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Comparison of the Crystal Structures of $Co_2(X_2O_7)\cdot 2H_2O$, $X = P$ and As

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Summary. Crystals of $Co_2(X_2O_7)\cdot 2H_2O$, $X = P/As$ were synthesized under hydrothermal conditions. Their crystal structures were determined by single crystal X-ray diffraction: $a = 6.334(1)/6.531(2)$, $b = 13.997(2)/14.206(4)$, $c = 7.637(1)/7.615(2)$ Å, $\beta = 94.77(2)/94.74(2)°$, space group $P2_1/n$, $R = 0.032/0.046$, $R_w = 0.028/0.034$ for 2423/2042 reflections and 131/119 variables. Within the two XO_4 tetrahedra connected via a common corner to an X_2O_7 group the average ⟨P–O⟩ bond lengths are approximately equal (1.540 and 1.543 Å), but ⟨As–O⟩ differs significantly (1.685 and 1.696 Å). A comparison with the isotypic Mn and Mg pyrophosphates shows a correlation between the ratio ⟨*Me*–O⟩/⟨*X*–O⟩ and the angle O–*X*–O.

Keywords. $Co_2(P_2O_7)\cdot 2H_2O$; $Co_2(As_2O_7)\cdot 2H_2O$; Pyrophosphate; Pyroarsenate; $Co(II)O_6$ octahedron.

Vergleich der Kristallstrukturen von $Co_2(X_2O_7)\cdot 2H_2O$, $X = P$ und As

Zusammenfassung. Kristalle von $Co_2(X_2O_7)\cdot 2H_2O$, $X = P/As$ wurden unter Hydrothermalbedingungen synthetisiert. Ihre Kristallstrukturen wurden mittels Röntgenbeugung an Einkristallen bestimmt: $a = 6.334(1)/6.531(2)$, $b = 13.997(2)/14.206(4)$, $c = 7.637(1)/7.615(2)$ Å, $\beta = 94.77(2)/94.74(2)°$, Raumgruppe $P2_1/n$, $R = 0.032/0.046$, $R_w = 0.028/0.034$ für 2423/2042 Reflexe und 131/119 Variable. In den beiden über eine gemeinsame Ecke zu X_2O_7-Gruppen verknüpften XO_4-Tetraedern sind die mittleren ⟨P–O⟩-Abstände ungefähr gleich (1.540 und 1.543 Å), hingegen differiert ⟨As–O⟩ signifikant (1.685 und 1.696 Å). Ein Vergleich mit den isotypen Mn- und Mg-Pyrophosphaten zeigt eine Korrelation zwischen dem Quotienten ⟨*Me*–O⟩/⟨*X*–O⟩ und dem Winkel *X*–O–*X*.

Introduction

Pyrophosphate anions exhibit a wide range of conformations. For example the anhydrous pyrophosphates of alkaline earth elements or of first row transition metal elements have been studied in detail [1–5]. Already these compounds show one of the most peculiar features of the P_2O_7 group: the P–O–P angle varies on a wide range from 180° (at least symmetrically restricted) to ~120°. Compilations of the crystal chemistry of phosphates and even pyrophosphates are given in [6, 7]. On the contrary, structural investigations on pyroarsenates are rare: crystal structure determinations have been performed on $Mg_2(As_2O_7)$ [8], $Na_4As_2O_7$ [9], $CaK_2(As_2O_7)$ [10], $Cr_2H_2(As_2O_7)(As_4O_{12})$ [11], $Ca_2(As_2O_7)$ [12], $PbCu(As_2O_7)$

[13], $Na(Al_{1.5}As_{0.5})(As_2O_7)$ [14], $Co_2(As_2O_7)$, $Mn_2(As_2O_7)$ and $Ni_2(As_2O_7)$ [15], $Ag_5Cu(AsO_4)(As_2O_7)$ and $Ag_7Cu(As_2O_7)_2Cl$ [16].

