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Synthesis and crystal structures of two new cobalt 42-oxododecatungstates, $[Co_4Na(H_2O)_{21}][H(H_2W_{12}O_{42})].18H_2O$ and $[Co_5(H_2O)_{22}][H_2W_{12}O_{42}].12H_2O$

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Abstract

The title compounds $[Co_4Na(H_2O)]$ $[H(H_2W_{12}O_{42})].18H_2O$ (I) and $[Co_5(H_2O)_{22}]$ $[H_2W_{12}O_{42}].12H_2O$ (II) were synthesized and their crystal structures determined. The structures are built from paradodecatungstate anions joined by Co and Na cations into three-dimensional networks. The Co and Na cations are coordinated both by O atoms of the anions and by water molecules. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction,

The chemistry of polynuclear oxometalate anions, polyoxometalates, have attracted much attention in recent years. This is mainly due to their possibility of versatile applications in analytical chemistry, biology, clinical research, and in homogeneous and heterogeneous catalysis. Polyoxometalates of transition metals can have another important application: their reduction can produce a mixture of metals, which otherwise do not make alloys, evenly dispersed on an 'atomic scale' ready for powder metallurgy processing. An excellent review covering all aspects of polyoxometalates has been very recently published in Chemical Reviews [1].

A recent detailed study of complexation of tungstate with tartrate (L^{2-}) in 1 M KNO_3 at 25°C by potentiometry [2] proved an existence of species $(H^+)_p$ $(WO_4^{2-})_q$ $(L^{2-})_r^{(p-2g-2r)}$ with $\log \beta_{212}=18.82\pm0.05$, $\log \beta_{422}=31.3\pm0.1$, and $\log \beta_{522}=33.0\pm0.1$. After an addition of Co(II) to the solution and standing for a prolonged period of time, tartrate was removed from a coordination sphere of W and dimeric tungstate species oligomerized under the formation of new Co(II) paradodecatungstates which crystallized out of the solution.

However, since this preparation was an accidental one and yielded only a very small amount of the substances, we attempted to obtain the compounds on a preparative scale. Therefore, we prepared rather concentrated solutions of Na_2WO_4 and $Co(NO_3)_2$ from which yellow–orange crystals crystallized during a few days. We have found that in the first step mixed cobalt–sodium paratungstate $[Co_4Na(H_2O)_{21}]$ $[H(H_2W_{12}O_{42})].18H_2O$ (I) is formed which on prolonged stay in the mother liquid is transformed into cobalt paratungstate $[Co_5(H_2O)_{22}]$ $[H_2W_{12}O_{42}].12H_2O$ (II). The identity of the compounds was established by their X-ray structure determination and by a qualitative analysis of their metal contents.

2. Experimental details

2.1. Preparation

In a typical preparation, 6 g of $Na_2WO_4.2H_2O$ was dissolved in 150 ml of water in a 400 ml beaker and its pH adjusted to 5.5 by addition of diluted HNO_3, brought to boil and a solution of 2.2 g of $Co(NO_3)_2.6H_2O$ in 75 ml of

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water was added dropwise. The solution turned blue and if a light turbidity occurred it was waited until it cleared again before the next drop was added. The solution was removed from the heat and the beaker was covered with a watch-glass and left. During a few days, yellow–orange crystals of (I) crystallized out of the solution in the form of perfectly developed parallepipeds. It was not possible to isolate the compound since it loses crystal water and disintegrates within a few seconds after being dry.

If the crystals of (I) are left in the mother liquid for a prolonged period of time (several weeks) they are transformed into light orange hexagonal columns of the compound (II). However, this transformation proceeds only slowly and is never complete. The compound (II) is stable when dry and can be isolated from a dry crystalline mass by treating it with water: compound (I) disintegrates into a fine powder which can be washed out or filtered through a thin sintered glass filter.

The stoichiometry of both substances was mainly derived from the results of the X-ray structure analysis. However, we attempted to determine their metal contents by ICP and flame spectrophotometry. Since the compound (I) decomposes on drying, only an approximate molar ratio of the metals could be determined. The results are not very conclusive, Na:Co:W=2.73:3.73:12, but nevertheless they confirm a presence of sodium cations in the compound. The analysis of (II) did not find any sodium, the content of W and Co is consistent with the formula. Found: W 62.4%; Co 7.32%; Calc.:W 59.36%, Co 7.93%.

