H in Oe). Actually, the value of the moment (*ca.* 1.25 μ_B under 4 T) is much lower than expected for three cobalt(II) ions, *i.e.* about 8–9 μ_B depending on the g values.[10,11] The magnetization curves below T_C exhibit an hysteresis effect with a coercive field H_c and a small net magnetization M_r. For instance, $H_c=5000$ Oe and $M_r=0.43$ μ_B mol^{-1} at 2 K. These features are characteristic of weak ferromagnetic behaviour and are observed up to the critical temperature T_C. The H_c and M_r values decrease regularly to vanish at T_C, and an S shape of the hysteresis loop is observed above 7 K [Fig. 4(a) and (b)].

The ac susceptibility has been measured under a 3.5 Oe alternative field at various frequencies (Fig. 5). A maximum of χ' is observed at 15.5 K. In the range 1–100 Hz, the ac susceptibility exhibits an out of phase signal denoted by a peak of χ''. This signal is in agreement with the occurrence of an hysteresis in the magnetization *versus* field curves, and is the signature of ferromagnetic-like behavior. The maximum value of χ' gives the critical temperature $T_C=15.5$ K, in full agreement with the above results. There is no frequency dependence of χ'' below 100 Hz. For higher frequencies (200 Hz and above), the imaginary component seems to disappear but this is difficult to confirm because the measurements become very noisy.

The results of specific heat measurements are plotted in the range 1.2–40 K in Fig. 6. A λ-type anomaly is noted with a maximum at 15.2 K, which agrees well with the T_C value deduced from the ac susceptibility signal. At higher temperatures, the increase of C_p is mainly due to the lattice contribution; however short-range 2D magnetic interaction effects are expected to contribute also above T_C.[12] Accordingly, the high temperature data ($T>30$ K) have been fitted to the relationship $C_p(T)=AT^{-2}+BT^3-CT^5$, where the first term is ascribed to the 2D correlations (Schottky tail) while the others deal with the lattice contribution. After subtracting the latter (solid line in Fig. 6), the magnetic specific heat contribution is deduced. The bumped tail observed above 20 K suggests the existence of significant short-range order effects.

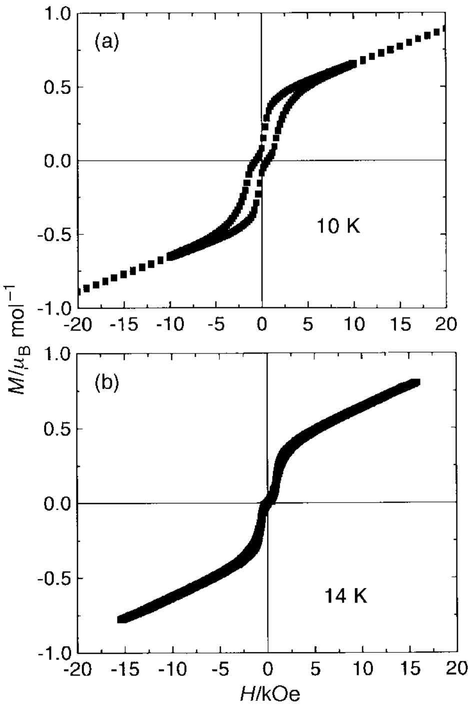

Fig. 4 Magnetization *versus* field cycle for $Co_3(O_3PC_2H_4CO_2)_2$ at (a) 10 K and (b) 14 K.

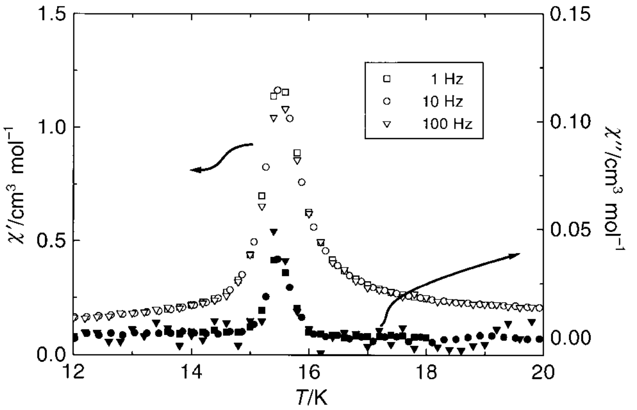

Fig. 5 ac Susceptibility of $Co_3(O_3PC_2H_4CO_2)_2$ under a 3.5 Oe alternative field at 1, 10 and 100 Hz.

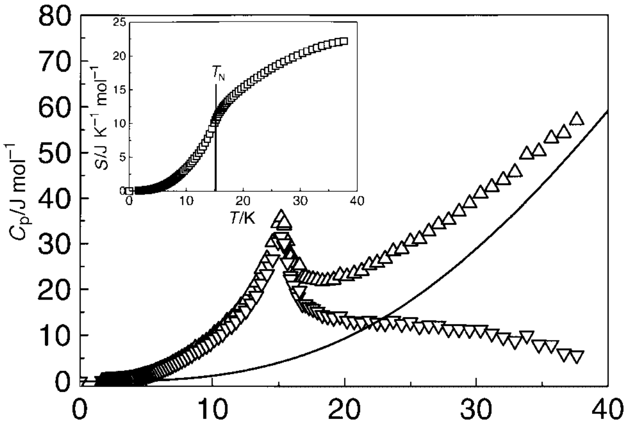

Fig. 6 Low temperature specific heat measurements for $Co_3(O_3PC_2H_4CO_2)_2$: (△) experimental result, (▽) deduced magnetic contribution. The solid line represents the lattice contribution, the corresponding magnetic entropy is plotted in the insert (see text).