In connection with syntheses in parts of the system $CoO–P_2O_5–H_2O$ under hydrothermal conditions [17, 18] crystals of $Co_2(P_2O_7)\cdot 2H_2O$ were obtained. They proved, together with those of $Co_2(As_2O_7)\cdot 2H_2O$, to be isotypic with $Mn_2(P_2O_7)\cdot 2H_2O$ and $Mg_2(P_2O_7)\cdot 2H_2O$ [19, 20]. The aim of the present paper is to compare the geometry of the pyrophosphate and pyroarsenate anions within one structure type in detail.

As a convenience throughout this paper the following abbreviations were used for the compounds $Me_2(X_2O_7)\cdot 2H_2O$ with Me=Mg, Mn, Co and X = P, As: *MGP* for $Mg_2(P_2O_7)\cdot 2H_2O$, *MNP* for $Mn_2(P_2O_7)\cdot 2H_2O$, *COP* for $Co_2(P_2O_7)\cdot 2H_2O$, and *COA* for $Co_2(As_2O_7)\cdot 2H_2O$. For *MGP* and *MNP* data refer to [20] and [19], respectively.

Experimental Part

Single crystals of *COP* and *COA* were synthesized under hydrothermal conditions from mixtures of $Co_3(OH)_2(PO_3OH)_2$ [18] $+ 0.5n$ H_3PO_4 and $Co(OH)_2 + As_2O_3$ $+0.1n$ HNO_3, respectively, in "teflon" lined stainless steel autoclaves (temperature range from 190 °C to 230 °C, saturation vapour pressure, reaction time 4 days). Preliminary investigations were made with a Weissenberg type film camera equipped with a Cu tube. Details on the experimental work are summarized in Table 1. For the cobalt(II) pyrophosphate compound the hydrogen atoms were located by the means of a difference Fourier summation, their atomic coordinates were allowed to vary during the final stages of least-squares refinements. The location of hydrogen atoms in the pyroarsenate compound failed due to the higher atomic number of arsenic and the poor crystal quality. Data on the least-squares structure refinements are compiled in Table 2.

Results and Discussion

The most prominent features of the structure type $Me_2(X_2O_7)\cdot 2H_2O$ have been mentioned in [19, 20]. Figure 1 depicts some details of the structure. Relevant crystal chemical data on *COP* and *COA* are compiled in Table 3.

The crystal structures of the title compounds are characterized by two crystallographically independent Co(II) atoms; they are octahedrally coordinated to five oxygen atoms of X_2O_7 groups and to one water molecule. These $Co(1)O_6$ and $Co(2)O_6$ octahedra are chelated across a O(3)–X–O(5) and O(2)–X–O(6) bridge, respectively, with the X_2O_7 groups. The CoO_6 octahedra are alternatingly connected via O(2)–O(5) and O(3)–O(6) edges to each other forming infinite zig-zag chains in $[10\bar{1}]$ with formula Co_2O_8. There are no further connections among the CoO_6 octahedra. Bond lengths, bond angles as well as distortion parameters of the CoO_6 coordination polyhedra are within the range of values calculated from 112 CoO_6 polyhedra in 73 crystal structures determined with high accuracy [25].

An empirical crystal chemical rule concerning coordination polyhedra says that the O–O distances of shared edges are "short", the corresponding bond angles ligand-central atom-ligand are "small" as compared to the unshared edges and their angles. Nevertheless, in the $Co(1)O_6$ and $Co(2)O_6$ octahedra of *COP* the unshared edges O(2)–O_w(1) and O(2)–O(4) are shorter than one of the two shared O–O edges. The O atoms of the two "short unshared" edges belong to two different pyrophosphate groups or to one pyrophosphate group and the water molecule. Also

Table 1. Summary of crystal data, X-ray measurements and structure refinements (STOE four-circle diffractometer AED2, Mo tube, graphite monochromator, min. scan width increased for α_1–α_2 dispersion and for background correction, scan speed 0.02 to 0.06° s^{-1}; correction for Lorentz and polarization effects; calculations performed on an ECLIPSE S140 computer, program system STRUCSY [21], neutral complex scattering functions [22] used)