Table 1
Crystal data and structure refinement

	(I)	(II)
Formula	$H_{81}O_{81}Co_4NaW_{12}$	$H_{70}O_{76}Co_5W_{12}$
Formula weight	3842.56	3787.41
Temperature [°C]	−123(2)	25(2)
λ [Å]	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	12.109(4)	26.143(4)
b [Å]	13.092(4)	14.998(3)
c [Å]	14.821(5)	22.038(4)
α [°]	106.82(3)	90
β [°]	100.20(3)	90
γ [°]	111.26(3)	90
Volume [Å]	1988.5(10)	7021(2)
Z	1	4
$F(000)$	1736	6804
D_x [Mg m^{-1}]	3.209	3.583
μ [mm^{-1}]	18.209	20.839
Crystal size [mm]	0.19×0.15×0.08	0.20×0.20×0.20
ϑ range	2.87–28.30	1.66–22.98
Measured data	15817	5257
Unique data	8199	4894
R_{int}	0.0412	0.0238
Refinement	Full matrix least-squares on F	
Weight	$w=1/[\sigma^2(F_0^2)+aP^2+bP]$ where $P=0.333$ [max of (0 or F_0^2)]$+0.667F_c^2$	
Data/parameters	8186/450	4869/398
S on F^2	0.977	1.116
[a]$R1$ [for $I>2s(I)$]	0.0449	0.0454
[b]$wR2$ [for $I>2s(I)$]	0.1174	0.1240
$R1$ all data	0.0610	0.0597
$wR2$ all data	0.1234	0.1292
$\Delta\rho_{max}/\Delta\rho_{min}$ [eÅ^{-3}]	4.489/−3.189	3.398/−1.922

[a] $R1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$.
[b] $wR2=[\Sigma w(F_0^2-F_c^2)^2/\Sigma wF_0^4]^{1/2}$.

2.2. X-ray analysis

A suitable crystal of (I) was chosen in a drop of mother liquid, covered with a layer of Apiezon grease while still wet, and transferred on a diffractometer and cooled to 150 K. The diffraction data were collected on the Nonius diffractometer equipped with a CCD area detector and the Oxford Cryosystem LT device. The images were obtained by 360° ϕ-scan with 1° frame width and 30 s exposure time.

The crystal of (II) was chosen from a dry crystalline mass. The diffraction data were collected on a conventional κ-axis Nonius diffractometer at room temperature. The stability of the crystal was monitored by measuring three standard reflections every 3 h but no decay of the crystal was observed.

The intensity data of (I) were partially corrected for absorption by an internal scaling procedure between groups of frames, for (II) a Gaussian integration procedure was employed. Since in both cases the absorption correction left some residual effects, an empirical absorption correction based on a structural model using the program XABS2 [3] was later used.

The structures were solved by direct methods and anisotropically refined (except water molecules of disordered Co4 cation in (I) and O1, O2 atoms in (II)) using SHELXL-97 [4] program system and the drawings were made by ORTEP [5]. The hydrogen atoms were not localized.

Crystal data and some details of the intensity measurements and structure refinements are in the Table 1. In Tables 2 and 3 atomic parameters for (I) and (II), respectively, are contained.

3. Description and discussion of the structures

Both structures are formed by dodecatungstate anions lying on symmetry centres joined by the cations into an infinite three-dimensional network. The cations are coordinated octahedrally both by O atoms of the anions and by water molecules. The symmetry and a general shape of the $[H_2W_{12}O_{42}]^{10-}$ anions is the same as observed in other paradodecatungstates, e.g. $Mg_5[H_2W_{12}O_{42}].38H_2O$ [6], $Na_{10}[H_2W_{12}O_{42}].20H_2O$ [7], and $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}].14H_2O$ [8].

