DALTON
FULL PAPER

Chains, planes, and tunnels of metal diphosphonates: synthesis, structure, and characterization of $Na_3Co(O_3PCH_2PO_3)(OH)$, $Na_3Mg(O_3PCH_2PO_3)F{\cdot}H_2O$, $Na_2Co(O_3PCH_2PO_3){\cdot}H_2O$, $NaCo_2(O_3PCH_2CH_2CH_2PO_3)(OH)$, and $Co_2(O_3PCH_2PO_3)(H_2O)$

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Received 10th December 1998, Accepted 23rd March 1999

Four cobalt(II) and one magnesium diphosphonates with one-, two-, and three-dimensional structures have been synthesized and characterized structurally, thermally, magnetically, and spectroscopically (IR and UV-VIS). Isolated chains of corner-sharing octahedra (*trans* OH or F groups) are observed in the colorless $Na_3Co(O_3PCH_2PO_3)(\mu\text{-}OH)$ **1** and in the nearly isostructural $Na_3Mg(O_3PCH_2PO_3)(\mu\text{-}F){\cdot}H_2O$ **2**. Planes characterize the structures of the layered $Na_2Co(O_3PCH_2PO_3){\cdot}H_2O$ **3** with square-pyramidal cobalt, and of $NaCo_2(O_3PCH_2CH_2CH_2PO_3)(\mu_3\text{-}OH)$ **4** with octahedral and trigonal-bipyramidal cobalt. Hydrophobic tunnels are found in $Co_2(O_3PCH_2PO_3)(H_2O)$ **5**. The diphosphonates co-ordinate as tetradentate ligands in **1** and **2**, pentadentate ligands in **3**, and hexadentate ligands in **4** and **5**. Four of the six Co–O distances of the CoO_6 octahedra in **1** are anomalously long. Remarkably, the compound is colorless, a quite unusual phenomenon for a cobalt(II) compound. Magnetic measurements showed Curie–Weiss behavior for **1**, **3**, **4**, and **5**, but also some unusual transitions at low temperatures for compound **1**.

Introduction

Diphosphonic acids are remarkably versatile building blocks for assembling extended structures. The two phosphonic groups with their six oxygen atoms provide a variety of possible modes for co-ordination to more than one transition metal; they are the "cement" in a number of one-, two-, and three-dimensional constructions.[1–15] Possible potential applications of such compounds include molecular sieving, catalysis, ion exchange, sensing, intercalation, ion (including proton) conduction, *etc.*[16–22] In addition to this, the tendency for low dimensionality in many of these compounds provides potential for interesting magnetic properties.[3,7,11,23–28] Novel transition metal diphosphonates with new structures, and therefore properties, can be achieved by changing one or more of the large number of available variables. Some of these variables are: the kind of organic group between the phosphonic groups, and therefore the distance between them; the transition metal, and therefore the preferred oxidation state and co-ordination geometry; the pH of the system, and therefore the degree of protonation/deprotonation of the phosphonate; the presence or not of other cations and anions in the starting mixtures. Furthermore, the large number of co-ordinating atoms and possible co-ordination modes of the diphosphonates bring additional structural richness. Typically the diphosphonates are found as hexadentate ligands co-ordinated in a bis-tridentate mode, but examples of bis-monodentate, bis-bidentate, and different asymmetrical modes are also known. The bis-tridentate mode generates mainly layered- or pillared-type structures with alternating "inorganic" and "organic" layers. This is the predominant structural type observed for the diphosphonates. The inorganic portion consists of metal atoms co-ordinated by oxygen and is generally hydrophilic, while the organic part is hydrophobic and contains the organic, covalently bonded part of the diphosphonate. This segregation is driven in part by the different polarities of the groups, and their different affinity to each other and towards the solvent. This principle, *i.e.* "like are adjacent to like", is followed not only for the lamellar structures but also for many compounds of the hybrid inorganic–organic type with different structures. The same principle applies for the five diphosphonates with one-, two-, and three-dimensional structures reported here.

Following the synthesis of an unusual cobalt methylenediphosphonate with framework structure and hydrophobic channels,[15] we undertook a more detailed and systematic study of this system. The structures and some important properties of four new compounds are reported here. One of them, $Na_3Co(O_3PCH_2PO_3)(\mu\text{-}OH)$ **1**, is quite remarkable in the fact that it is colorless despite the presence of octahedral cobalt(II) atoms. Structurally and magnetically this compound is also interesting. It contains isolated chains of corner-connected cobalt octahedra with unusually long Co–O distances, perhaps the reason behind the lack of color. Magnetically the compound behaves as a canted ferromagnet at higher temperatures, while at low temperatures it experiences a magnetic phase transition indicated by a sharp peak in the magnetic susceptibility data.

Experimental

Materials and methods

All four compounds were made hydrothermally in nearly 100% yield. The reaction mixtures were placed in stainless-steel autoclaves with Teflon inserts (23 ml capacity), and were heated for 2 to 3 d at temperatures of 160 to 190 °C. In a typical reaction, methylenediphosphonic or propylene-1,3-diphosphonic acid (Alfa-Æsar) is mixed with tris(ethylenediamine)cobalt(III) chloride or magnesium acetate tetrahydrate (both from Aldrich) in 10 mL of water (the same volume was used for all reactions), HF added (sometimes), and, if necessary, the pH adjusted with sodium hydroxide. Compound **5** forms at pH 12, but is most efficiently made at pH 4. Compound **4** forms in a very narrow range of pH, between 12 and 12.5, while **1**, **2**, and **3** form at pH 13. We have previously used $[Co(en)_3]Cl_3$ as the cobalt source in other reactions, and this was the only reason to use it initially for the syntheses of the products described here. Later, we discovered that although the compounds are of Co^{II} we could not synthesize them using cobalt(II) compounds as the cobalt source, and we have no explanation for this at this time. X-Ray powder diffraction patterns (Enraf-Nonius, Guinier camera) of the products were taken with Cu-Kα_1 radiation and silicon (NIST) as an internal standard. The IR spectra were obtained (Perkin-Elmer, PARAGON 100) by the KBr disk method, UV-VIS spectra in transmission and reflection modes in the range 400–700 nm (Perkin-Elmer, Lambda 6) from samples that were powdered onto an oiled (natural oil) surface of a quartz plate. Thermogravimetric analyses (CAHN, TG-131) were carried out under a flow of air at a heating rate of 5 °C min^{-1}. The magnetization of the compounds was measured (Quantum Design, MPMS SQUID) over the temperature range 2–300 K at different fields.