Compound Abbreviation	$Co_2(P_2O_7)\cdot 2H_2O$ *COP*	$Co_2(As_2O_7)\cdot 2H_2O$ *COA*
a (Å)	6.334(1)	6.531(2)
b (Å)	13.997(2)	14.206(4)
c (Å)	7.376(1)	7.615(2)
β (°)	94.77(2)	94.74(2)
V (Å^3)	651.7	704.1
Z	4	4
Space group	$P2_1/n$	$P2_1/n$
D_x (g cm^{-3})	3.34	3.92
μ(MoKα) (cm^{-1})	53.7	136.7
Reflections for lattice parameters	75	35
2Θ-Range for lattice parameters (°)	40.2 to 45.4	25.2 to 29.7
Crystal dimensions (mm)	0.04 × 0.011 × 0.14	0.18 × 0.12 × 0.14
Colour	pink	pink
Crystallographic forms	{010}, {011}, $\{11\bar{1}\}$	{010}, {001}, {011}, {100}
2Θ max for data collection (°)	70	65
2Θ/ω Scan, min. scan with (°)	1.26	1.20
Back ground (each side) (°)	0.24	0.18
Reflections measured	6360	5274
Unique reflections	2868	2548
Reflections with $F_0 > 3\sigma(F_0)$	2423	2042
Absorption correction	crystal form	crystal form
Transmission factors	0.721 to 0.910	0.238 to 0.290
R/R_w, $w = [\sigma(F_0)]^{-2}$, $F_0 > 3\sigma(F_0)$	0.032/0.028	0.046/0.033
R/R_w, $w = [\sigma(F_0)]^{-2}$, all data	0.044/0.028	0.066/0.034
max Δ/σ	<0.01	<0.01
Variable parameters	131	119
Final difference Fourier map (e Å^{-3})	−0.82 to 0.61	−2.55 to 1.43
Extinction g [23]	$6.8(8)\cdot 10^{-5}$	$2.48(7)\cdot 10^{-5}$

MGP and *MNP* show the same features, but they have not been mentioned in literature yet. On the contrary for *COA* both the "shared" edges are shorter than the "unshared" ones. Obviously the shortening of the "unshared" edges result from a minimization of the cation-anion repulsion in the prophosphate compounds; the larger pyroarsenate group avoid the short unshared edges.

Worthy to note is that the edge O(2)–O(4) is approximately parallel to [010]: angles are 11.1(2)° and 7.3(3)° in *COP* and *COA*; O(2)–O_w(1) is inclined to [010] with 45.7(2) and 43.2(3)°. The cell parameters *a* and *c* increase from *COP* to *COA* for 3.11% and 3.24%, *b* only for 1.49%. This indicates an appreciable torsion of the coordination polyhedra between *COP* and *COA*.