The anions $[H(H_2W_{12}O_{42})]^{9-}$ of (I) are surrounded by six Co (Co1, Co2, Co3+3 symmetry equivalent) and two

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (I)[a]

	x	*y*	*z*	U_{eq}
W(1)	3074(1)	1736(1)	9385(1)	14(1)
W(2)	2788(1)	2478(1)	11903(1)	14(1)
W(3)	437(1)	2357(1)	10250(1)	13(1)
W(4)	−2065(1)	376(1)	7804(1)	15(1)
W(5)	799(1)	1740(1)	7759(1)	15(1)
W(6)	143(1)	−1089(1)	8104(1)	14(1)
O(1)	4066(7)	1069(7)	9172(7)	21(2)
O(2)	1388(7)	2134(6)	9392(6)	16(2)
O(3)	1524(7)	31(6)	9087(6)	15(2)
O(4)	4006(7)	3175(7)	9519(6)	20(2)
O(5)	2127(7)	1295(6)	8000(6)	16(2)
O(6)	3278(6)	2017(6)	10736(6)	14(2)
O(7)	4184(7)	3555(7)	12777(6)	22(2)
O(8)	2169(7)	3366(7)	11350(6)	19(2)
O(9)	892(7)	1084(6)	10765(6)	16(2)
O(10)	−147(7)	2303(6)	11401(6)	17(2)
O(11)	303(7)	3621(6)	10189(6)	18(2)
O(12)	−1005(7)	1149(7)	9396(6)	19(2)
O(13)	−2606(7)	−194(7)	6509(6)	22(2)
O(14)	−2847(7)	−1018(7)	8016(6)	18(2)
O(15)	−679(7)	1845(7)	7923(6)	20(2)
O(16)	−413(7)	−3(7)	7840(6)	17(2)
O(17)	−3039(7)	1041(7)	8105(7)	21(2)
O(18)	1625(7)	3236(7)	7986(7)	21(2)
O(19)	335(7)	1049(7)	6455(6)	17(2)
O(20)	681(7)	−1500(7)	7112(6)	21(2)
O(21)	−1696(7)	−2312(7)	7349(6)	19(2)
Co(1)	0	5000	10000	16(1)
O(1C1)	1470(8)	5342(8)	9396(8)	29(2)
O(2C1)	−1219(8)	3789(7)	8606(7)	27(2)
Co(2)	5000	5000	10000	19(1)
O(1C2)	3963(10)	4995(9)	8740(10)	64(4)
O(2C2)	3719(12)	5134(9)	10747(13)	74(5)
Co(3)	0	0	5000	19(1)
O(1C3)	1756(8)	1101(9)	4986(7)	33(2)
O(2C3)	−754(10)	1035(9)	4560(8)	39(2)
Co(4)	380(7)	4974(6)	6080(6)	89(2)
O(1C4)	930(2)	6033(18)	7706(18)	45(5)
O(2C4)	−300(2)	6032(19)	5548(18)	47(6)
O(3C4)	2430(3)	6300(3)	6010(3)	112(12)
O(4C4)	−1500(3)	3850(3)	5950(2)	82(9)
O(5C4)	160(4)	3640(4)	6420(4)	151(17)
Na	5000	0	10000	29(2)
O(1NA)	5085(8)	1139(8)	11547(8)	34(2)
O(2NA)	7047(9)	1340(9)	10281(9)	44(3)
OW1	3458(9)	1657(11)	6725(8)	48(3)
OW2	3664(9)	7172(9)	10902(10)	44(3)
OW3	6910(12)	1347(14)	13100(11)	76(4)
OW4	5194(13)	−440(15)	13361(13)	85(5)
OW5	−2288(16)	4576(12)	7374(10)	87(6)
OW6	3497(11)	6714(12)	8392(15)	100(7)
OW7	−2170(2)	1590(19)	5637(14)	130(9)
OW8	−2140(2)	−3210(2)	5364(13)	136(8)
OW9	4730(2)	3970(15)	7059(15)	153(10)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (II)[a]