Syntheses

$Na_3Co(O_3PCH_2PO_3)(\mu\text{-}OH)$ 1. High yields were obtained from a mixture of methylenediphosphonic acid, $[Co(en)_3]Cl_3$, NaOH, and HF in the molar ratio 2 : 1 : 33 : 11, which results in pH 14. The product is colorless and semitransparent, and the crystals are very small elongated plates. Often they have macro inclusions of a black substance, most likely to be the residue of partially decomposed diphosphonic acid. Much larger crystals of the compound, of the order of 2 mm, were synthesized without the presence of HF. These well shaped pseudo-hexagonal plates were used for the structural studies. Elemental analysis (Galbraith Laboratories) for eventual adventitious fluorine in the product synthesized without HF showed virtually zero concentration of this element, 0.67 wt.%.

$Na_3Mg(O_3PCH_2PO_3)(\mu\text{-}F)\cdot H_2O$ 2. Methylenediphosphonic acid, magnesium acetate, NaOH, and HF were mixed in the same molar ratio as for compound **1**. The product forms as colorless transparent bars.

$Na_2Co(O_3PCH_2PO_3)\cdot H_2O$ 3. Methylenediphosphonic acid, $[Co(en)_3]Cl_3$, and HF were mixed in a molar ratio 3 : 1 : 25, and the pH was adjusted to 12 with NaOH. The compound crystallizes as purple needles.

$NaCo_2(O_3PCH_2CH_2CH_2PO_3)(\mu_3\text{-}OH)$ 4. Propylene-1,3-diphosphonic acid, $[Co(en)_3]Cl_3$, NaOH, and HF were mixed in a molar ratio 1 : 2 : 30 : 5. The resulting pH was 14. The compound crystallizes as purple-blue flakes.

$Co_2(O_3PCH_2PO_3)(H_2O)$ 5. The synthesis and structure of compound **5** were described elsewhere.[15]

Crystallographic studies

X-Ray diffraction data sets were collected at 293 K from single crystals of the compounds with monochromated Mo-Kα radiation (λ 0.71073 Å) on a CAD4 diffractometer (ω–2θ scans, $2\theta_{max} = 50°$). No absorption corrections were applied to the data for **3**, while the program XABS2[29] was used for the remaining data sets (normalized minimum transmissions: 0.5425, 0.8633, and 0.4656 for **1**, **2**, and **4**, respectively). The structure solutions (direct methods) and refinements were handled with the SHELXTL V5.0 software package.[30] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **1**, **2**, and **3** were located from the difference Fourier maps and refined independently (including thermal parameters), while those in **4** were located and refined using a constrained “riding” model. Specific crystallographic data for the four compounds are listed in Table 1, while important distances and angles are presented in Table 2. (The structure determination of **5** was reported elsewhere.[15]) In order to confirm the structural details of **1**, a second data set was collected from a crystal from another synthesis, also without HF. It refined to slightly better R factors, $R1/wR2 = 3.08/8.02$ with positive and negative peaks of $+0.22/-0.40$ e Å^{-3} in the Fourier-difference map.

CCDC reference number 186/1413.