Table 2. Structural parameters for $Co_2(P_2O_7)\cdot 2H_2O$ (upper row) and $Co_2(As_2O_7)\cdot 2H_2O$ (lower row), e.s.d.'s in parentheses. Anisotropic displacement parameters are defined as $\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}h_ih_ja_i^*a_j^*\right)$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	0.23503(5)	0.38805(2)	0.41759(4)	0.0127(1)	0.0152(1)	0.0108(1)	0.0001(1)	0.0013(1)	−0.0003(1)
	0.23837(10)	0.38477(5)	0.41376(9)	0.0106(3)	0.0115(3)	0.0104(3)	0.0003(2)	0.0006(2)	−0.0002(2)
Co(2)	0.45102(5)	0.24884(2)	0.14960(3)	0.0130(1)	0.0159(1)	0.0104(1)	0.0000(1)	0.0013(1)	−0.0007(1)
	0.45716(11)	0.24766(5)	0.14385(8)	0.0112(3)	0.0128(3)	0.0102(3)	−0.0002(2)	0.0011(2)	−0.0008(2)
P(1)	0.24102(9)	0.08420(4)	0.84941(6)	0.0118(3)	0.0134(2)	0.0097(2)	−0.0001(2)	0.0006(2)	0.0005(2)
As(1)	0.23862(8)	0.08008(3)	0.84910(6)	0.0088(2)	0.0097(2)	0.0097(2)	−0.0001(2)	0.0002(2)	0.0008(2)
P(2)	0.43476(9)	0.18793(4)	0.57137(6)	0.0121(3)	0.0141(2)	0.0093(2)	0.0002(2)	0.0011(2)	0.0003(2)
As(2)	0.44271(8)	0.18561(3)	0.55966(6)	0.0099(2)	0.0109(2)	0.0083(2)	0.0000(2)	0.0007(2)	0.0001(2)
O(1)	0.2011(3)	−0.0206(1)	0.8724(2)	0.0199(8)	0.0158(6)	0.0142(6)	−0.0024(6)	0.0003(5)	0.0015(5)
	0.1773(6)	−0.0312(2)	0.8751(4)	0.019(2)	0.010(2)	0.014(2)	−0.001(1)	−0.003(1)	0.004(1)
O(2)	0.0379(3)	0.1427(1)	0.8402(2)	0.0131(7)	0.0164(7)	0.0162(6)	0.0012(6)	0.0032(5)	0.0018(5)
	0.0318(5)	0.1492(2)	0.8379(4)	0.014(2)	0.014(2)	0.013(2)	0.005(1)	0.005(1)	0.003(1)
O(3)	0.4135(2)	0.1271(1)	0.9817(2)	0.0135(7)	0.0182(7)	0.0122(5)	−0.0012(6)	0.0009(5)	−0.0021(5)
	0.4296(5)	0.1256(2)	0.9824(4)	0.011(2)	0.014(2)	0.012(2)	0.000(1)	0.001(1)	−0.003(1)
O(4)	0.4697(3)	0.1618(1)	0.3776(2)	0.0201(8)	0.0172(7)	0.0105(5)	−0.0011(6)	0.0039(5)	0.0008(5)
	0.4820(6)	0.1551(2)	0.3536(4)	0.020(2)	0.015(2)	0.010(2)	−0.001(1)	0.001(1)	0.000(1)
O(5)	0.6380(2)	0.2079(1)	0.6918(2)	0.0125(7)	0.0190(7)	0.0119(5)	−0.0019(6)	−0.0008(5)	0.0010(5)
	0.6547(5)	0.2095(3)	0.6928(4)	0.010(2)	0.019(2)	0.013(2)	−0.003(1)	−0.005(1)	0.004(1)
O(6)	0.2740(3)	0.2681(1)	0.5912(2)	0.0152(7)	0.0157(6)	0.0140(6)	0.0008(6)	0.0034(5)	0.0013(5)
	0.2659(6)	0.2697(2)	0.5840(5)	0.012(2)	0.014(2)	0.018(2)	0.005(1)	0.002(1)	0.002(1)
O(7)	0.3321(3)	0.0939(1)	0.6524(2)	0.0142(7)	0.0155(6)	0.0104(5)	−0.0017(6)	0.0020(5)	0.0001(5)
	0.3336(5)	0.0832(2)	0.6401(4)	0.014(2)	0.013(2)	0.011(2)	−0.003(1)	0.001(1)	−0.001(1)
$O_w(1)$	0.2573(3)	−0.0037(1)	0.2780(2)	0.0202(9)	0.0218(8)	0.0245(8)	−0.0024(7)	0.0013(7)	−0.0056(7)
	0.2541(6)	−0.0021(3)	0.2630(5)	0.024(2)	0.019(2)	0.022(2)	−0.003(2)	0.005(2)	−0.007(2)
$O_w(2)$	0.9354(3)	0.1503(1)	0.4367(2)	0.0201(9)	0.0300(9)	0.0154(6)	−0.0007(7)	−0.0001(6)	−0.0010(7)
	0.9371(6)	0.1565(3)	0.4318(5)	0.024(2)	0.027(2)	0.021(2)	0.001(2)	−0.003(2)	−0.009(2)
H(1)	0.359(5)	0.051(2)	0.298(3)	0.012*					
H(2)	0.157(5)	0.010(2)	0.289(4)	0.012*					
H(3)	0.912(4)	0.179(2)	0.327(3)	0.012*					
H(4)	0.855(5)	0.117(2)	0.428(4)	0.012*					