	x	*y*	*z*	U_{eq}
W(1)	1061(1)	1007(1)	−402(1)	14(1)
W(2)	1309(1)	3343(1)	206(1)	16(1)
W(3)	2578(1)	2063(1)	1290(1)	13(1)
W(4)	3659(1)	477(1)	1233(1)	17(1)
W(5)	2266(1)	−314(1)	695(1)	15(1)
W(6)	2270(1)	886(1)	−800(1)	12(1)
O(1)	429(7)	787(10)	−1342(9)	23(4)
O(2)	2016(6)	1137(9)	648(8)	13(3)
O(3)	1642(7)	1345(10)	−802(9)	22(4)
O(4)	741(8)	686(11)	71(8)	25(4)
O(5)	1487(7)	−116(10)	−268(8)	22(4)
O(6)	981(6)	2234(9)	−368(8)	13(3)
O(7)	685(7)	3717(11)	200(9)	25(4)
O(8)	1751(7)	2641(10)	1057(9)	18(3)
O(9)	2165(6)	2873(9)	256(8)	13(3)
O(10)	2880(7)	3274(10)	1571(8)	17(3)
O(11)	2830(7)	1698(10)	2168(8)	21(4)
O(12)	3198(7)	1722(9)	1222(8)	16(3)
O(13)	3837(8)	−581(11)	1069(10)	29(4)
O(14)	3902(6)	1180(10)	721(8)	18(3)
O(15)	3095(7)	29(11)	1475(8)	21(4)
O(16)	2715(6)	425(9)	168(7)	11(3)
O(17)	4288(7)	664(11)	2152(10)	35(5)
O(18)	1976(7)	−593(10)	1204(9)	23(4)
O(19)	2434(8)	−1336(10)	490(9)	26(4)
O(20)	1925(7)	−72(10)	−1386(8)	19(3)
O(21)	3117(7)	724(10)	−685(8)	21(4)
Co(1)	0	743(3)	−2500	21(1)
O(1C1)	−628(8)	−283(11)	−2678(10)	37(5)
O(2C1)	−652(8)	1685(12)	−2645(9)	32(4)
Co(2)	0	0	0	21(1)
O(1C2)	440(12)	−1204(15)	71(13)	61(6)
O(2C2)	503(9)	−15(13)	1173(9)	35(4)
Co(3)	2500	−2500	0	20(1)
O(1C3)	2023(10)	−1889(12)	−1045(10)	41(5)
O(2C3)	1637(8)	−2949(12)	−234(11)	36(5)
Co(4)	3266(2)	1288(2)	3262(2)	24(1)
O(1C4)	4042(9)	2114(13)	3656(10)	39(5)
O(2C4)	2900(9)	2343(14)	3507(11)	45(5)
O(3C4)	2448(10)	497(13)	2830(10)	48(6)
O(4C4)	3677(11)	273(13)	3038(11)	48(5)
O(5C4)	3684(12)	841(14)	4359(10)	60(7)
OW1	4208(11)	−3368(18)	970(2)	129(16)
OW2	1254(14)	−3000(2)	−2233(18)	99(10)
OW3	1391(11)	1362(16)	1684(13)	62(7)
OW4	2066(11)	3510(15)	2368(12)	57(6)
OW5	−179(8)	3112(12)	−1767(10)	35(4)
OW6	−1451(8)	1186(11)	−1919(9)	31(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Na cations (symmetry equivalent included), all of them bridging to neighbouring anions. The cations Co1, Co2, Co3, and Na are coordinated octahedrally by four water molecules (subsequently abbreviated as OW) and by two O atoms of the anions in the equatorial and axial positions, respectively, and are situated on the centres of symmetry. Co4 cation is isolated and octahedrally coordinated by water molecules only and is disordered across a center of symmetry. A schematic drawing of a molecule of (I) is in Fig. 1.

The anions are connected by bridging Co1–O and Co3–O octahedra into layers parallel to (100) plane. These layers are further bound by Co2–O and Na–O octahedra

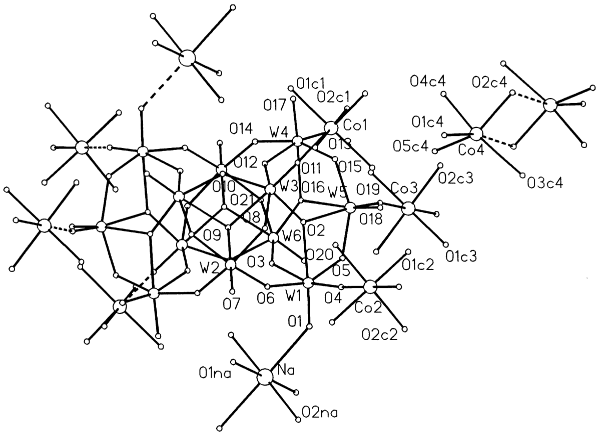

Fig. 1. An ORTEP representation of a ‘molecule’ of (I). Co–O and Na–O octahedra from a neighbouring molecule are attached by dashed lines. Water molecules are omitted.