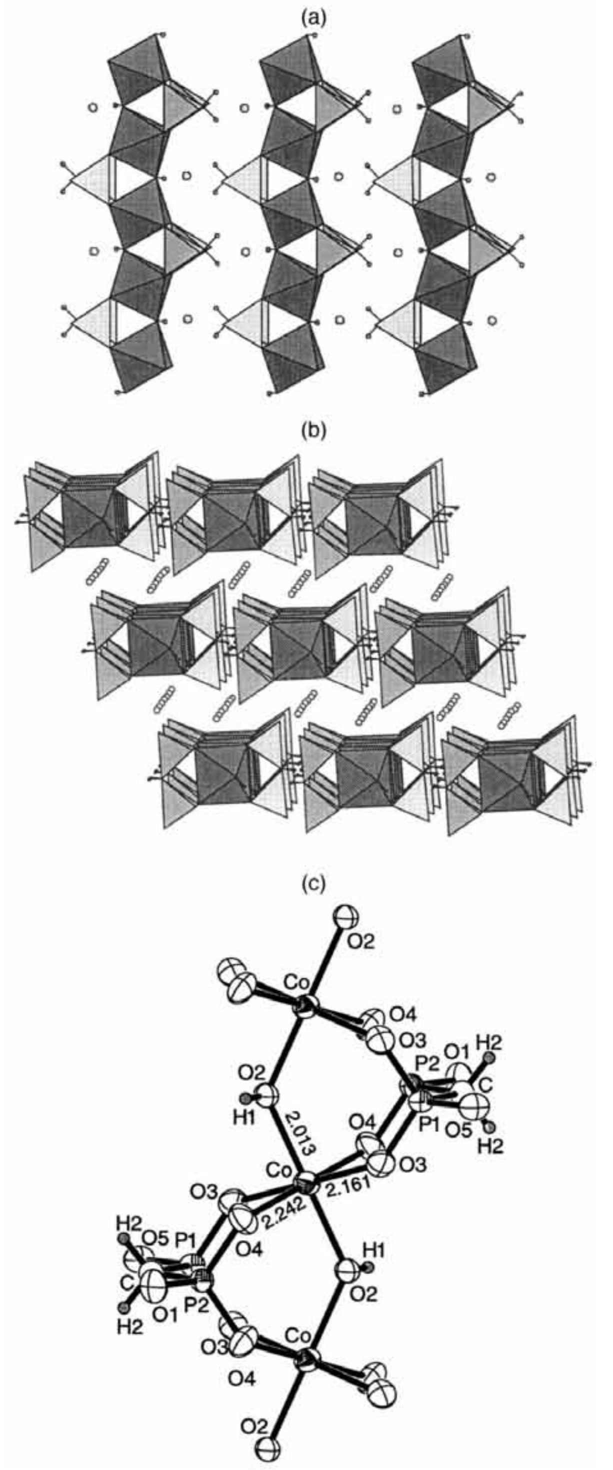

Fig. 1 Views of the structure of $Na_3Co(O_3PCH_2PO_3)(OH)$ **1**. (a) Three isolated chains of vertex-sharing $CoO_4(OH)_2$ octahedra (dark) held together by the $O_3PCH_2PO_3$ groups. The hydrogen and sodium atoms are shown as small and large spheres, respectively. (b) A view along the chains with the sodium cations shown as isolated spheres. The chains are “close-packed” in bundles resulting in a nearly 120° angle between a and c. (c) An ORTEP[31] plot of a section of the chain with 90% probability thermal ellipsoids.

See http://www.rsc.org/suppdata/dt/1999/1805/ for crystallographic files in .cif format.

Structural results

Chains

Aside from two minor differences, the structures of compounds **1** and **2** are identical. The two differences are: (a) in **2** fluorine occupies the positions of the hydroxyl groups of **1**; (b) a molecule of non-co-ordinated water found in **2** does not exist in **1**. Both compounds consist of parallel, discrete chains of corner-sharing octahedra along the twofold axis of the monoclinic cell (Fig. 1). The shared *trans* corners are the two OH groups of the $CoO_4(OH)_2$ octahedra in **1** or the two F atoms of the MgO_4F_2 octahedra in **2**. The remaining four vertices are oxygen atoms of the diphosphonate. Fig. 1(b) shows a view along the direction of the chains, the *b* axis of the structure. It can be seen that the chains form a pseudo closest-packed bundle, *i.e.* there are six neighbors around each chain, and as a result of this the monoclinic angles of the two structures are very close to 120°, 118.65(1) and 118.73(1)° for **1** and **2**, respectively. As expected, the non-polar hydrophobic parts of the chains, *i.e.* the CH_2 groups of the methylenediphosphonates, are close to each other, and are far from the more polar parts such as oxygen atoms, sodium cations and water molecules [Fig. 1(b)]. The cations in **1** and the cations and water molecules [not shown in Fig. 1(b)] in **2** are positioned between the chains but near their hydrophilic (polar) sides.

A closer view of a part of the chain of compound **1** is shown in Fig. 1(c). The same segment can be used to illustrate the structure of **2** as well after imaginary substitution of O2 by F, Co by Mg, and the removal of H1. (The atoms in Table 2 are numbered in the same manner for the two compounds, *i.e.* there is no O2 in **2**, and the extra oxygen in **2** is labeled O6.) Perpendicular to the chain direction there is a mirror plane through atoms P1, P2, O1, O5, C, O2 (or F), and H1. The position of the H1 atom (refined independently, and without disorder) clearly indicates an sp^3-type hybridization of O2 with Co–O2–Co and Co–O2–H1 angles of 131.1(3) and 106(2)°, respectively. The angle at the fluorine atom in **2** is very similar, 133.8(2)°. The metal atoms in **1** and **2** are at inversion centers, and the octahedra around them have nearly perfect angles: between 86.6(2) and 89.2(2)° for the cobalt, and between 87.9(1) and 89.0(1)° for the magnesium. Some of the distances of the octahedron in **1**, on the other hand, are somewhat longer than expected. Thus, the two Co–(μ-OH) distances, 2.013(3) Å, are quite normal and somewhat shorter (−0.072 Å) than the sum of the crystal radii, 2.085 Å.[32] The four distances to the diphosphonate oxygen atoms, on the other hand, are longer than expected and also longer than the sum of the crystal radii, 2.095 Å. Two of these, Co–O3, are 2.161(4) Å (0.066 Å), and the other two, Co–O4, are even longer, 2.242(4) Å (0.147 Å). Therefore, the cobalt–oxygen octahedron is nearly perfect on angles but quite two-dimensionally expanded on distances. The magnesium–oxygen octahedron, at the same time, is only somewhat "compressed" along the F–Mg–F axis with distances of 1.944(1) Å to the fluorine atoms (−0.061 Å from the sum of crystal radii). This distance is shorter than the Co–OH distance, and as a result of this the magnesium distances to O3 and O4, 2.091(3) and 2.149(3) Å, respectively, do not deviate as much as in **1** (0.021 and 0.079 Å, respectively).

The water molecule in compound **2** is strongly hydrogen bonded to two O4 atoms from two different diphosphonates. The OH group in **1** on the other hand is free of hydrogen bonding.

Planes

The structure of compound **3** is of the layered type (Fig. 2) but with layers that are not covalently bonded as in most diphosphonates (discussed in the Introduction). The layers, stacked along *c* of the orthorhombic cell, are extensively puckered along *a* but straight along the *b* axis [the viewing direction in Fig. 2(a)]. Their jagged "terrain" and the way they are stacked results in a zigzag shaped interlayer space.