* Fixed

Table 3. Interatomic distances (Å), bond angles (°), bond valences v (v.u.) [24], distortion parameters [6, 25]. $DI_d = \left(\sum_{i=1}^{n_1} |d_i - d_m| \right) \Big/ n_1 d_m$; $DI_{\sphericalangle} = \left(\sum_{i=1}^{n_2} |\sphericalangle_i - \sphericalangle_m| \right) \Big/ n_2 \sphericalangle_m$; $DI_e = \left(\sum_{i=1}^{n_2} |e_i - e_m| \right) \Big/ n_2 e_m$. d, $\sphericalangle$, e signifies Co/P/As–O bond distances, O–Co/P/As–O angles, and O–O edges within the relevant polyhedron; indices i and m indicate individual and mean values. n_1 and n_2 is 4 and 6 for the phosphate and arsenate tetrahedra and 6 and 12 for the cobalt octahedra

	$Co_2(P_2O_7)\cdot 2H_2O$ (*COP*)		$Co_2(As_2O_7)\cdot 2H_2O$ (*COA*)	
Co(1)–O(1), v	2.024(1)	0.408	2.041(3)	0.389
Co(1)–O(2), v	2.091(1)	0.340	2.103(3)	0.329
Co(1)–O(3), v	2.139(1)	0.299	2.130(3)	0.306
Co(1)–O(5), v	2.188(1)	0.262	2.184(4)	0.265
Co(1)–O(6), v	2.113(1)	0.321	2.085(3)	0.346
Co(1)–O_w(1), v	2.096(1)	0.336	2.099(3)	0.333
⟨Co(1)–O⟩, Σv	2.109	1.966	2.107	1.968
DI_d	0.0191		0.0158	
$DI_{\sphericalangle}$	0.0670		0.0569	
DI_e	0.0415		0.0433	
O–O (shared edges)	2.777(2) and 2.826(2)		2.752(5) and 2.712(5)	
O–Co(1)–O (shared)	81.52(6) and 82.64(6)		79.8(1) and 80.1(1)	
O–O (unshared edges)	2.788(2) to 3.416(2)		2.864(5) to 3.388(5)	
O–Co(1)–O (unshared)	83.50(7) to 107.51(7)		85.9(2) to 106.5(2)	
Co(2)–O(2), v	2.111(1)	0.322	2.110(3)	0.323
Co(2)–O(3), v	2.108(1)	0.325	2.125(3)	0.310
Co(2)–O(4), v	2.072(1)	0.358	2.064(3)	0.366
Co(2)–O(5), v	2.121(1)	0.314	2.129(3)	0.307
Co(2)–O(6), v	2.139(1)	0.299	2.118(4)	0.316
Co(2)–O_w(2), v	2.108(1)	0.325	2.108(4)	0.325
⟨Co(2)–O⟩, Σv	2.110	1.943	2.109	1.947
DI_d	0.0066		0.0073	
$DI_{\sphericalangle}$	0.0563		0.0706	
DI_e	0.0439		0.0552	
O–O (shared edges)	2.777(2) and 2.826(2)		2.712(5) and 2.752(5)	
O–Co(2)–O (shared)	81.66(6) and 83.80(6)		79.5(1) and 81.0(1)	
O–O (unshared edges)	2.788(2) to 3.351(2)		2.803(5) to 3.429(5)	
O–Co(2)–O (unshared)	83.57(6) to 104.82(7)		84.4(2) to 107.4(1)	
X(1)–O(1), v	1.500(1)	1.372	1.647(3)	1.383
X(1)–O(2), v	1.522(1)	1.293	1.666(3)	1.314
X(1)–O(3), v	1.526(1)	1.279	1.672(3)	1.293
X(1)–O(7), v	1.613(1)	1.011	1.756(3)	1.030
⟨X(1)–O⟩, Σv	1.540	4.955	1.685	5.020
DI_d	0.0235		0.0210	
$DI_{\sphericalangle}$	0.0366		0.0411	
DI_e	0.0088		0.0142	
O–O(7)	2.473(2) 2.508(2)		2.681(5) to 2.744(5)	
O–X(1)–O(7)	104.61(8) to 106.20(8)		103.8(2) to 106.6(2)	
O–O (others)	2.511(2) to 2.560(2)		2.740(5) to 2.850(5)	
O–X(1)–O (others)	111.97(9) to 115.55(9)		111.4(2) to 118.3(2)	