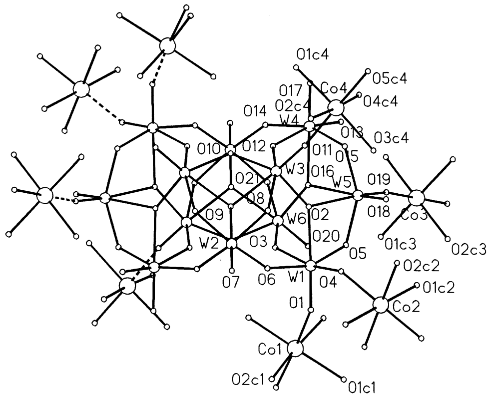

Fig. 3. An ORTEP representation of a ‘molecule’ of (II). Co–O octahedra from a neighbouring molecule are attached by dashed lines. Water molecules are omitted.

into a three-dimensional structure. A polyhedral representation of a layer is depicted in Fig. 2.

Each $[H_2W_{12}O_{42}]^{10-}$ anion of (II) is surrounded by eight Co atoms, six of them being bridging (Co1, Co2, Co3+3 symmetry equivalent) and two being terminal (Co4+symmetry equivalent). Co1, Co2, and Co3 are situated on symmetry centres and coordinated by four water molecules and two O atoms as in (I), Co4 is in a general position and coordinated by five water molecules and one O atom of the anion. A drawing of a molecule of (II) is in Fig. 3.

Paradodecatungstate anions of (II) are joined by Co1–O and Co3–O bridging octahedra into layers parallel to (10–1) plane which are further connected by Co2–O octahedra into a three-dimensional network. Co4–O octahedra do not participate in any bridging. A polyhedral representation of such a layer is given in Fig. 4.

Similar three-dimensional network via Co–O and Na–O polyhedra has been also observed in $(Me_4N)_2Na_2[Na_2Co_2H_2W_{12}O_{42}(H_2O)_{12}].16H_2O$, and $Na_3[NaCo_3H_2W_{12}O_{42}(H_2O)_{16}].22H_2O$ [9], while $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}].14H_2O$ [8], exhibits only a two-dimensional structure.

The W–O distances in the paradodecatungstate anions follow the same tendencies noted by Tsay and Silverton [6] in $Mg_5[H_2W_{12}O_{42}].38H_2O$: the shortest are those to single bonded, terminal, oxygens (mean values 1.74(1) in (I), 1.74(2) Å in (II)), followed by double bonded μ_2–O (1.95(13) (I), 1.95(12) Å (II)), and the longest being to triple bonded μ_3–O oxygens (2.17(17) (I), 2.17(17) Å (II)). There is no difference in W–O bond lengths for oxygens bonded to Co or Na atoms, respectively. However, despite a smooth change in W–O distances with respect to the hapticity of the O atoms, there is a

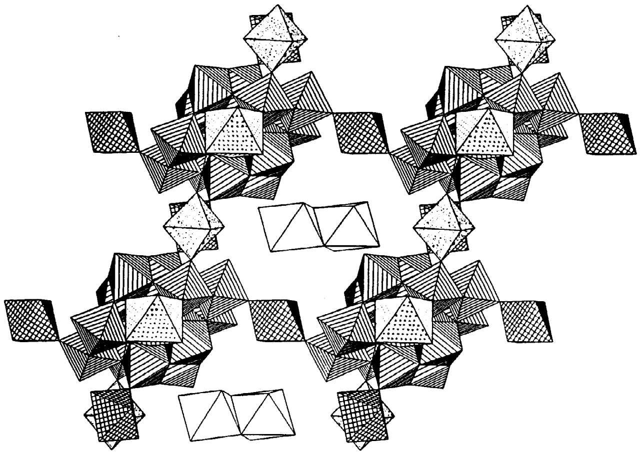

Fig. 2. A polyhedral representation of the structure of (I). Bridging Co–O (Co1, Co3) octahedra in the layer are cross-hatched, bridging Co–O (Co2) and Na–O octahedra to adjacent layers are dotted (Co random, Na regular dot pattern), and disordered Co4–O octahedra are blank. Free water molecules are omitted.