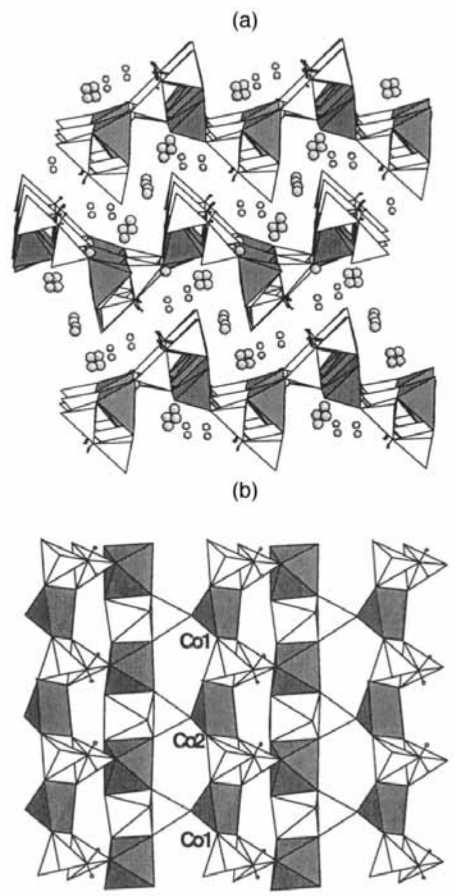

Fig. 2 Two views of the structure of $Na_2Co(O_3PCH_2PO_3)\cdot H_2O$ **3**. (a) Shown are three zigzag layers of CoO_5 square pyramids (shaded) and $O_3PCH_2PO_3$ groups. The water molecules and the sodium cations are shown as isolated small and large spheres, respectively. (b) A view normal to the layer with *b* vertical. The two types of cobalt atoms are labeled.

The two types of cobalt atoms are five-co-ordinated by oxygen, both in a geometry that is somewhat closer to square pyramidal than to trigonal bipyramidal (Fig. 2). The latter is quite clear from the dihedral angles at the base of the pyramid, 12.7(4) and 0.4(4)° for the polyhedra around Co1 and Co2, respectively. These angles for the ideal square pyramid and trigonal bipyramid are 0 and 53.1°, respectively. All five oxygens are from the diphosphonate, and the distances, except one per each cobalt, are within the normal range (Table 2). The two exceptions are somewhat longer than usual, 2.176(7) and 2.139(7) Å for Co1 and Co2, respectively. The two cobalt atoms are identically co-ordinated by the diphosphonate molecules [Fig. 2(b)]. Furthermore, although there are two crystallographically different diphosphonates in the structure, they are also identically connected to the cobalt atoms. The bases of the square prisms around the cobalts are two pairs of oxygen atoms, each pair from different diphosphonates, and each oxygen within the pair from different phosphonic groups within the diphosphonate. The apex of the pyramid is an oxygen atom from a third diphosphonate. Thus each diphosphonate connects three cobalt atoms, and acts as a pentadentate ligand in an asymmetrical tris-bidentate mode. The sixth oxygen is nonbonded and points between the layers.

The interlayer space is filled by the water molecules (O13, O14) and the sodium cations [Fig. 2(a)]. They are positioned away from the hydrophobic parts of the structure that protrude into the open space. The structure shows "segregation" of hydrophobic and hydrophilic parts. The CH_2 groups of the diphosphonates from two adjacent layers point directly at each other and are very close. At the same time the water molecules and the sodium cations are grouped in places closer to the oxygen atoms of the layer. The one-bonded oxygen of the methylenediphosphonate, O6, points directly to a sodium cation, Na4, and is very close to it, 2.231(7) Å. The same oxygen

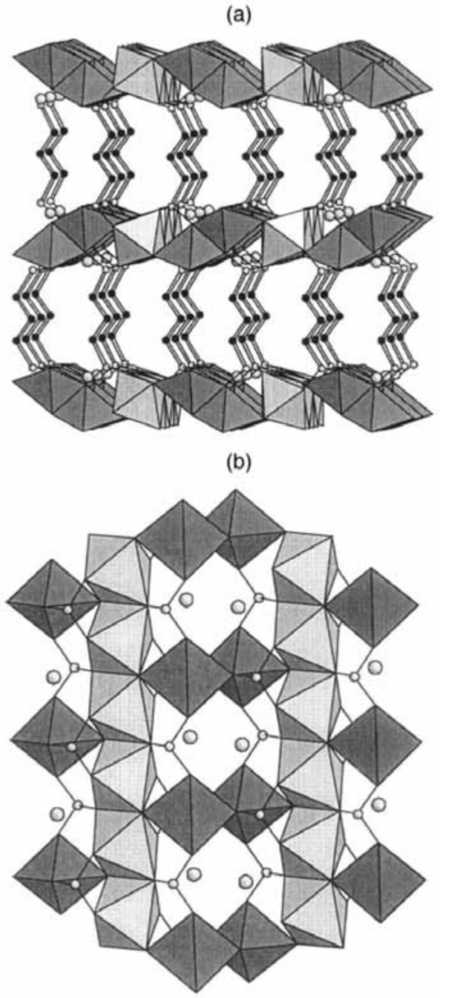

Fig. 3 Two views of the structure of $NaCo_2(O_3PCH_2CH_2CH_2PO_3)(OH)$ **4**. (a) A view parallel to the layers showing the inorganic layers of CoO_5 trigonal bipyramids (darker polyhedra) and CoO_6 octahedra sandwiched between the organic layers of $O_3PCH_2CH_2CH_2PO_3$ groups. The carbon atoms and the sodium cations are shown as black circles and isolated spheres, respectively. (b) A view normal to the inorganic layer showing the pairs of edge-fused CoO_5 trigonal bipyramids, and chains of edge-fused CoO_6 octahedra. The μ_3-OH groups are at the places where two octahedra and a trigonal bipyramid share a corner. The sodium cations and the phosphorus atoms from the diphosphonate are shown as large and small spheres, respectively.

atom is also hydrogen bonded to one of the water molecules, O14 at 2.80(1) Å. That water molecule is also hydrogen bonded to O3 at the same distance. The second water molecule does not participate in such bonding.