Table 3. (*Continued*)

	$Co_2(P_2O_7)\cdot 2H_2O$ (*COP*)		$Co_2(As_2O_7)\cdot 2H_2O$ (*COA*)	
X(2)–O(4), v	1.509(1)	1.339	1.668(3)	1.307
X(2)–O(5), v	1.528(1)	1.272	1.682(3)	1.258
X(2)–O(6), v	1.531(1)	1.262	1.682(3)	1.258
X(2)–O(7), v	1.605(1)	1.033	1.753(3)	1.039
$\langle X(2)–O\rangle$, Σv	1.543	4.906	1.696	4.862
DI_d	0.0200		0.0167	
DI	0.0347		0.0427	
DI_e	0.0109		0.0201	
O–O(7)	2.462(2) to 2.508(2)		2.664(6) to 2.764(5)	
O–X(2)–O(7)	104.44(8) to 106.36(9)		102.1(2) to 107.2(2)	
O–O (others)	2.508(2) to 2.561(2)		2.742(5) to 2.851(6)	
O–X(2)–O (others)	110.19(9) to 114.80(9)		109.2(2) to 116.7(2)	
X(1)–X(2)	2.870(1)		3.061(1)	
X(1)–O(7)–X(2)	126.20(7)		121.2(1)	

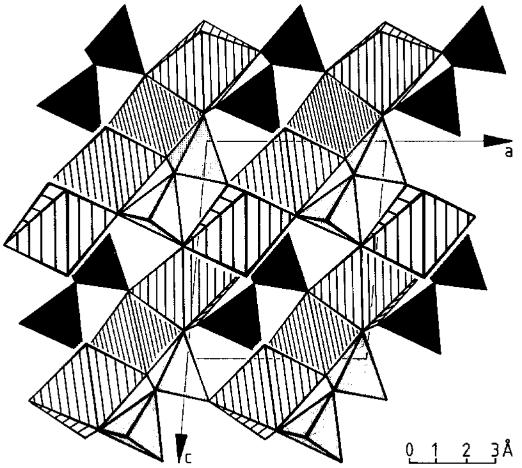

Fig. 1. The connection of the MeO_6 octahedra and the X_2O_7 groups in the structure of type $Me_2(X_2O_7)\cdot 2H_2O$: Projection of the coordination polyhedra around cations with $0 < y < 1/2$ onto [010]

Bond distances and bond angles of the pyrophosphate and pyroarsenate group agree with well known X_2O_7 groups [6, 7]. The angular and edge distortions of the AsO_4 tetrahedra are larger than for the PO_4 tetrahedra, the bond length distortions retain vice versa. The variability of the X–O–X angles is on special interest: in *MGP*/*COP*/*MNP* these angles P–O–P are 125.7(2)°/126.20(7)°/130.2(6)° which correlates with the average $\langle Me–O\rangle$ bond distances of 2.088 and 2.091 Å/2.109 and 2.110 Å/2.191 and 2.194 Å. In *COA* As–O–As is lowered to 121.2(1)°. The ratio $\langle Me–O\rangle/\langle X–O\rangle$ obviously controlls the angle X–O–X.