However, the uncertainties in the evaluation of the lattice contribution in this temperature region compel us to be cautious towards a detailed analysis.

Discussion

The minimum of χT at 20 K can be linked to a spin–orbit coupling effect for octahedral Co(II).[11,13] However, with this contribution involving only 1/3 of the cobalt ions, the decrease of χT should be less important than is observed. Thus, this decrease is merely due to antiferromagnetic interactions within the plane where the cobalt(II) ions are found alternately in octahedral and pairs of tetrahedral sites. The magnetic coupling occurs through a rather complex network, involving Co–O–Co superexchange pathways (Fig. 7). In this context, the two neighboring Co(1) tetrahedral sites within pairs are coupled through two oxygen bridges [O(1)] and are also coupled with the Co(2) octahedral sites *via* an additonal oxygen bridge [O(2)]. The contribution of the Co–O–P–O–Co and Co–O–C–O–Co exchange pathways has also to be considered, although these are probably weaker.

Below T_C, $Co_3(O_3PC_2H_4CO_2)_2$ behaves as a weak ferromagnet. The decrease of χT along with the very sharp peak at 15.5 K, the weakness of the magnetic moment and the absence of saturation are characteristic of canted antiferromagnetism.[14,15] This situation arises in antiferromagnets when the moments of the antiparallel sub-networks are not strictly aligned (with an angle other than 180°). The extrapolated value of M for $H=0$ at 2 K ($M=0.43\,\mu_B$ mol^{-1}, Fig. 3) compared to the 9 μ_B expected for saturated $Co_3(O_3PC_2H_4CO_2)_2$ gives the mean canting angle $\varphi_m \approx 4°$. The canting effect is due to antisymmetric interactions linked to the symmetry of the exchange pathways joining the magnetic centers, and also to single ion anisotropy.[10,13–15] Many examples of cobalt salts are known to be canted antiferromagnets, such as $CsCoCl_3{\cdot}2H_2O$[16] or $[(CH_3)_3NH]CoCl_3{\cdot}2H_2O$.[17] In $Co_3(O_3PC_2H_4CO_2)_2$, the single ion anisotropy of cobalt(II)[10,11,13] should play a key role. Indeed, the structural features indicate octahedral and tetrahedral environments for the metal atoms, and a noticeable angle between their respective anisotropy axes is expected. It has been shown that both

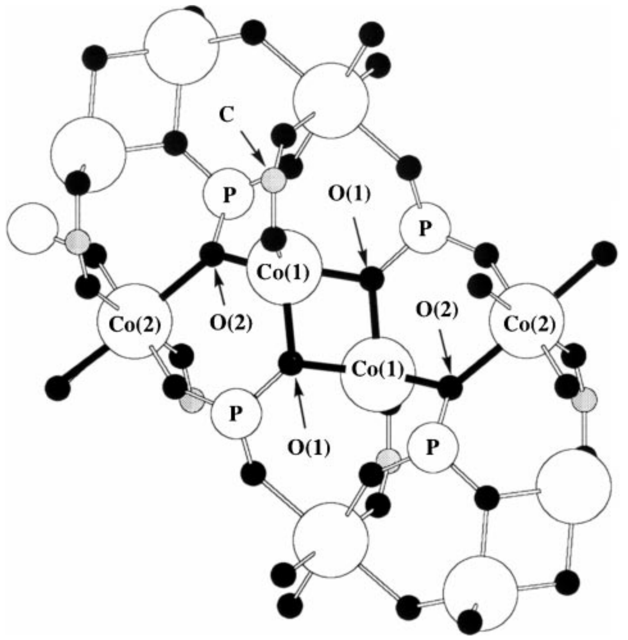

Fig. 7 Representation of the structure of $Co_3(O_3PC_2H_4CO_2)_2$ showing the possible exchange pathways involved in the magnetic properties of this compound (the Co–O–Co superexchange pathways are indicated as bold lines).

antisymmetrical and single ion anisotropy effects are proportional to $\Delta g/g$, where $\Delta g = g - 2$.[15] Thus, the antisymmetrical interaction between the magnetic centers is strongly favoured by the alternation of both types of site, and a competition between the different single ion anisotropies may occur.

On the other hand, the S shape of the magnetization curve occuring at relatively low field ($H < 1000$ Oe) is quite unusual. It looks like a spin flop effect,[10,18] suggesting a quite complex magnetic phase diagram. In the absence of single crystal (anisotropy) measurements it is difficult to conclude definitively on the magnetic structure of $Co_3(O_3PC_2H_4CO_2)_2$. In particular the low-dimensional character of the structure might have a noticeable importance as suggested by the magnetic specific heat, which exhibits a λ-type maximum at T_C and a broad peak at higher temperature. The analysis of the magnetic entropy S (Fig. 6) reveals that the experimental values are below the expected value $R(\log(2\times1/2+1)+2\log(2\times3/2+1)) = 28.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$. This is essentially due to the rough nature of the evaluation of the lattice contribution and also to the fact that the whole magnetic contribution is not achieved at 40 K [$C_p(T)$ is not zero at this temperature]. Nevertheless, it is clear that only a small part of the entropy (less than 50%) is spent at the transition, confirming the occurrence of a large amount of short-range order above T_C.

Thus $Co_3(O_3PC_2H_4CO_2)_2$ appears as a nice example of a 2D canted antiferromagnet with a strong effect of the single ion anisotropy of the cobalt(II) ions on the magnetic behaviour. Neutron diffraction studies should be of great interest in order to detail the arrangement and mutual orientation of the moments within the structure.

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