Compound **4** is also lamellar, but of the type that is more common for diphosphonates (Fig. 3). It is built of alternating "organic" and "inorganic" layers that are connected in an extended three-dimensional structure. The inorganic part consists of cobalt–oxygen polyhedra of two types, trigonal bipyramids and octahedra. The former are paired through a shared edge [Fig. 3(b)], the non-equatorial one, where an apex of one bipyramid is a waist atom of the second one and *vice versa*. The remaining two apices of the pair are the OH groups, each shared with two CoO_6 octahedra. The octahedra form chains along *a* [vertical in Fig. 3(b)] by sharing opposite parallel edges. All oxygen atoms, except O4 of the hydroxyl group, belong to phosphonate groups. Each of the two PO_3 groups of the propylene-1,3-diphosphonate co-ordinates to a different layer forming the observed "pillared"-type structure. The sodium cations are nested near oxygen atoms of the inorganic layer. The hydrophilic and hydrophobic parts of the structure are segregated, and this clearly determines the formation of such a layered, sandwich-type structure.

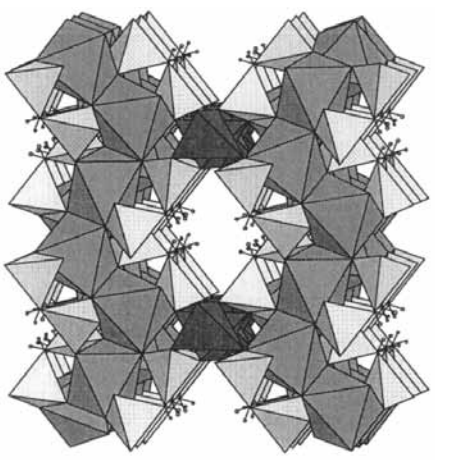

Fig. 4 A view of $Co_2(O_3PCH_2PO_3)(H_2O)$ **5** along the tunnels. Zigzag chains of CoO_6 octahedra (medium shading) run vertical and are joined together by the CoO_4 tetrahedra (dark) at the points of closest approach. The methylenediphosphonate groups line the channels with the hydrophobic CH_2 groups pointing towards the center.

The apical Co–O distances in the trigonal bipyramid, 2.083(8) and 2.110(9) Å, are longer than the equatorial ones, 2 × 1.968(8) and 1.999(9), as could be expected for a high-spin d^7 metal. The distances in the octahedra are within the normal range with two of them, 2 × 2.162(6) Å, somewhat on the upper side. The oxygen of the hydroxyl group, O4, is three-bonded with distances of 2.083(8) and 2.055(6) within the trigonal bipyramids and the octahedra, respectively, and is free of hydrogen bonding.

Tunnels

Lastly, the structure of compound **5** can be described as a three-dimensional framework of cobalt–oxygen octahedra and tetrahedra (Fig. 4). The octahedra form zigzag chains through sharing opposite edges. The chains run parallel and out-of-phase to each other, and are connected by the CoO_4 tetrahedra at the points of closest approach. The so-formed sheets are connected to each other through phosphate groups. The structure has one-dimensional openings, tunnels, that are covered by the methylenediphosphonate groups. The CH_2 groups form the walls of these tunnels and point radially towards its center line. Again, the separation into hydro-phobic and -philic regions of the structure is clearly visible.

Spectroscopic results

Infrared

The IR spectra of the five compounds (Fig. 5) have many similar features corresponding to the common groups: P–O bands of the phosphonate in the region 900–1200 cm^{-1}, the C–H bending and stretching bands at *ca.* 1370 and 2950 cm^{-1}, respectively, and the broad O–H stretching bands of H_2O in the region 3000–3500 cm^{-1}, or the sharp OH band at *ca.* 3600 cm^{-1}. The spectra confirm the presence of water in **2**, **3**, and **5**. More importantly, they show very clearly the presence of non-hydrogen-bonded OH groups in **1** and **4**, and the lack of water in these compounds. The corresponding peaks at 3626 cm^{-1} of **1** and at 3602 cm^{-1} of **4** are extremely sharp and at very high energies. This is consistent with the structures of the two compounds where the OH groups are free of any interactions through the hydrogen atoms since there are no other electronegative (polar) species in their vicinities (see Structural results). Aside from the O–H stretching area, the spectrum of **2** is identical to that of **1** as can be expected from the structural and compositional similarities between these two compounds. The sharp OH peak observed in **1** is clearly missing in **2**. Instead, a broad water band is present for the latter. This is in perfect

Table 1 Data collection and refinement parameters for $Na_3Co(O_3PCH_2PO_3)(OH)$ **1**, $Na_3Mg(O_3PCH_2PO_3)F\cdot H_2O$ **2**, $Na_2Co(O_3PCH_2PO_3)\cdot H_2O$ **3**, and $NaCo_2(O_3PCH_2CH_2CH_2PO_3)(OH)$ **4**