Within the four compounds $Me_2(X_2O_7)\cdot 2H_2O$ the average bond lengths $\langle X(1)–O\rangle$ are smaller than $\langle X(2)–O\rangle$, the differences is 6.5‰ in *COA*, 4.6‰ in *MGP* and 3.9‰ in *MNP*, in *COP* the difference is less significant with 2.0‰. The O atoms of the two XO_4 tetrahedra show comparable environments: each one O atom is

Table 4. Hydrogen bonds for $Co_2(P_2O_7)\cdot 2H_2O$ (upper line) and $Co_2(As_2O_7)\cdot 2H_2O$ (lower line). $O_w\ldots O$ up to 3.20 Å is listed (edges in the CoO_6 octahedra excluded)

*D*onor	Hydrogen	*A*cceptor	*D*–H	*D*...*A*	H...*A*	*D*–H...*A*	H–*D*...*A*	H–*D*–*H*	*A*...*D*...*A*
$O_w(1)$	H(1)	O(4)	1.00(3)	2.747(2) 2.741(5)	1.78(3)	160(2)	13(3)	112(3)	O(4)/O(1) 115.78 113.9(2)
		O(3)	–	3.077(2) 3.094(5)	2.62(3)	108(1)	54(2)	–	
		O(7)	–	3.082(2) 3.120(5)	2.70(3)	103(1)	59(2)	–	
		O(7)	–	2.898(2) 2.965(5)	2.82(3)	85(2)	75(2)	–	
	H(2)	O(1)	0.68(3)	3.040(2) 2.963(5)	2.48(3)	142(3)	30(3)	–	
$O_w(2)$	H(3)	O(6)	0.90(2)	2.900(2) 2.979(5)	2.02(3)	164(3)	11(3)	99(3)	O(6)/O(1) 60.65(8) 57.5(2)
		O(5)	–	3.039(2) 3.064(5)	2.41(3)	127(2)	39(3)	–	
	H(4)	O(1)	0.69(3)	2.986(2) 2.983(5)	2.59(3)	119(2)	50(3)	–	O(6)/O(4) 64.78(8) 62.0(2)
		O(4)	–	2.951(2) 2.982(5)	2.52(3)	123(3)	46(4)	–	
		O(7)	–	2.966(2) 3.103(5)	3.34	52(4)	117(3)	–	

coordinated to one X and one Co atom, two O atoms are coordinated to one X and to two Co atoms, the fourth is the bridging X–O–X oxygen atom. The reason for the different $\langle X\text{–O}\rangle$ bond lengths seem to be a stronger interaction of the hydrogen atoms with the three not bridging O atoms of the $X(2)O_4$ tetrahedron.

Corner connection of the Co_2O_8 chains and the X_2O_7 groups forms a three-dimensional network. Dominant connection is observed in [010]: Each X_2O_7 group links to three O atoms in one chain and to two O atoms in a chain neighboured in [010], only the sixth O atom connects in [010] with a third chain; the bridging O atom between the two X atoms is not involved into the CoO_6 coordination polyhedra. In conformity with this connection type the crystals of the title compounds are flatened on [010].

As pointed out in [19, 20] for the majority of the hydrogen atoms of the water molecules there does not exist a specified hydrogen bonding schema in the $Me_2(X_2O_7)\cdot 2H_2O$ structure type. From O_w...O distances (see Table 4) and from the (of course inaccurate) positions of the H atoms determined for *COP* there is evidence for hydrogen bonds O_w(1)–H(1)...O(4), O_w(1)–H(2)...O(1) and O_w(2)–H(3)... O(6). O_w–H(4) forms a so-called bifurcated bond with O(1) and O(4) as the acceptor atoms. This assumption is supported by bond valence calculations (according to [24], in v.u.): For *COP* and *COA* the bond valences at the atoms O(1) are 1.78 and 1.77, at O(4) they are 1.70 and 1.67 and at O(6) 1.88 and 1.92. In addition H...O interactions are expected for the atoms O(5) (bond valences 1.85 and 1.83 v.u.) and with some respect for the atoms O(3) (1.90 and 1.91 v.u.). At the atoms O(2) values of 1.96 and 1.97 v.u. were observed – the atoms O(2) are too far from any H atom for a distinct interaction. The atoms O(7) have a sum of bond valences of 2.04 and 2.07 v.u. in *COP* and *COA* indicating that the bridging O atom within the X_2O_7 group does not act as an acceptor, which is in accordance with common crystal chemical experience.

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