	1	**2**	**3**	**4**
Formula	$CH_3CoNa_3O_7P_2$	$CH_4MgNa_3O_7P_2$	$CH_4CoNa_2O_7P_2$	$C_3H_7Co_2NaO_7P_2$
M	316.87	302.26	294.89	357.88
a/Å	7.789(1)	7.996(2)	8.997(1)	6.123(1)
b/Å	7.329(1)	7.1516(7)	10.348(2)	16.634(3)
c/Å	7.957(1)	8.100(2)	16.260(3)	18.780(4)
β/°	118.65(1)	118.73(1)		
V/Å^3	398.62(9)	406.2(1)	1513.8(4)	1912.7(7)
Crystal symmetry	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group, Z	$P2_1/m$, 2	$P2_1/m$, 2	$P2_12_12_1$, 8	$Cmcm$, 8
μ/cm^{-1}	27.19	8.01	28.03	38.57
Crystal size/mm	0.14 × 0.05 × 0.01	0.16 × 0.03 × 0.03	0.20 × 0.02 × 0.02	0.09 × 0.04 × 0.01
D_c/g cm^{-3}	2.640	2.471	2.588	2.486
$R1/wR2$ ($I > \sigma I$)	0.044/0.098	0.040/0.089	0.023/0.059	0.061/0.112
(all data)	0.072/0.118	0.063/0.100	0.026/0.063	0.112/0.147

Table 2 Important distances (Å) and angles (°) for compounds **1**–**4**

1		**2**		**3**		**4**	
Co–O2 × 2	2.013(3)	Mg–F × 2	1.944(1)	Co1–O1	2.023(7)	Co1–O2 × 2	1.968(8)
Co–O3 × 2	2.161(4)	Mg–O3 × 2	2.091(3)	Co1–O2	2.060(6)	Co1–O4	2.083(8)
Co–O4 × 2	2.242(4)	Mg–O4 × 2	2.149(3)	Co1–O5	1.999(6)	Co1–O5	1.999(9)
P1–O3 × 2	1.528(4)	P1–O3 × 2	1.529(3)	Co1–O9	2.028(6)	Co1–O5	2.110(9)
P1–O5	1.534(6)	P1–O5	1.519(4)	Co1–O10	2.176(7)	Co2–O1 × 2	2.162(6)
P1–C	1.820(9)	P1–C	1.816(6)	Co2–O4	2.019(4)	Co2–O3 × 2	2.086(6)
P2–O4 × 2	1.526(4)	P2–O4 × 2	1.530(3)	Co2–O7	2.092(6)	Co2–O4 × 2	2.055(6)
P2–O1	1.527(6)	P2–O1	1.522(4)	Co2–O8	2.017(7)	P1–O3 × 2	1.533(7)
P2–C	1.814(9)	P2–C	1.823(6)	Co2–O11	2.015(6)	P1–O5	1.542(9)
Na1–O3 × 2	2.506(4)	Na1–O3 × 2	2.494(3)	Co2–O12	2.139(7)	P1–C1	1.78(1)
Na1–O1	2.286(7)	Na1–O1	2.296(5)	P1–O9	1.525(7)	P2–O2 × 2	1.529(7)
Na1–O2	2.239(7)	Na1–F	2.185(4)	P1–O10	1.512(7)	P2–O1	1.53(1)
Na1–O5	2.351(7)	Na1–O5	2.293(5)	P1–O12	1.512(7)	P2–C2	1.81(1)
Na2–O1	2.270(4)	Na2–O1	2.394(3)	P1–C2	1.81(1)	C3–C2 × 2	1.50(2)
Na2–O3	2.320(4)	Na2–O3	2.329(3)	P2–O3	1.501(6)	C4–C1 × 2	1.50(2)
Na2–O4	2.301(4)	Na2–O4	2.500(3)	P2–O5	1.532(6)	Na–O1	2.500(11)
Na2–O5	2.280(4)	Na2–O5	2.379(3)	P2–O7	1.534(6)	Na–O2 × 2	2.624(9)
		Na2–O6	2.540(4)	P2–C2	1.82(1)	Na–O3 × 2	2.417(8)
O2–H1	0.78(9)			P3–O2	1.527(7)	O4–H	1.00(3)
				P3–O4	1.537(7)		
				P3–O6	1.504(6)		
				P3–C1	1.81(1)		
				P4–O1	1.521(7)		
				P4–O8	1.502(8)		
				P4–O11	1.530(7)		
				P4–C1	1.802(9)		
Co–O2–Co	131.1(3)	Mg–F–Mg	133.8(2)			Co1–O4–Co2	118.8(3)
Co–O2–H1	106(2)					Co2–O4–Co2	96.3(3)
						Co1–O4–H	95(1)
						Co2–O4–H	115(1)

agreement with the stoichiometries of the two compounds, $Na_3Co(O_3PCH_2PO_3)(OH)$ and $Na_3Mg(O_3PCH_2PO_3)F\cdot H_2O$.

Visible

The electronic spectra of compounds **3**, **4**, and **5** in the visible region show the expected d–d transitions for high-spin cobalt(II), and their coloration is consistent with the different co-ordinations of the metal. Compound **3** is deep purple, and for the five-bonded cobalt we observed four transitions at 495, 530, 602, and 626 nm. The color of **4** is also purplish but more on the pink side, and the observed transitions for the five- and six-co-ordinated cobalt are 482, 506, 580, and 592 nm. Compound **5**, on the other hand, is very bright blue since it contains tetrahedral cobalt, and the transitions are at 550, 581, and 632 nm.

A pink purplish coloration is expected for compound **1** as well since it contains high-spin octahedral Co^{II}, but most interestingly the compound is colorless and transparent. From a distance it looks somewhat steel-grayish, but this is more due to surface reflections and to the fact that some of the crystallites contain a macroscopic organic residue captured during the synthesis. Numerous UV-VIS spectra were taken in transmission and reflectance modes of many solid-state samples of this compound prepared by different techniques. None of them showed distinct absorption peaks, indicating that the compound either does not absorb at all in the visible region, or it absorbs but with extremely low efficiency. Nevertheless, two very small and broad humps can be imagined in a few of the spectra. These are centered at around 605 and 656 nm, and if real are quite atypical for octahedral high-spin Co^{II} because of their position at the very low energy end of the spectrum. This would indicate a very small crystal field splitting energy which is consistent with the unusually long Co–O distances in this compound.

Magnetic results

The magnetization of the four cobalt compounds was measured at 3 T in the range 10–293 K. Compounds **3** and **5** are

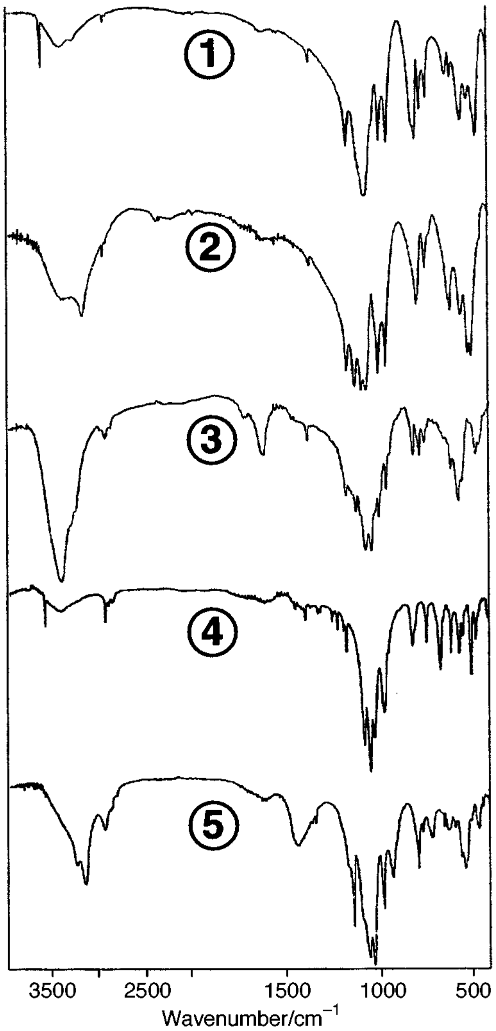

Fig. 5 The IR spectra of the five compounds.

Curie–Weiss paramagnetic throughout the whole temperature range, while **1** and **4** are such above ≈90 and 20 K, respectively. The inverse of the molar magnetic susceptibility was plotted *vs.* T for these regions, and the data were fitted with linear functions. The following effective magnetic moments per cobalt atom (μ_{eff}) and the Curie–Weiss temperatures (θ) were calculated from the fits: $\mu_{eff} = 5.23\ \mu_B$ and $\theta = -96.2$ K for **1**, $\mu_{eff} = 5.09\ \mu_B$ and $\theta = -17.6$ K for **3**, $\mu_{eff} = 4.98\ \mu_B$ and $\theta = -44.0$ K for **4**, and $\mu_{eff} = 5.22\ \mu_B$ and $\theta = -7.7$ K for **5**. Clearly the cobalt atoms experience substantial orbital contribution to the magnetic moments since the latter are significantly larger than the spin-only number of 3.87 μ_B for a high-spin d^7 atom. Nevertheless, these numbers are well within the range of moments typically observed for such ions, 4.3–5.2 μ_B.[33] The negative θ temperatures indicate antiferromagnetic coupling between the magnetic moments of adjacent atoms; the strongest is in **1** while the weakest is in **5**.

Compound **4** undergoes antiferromagnetic ordering below 20 K, and similar transitions may be expected for **3** and **5** as well. Compound **1**, on the other hand, behaves very differently at temperatures below the Curie–Weiss region, *i.e.* below *ca.* 90 K (Fig. 6). Its magnetic susceptibility rises sharply below that temperature indicating some sort of ferromagnetic interactions. For fields above 200 G this increase is steady down to 5 K where the moment seems to reach saturation at that temperature. Below 200 Oe (Oe = 10^3 A m^{-1}), on the other hand, another peculiar phenomenon is observed at low temperatures. The susceptibility reaches a maximum at 11.26 K, and then sharply drops below that temperature. Below *ca.* 7 K it drops more gradually, and reaches a plateau or a minimum at *ca.* 3 K.

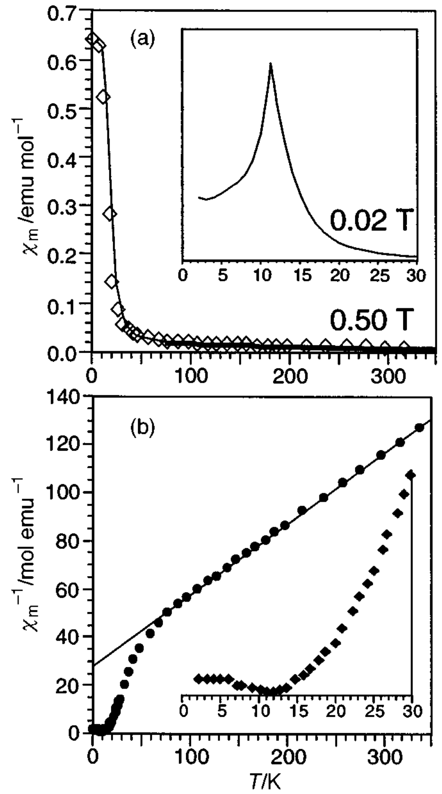

Fig. 6 Plots of the magnetic susceptibility (a) and its inverse (b) *versus* the temperature for $Na_3Co(O_3PCH_2PO_3)(OH)$ **1**. The line in (b) is the Curie–Weiss fit at temperatures above 90 K. The insert in (a) shows the behavior of χ_m below 30 K at a field of 200 Oe. The sharp maximum is at 11.6 K. The insert in (b) shows the corresponding $1/\chi_m$ for the same region and field.

Thermogravimetric results

Compounds **2**, **3**, and **5** lose their water at 350, 350, and 300 °C, respectively. All five compounds are structurally stable up to 450–500 °C. Compound **4** loses the hydrocarbon part of the composition at 500 °C and the structure breaks up, while **5** loses its organics 100 °C above the temperature of structural collapse at 500 °C.

Discussion

First, we would like to emphasize the profound significance of the pH of the reaction mixture in determining which of the three cobalt methylenediphosphonates will form. Moreover, the phosphonic groups in all three compounds are deprotonated, *i.e.* the pH apparently does not affect the protonation status of the acid. Particularly remarkable is the extremely narrow range of 12.0 to 12.5 for the stability of compound **3**.

Structurally the three methylenediphosphonates are also remarkably different. They are of the three possible dimensionalities for extended structures. This diversity is clearly due to: (a) the ability of cobalt to adopt different co-ordinations; and (b) the ability of the multidentate diphosphonate to adopt different modes of co-ordination. Perhaps the most interesting compound from the structure and properties points of view is **1**, $Na_3Co(O_3PCH_2PO_3)(OH)$. After its structure and stoichiometry were clarified, we attempted syntheses of isostructural analogs of Mn, Fe, Ni, and Mg since we have already observed such relations in other compounds for these elements and cobalt.[34] Nevertheless, only the synthesis with magnesium was successful in this case. Furthermore, this compound is not exactly the same since it contains fluorine instead of the hydroxyl group, and a water molecule is added to the stoichiometry. These differences were easily recognized from the structure refinement, and confirmed by the IR spectroscopy. The latter showed a sharp OH peak for **1** but a broad H_2O band for **2**. Moreover, compound **1** can be synthesized without HF while **2** cannot.

There are only three other chain-type compounds involving diphosphonates and corner-sharing octahedra: $Cs[(VO)(HO_3PCH_2PO_3H)]$,[3] $[Li(H_2O)_3][Tc(OH)(O_3PCH_2PO_3)]$,[6] and $Na_4[(WO_3)_2\{O_3PCHN(CH_3)_2PO_3\}]\cdot 11H_2O$.[5] Nevertheless, structurally each of them differs substantially from **1** and **2**. The shared OH groups in the technetium compound are in *cis* positions resulting in a completely different macrostructure.[6] While the shared atoms in the other two compounds are in *trans* positions, the diphosphonate in the tungsten compound bridges every other pair of octahedra,[5] and the octahedra in the vanadium compound are essentially square pyramids with alternating and substantially different V–O distances to the "shared" atoms, 1.60 and 2.40 Å.[3] In addition, due to the different co-ordinations and/or size of the metal in these three compounds, the M–O distances are well within the expected ranges. For **1**, on the other hand, four of these distances are somewhat longer than normal (see above), and this is most likely the reason for the lack of color for this compound. Lack of color is normal for a magnesium compound but quite abnormal for a high-spin cobalt(II) compound. This can be due to either absorption outside the visible range, presumably the near IR, or extremely weak absorption within it. However, the results from the UV-VIS measurements are quite ambiguous about this. The fact that four of the six Co–O distances in this compound are unusually long suggests that the energy of the d–d transitions should be smaller than usual. This may cause a substantial shift towards lower energies of the usually strong $^4T_{1g}(P) \longrightarrow {}^4T_{1g}$ transition, normally observed at around 500 nm [515 nm for $Co(H_2O)_6^{2+}$, for example]. Nevertheless, the expansion of the cobalt octahedron is perhaps not that extensive to account for a shift that is large enough to bring the band in the near IR region. It is more likely, therefore, that the ambiguous bands at 605 and 656 nm are real although at more than about 3000 cm^{-1} lower energy than expected. If that is the case, they correspond perhaps to transitions from the above mentioned state $^4T_{1g}(P)$ but tetragonally split to ^4E_g and $^4A_{2g}$. However, it is not clear why these transitions are so weak that the sample appears colorless.

The rather unusual magnetic behavior of compound **1** merits some more detailed discussion. Low dimensional systems with localized electrons generally attract much attention due to their potential for unusual magnetic properties such as low-dimensional magnetism, frustrated magnetic moments, large magnetic anisotropy, *etc*. From the powder data of **1** it is clear that at higher temperatures the compound is paramagnetic with a moment corresponding to $S = 3/2$, and that as expected the cobalt atoms interact antiferromagnetically through the shared OH groups.[33] At temperatures below *ca.* 90 K the effective moment starts to increase gradually and departs more and more from that value. Such behavior is consistent with canting of the spins, producing a net moment perpendicular to the spin alignment axis, presumably the direction of the chains. This "ordered" system is clearly field dependent since it is "stable" down to 2 K at fields above *ca.* 200 Oe, but undergoes a transition at weaker fields. This transition which occurs at *ca.* 11 K is a very sharp drop of the effective magnetic moment indicative of some sort of antiferromagnetic interactions, presumably between the chains. These interactions are of limited strength, and high fields override them. In order really to understand the magnetism of the system as a whole, we have undertaken a series of measurements (still in progress) on a large single crystal of the compound. Our preliminary results suggest that the effective moment below 90 K is indeed perpendicular to the direction of the chains. There are many more things to be learned from the complete single crystal measurements, but what is clear is that the system is a promising and interesting case from the theoretical point of view, and has the potential for unusual magnetic properties. Also in progress are experiments to synthesize diphosphonate compounds of Mn^{II}, Fe^{II}, and Ni^{II} with the same structure, and to study and compare their magnetic behavior with that of **1** since they carry different numbers of unpaired d electrons, 5, 4, and 2, respectively. The only other system with somewhat similar magnetism to that of **1**, that we have found, is anhydrous $Fe_2(SO_4)_3$.[35] The unusual transitions have been explained there by the two iron sublattices and their different connectivity, and therefore magnetization. Unfortunately this approach is obviously not applicable in our case.

Acknowledgements

We thank Evgeny Todorov and Peter Schiffer for the magnetic measurements, and the National Science Foundation for financial support (NSF-DMR9701550) and for an equipment grant for the SQUID (NSF-DMR9703732).

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Paper 8/09671F