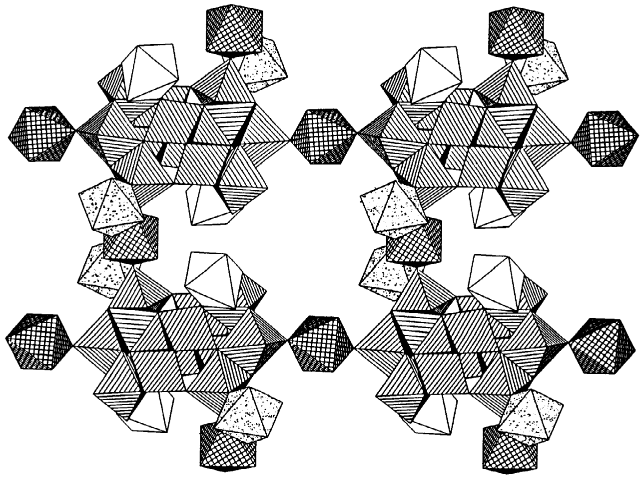

Fig. 4. A polyhedral representation of the structure of (II). Bridging Co–O (Co1, Co3) octahedra in the layer are cross-hatched, bridging Co–O (Co2) octahedra to adjacent layers are dotted, and terminal Co4–O octahedra are blank. Free water molecules are omitted.

Table 4
Important interatomic distances (Å) in (I) and (II)

	(I)	(II)
	$W–O_{term}$	
W(2)–O(7)	1.722(8)	1.719(15)
W(4)–O(13)	1.745(8)	1.750(16)
W(4)–O(17)	1.747(8)	1.732(16)
W(5)–O(18)	1.741(8)	1.735(15)
W(6)–O(20)	1.735(8)	1.785(15)
Mean	1.74(1)	1.74(2)
	$W–O_{Co}$	
W(1)–O(1)	1.744(8)	1.772(16)
W(1)–O(4)	1.740(8)	1.741(15)
W(3)–O(11)	1.746(7)	1.731(15)
W(5)–O(19)	1.762(8)	1.726(15)
Mean	1.748(10)	1.743(20)
	$W–\mu_2O$	
W(1)–O(3)	2.190(7)	2.215(16)
W(1)–O(5)	1.965(8)	1.944(14)
W(1)–O(6)	1.881(8)	1.859(14)
W(2)–O(6)	1.930(8)	1.959(14)
W(2)–O(8)	1.884(8)	1.854(15)
W(2)–O(14)#1	1.976(8)	1.916(15)
W(2)–O(21)#1	1.865(8)	1.865(14)
W(3)–O(8)	2.082(8)	2.098(15)
W(3)–O(10)	1.968(9)	1.934(15)
W(3)–O(12)	1.791(8)	1.786(14)
W(4)–O(12)	2.201(8)	2.216(14)
W(4)–O(14)	1.874(8)	1.903(15)
W(4)–O(15)	1.976(8)	1.955(15)
W(5)–O(5)	1.909(8)	1.923(15)
W(5)–O(15)	1.897(8)	1.890(14)
W(6)–O(3)	1.786(8)	1.778(15)
W(6)–O(10)#1	1.936(8)	1.961(14)
W(6)–O(21)	2.067(8)	2.090(16)
Mean	1.95(12)	1.95(13)
	$W–\mu_3O$	
W(1)–O(2)	2.284(8)	2.211(14)
W(2)–O(9)	2.292(8)	2.287(14)
W(3)–O(2)	1.890(8)	1.914(14)
W(3)–O(9)	2.218(7)	2.228(14)
W(4)–O(16)	2.223(8)	2.204(13)
W(5)–O(2)	2.244(8)	2.257(14)
W(5)–O(16)	2.273(7)	2.354(13)
W(6)–O(16)	1.885(8)	1.867(13)
W(6)–O(9)#1	2.264(8)	2.240(14)
Mean	2.18(20)	2.17(20)
	Co–O	
Co(1)–O(1)		2.107(16)
Co(2)–O(4)		2.117(15)
Co(3)–O(19)		2.112(16)
Co(4)–O(11)		2.070(15)
Co(1)–O(11)	2.051(7)	
Co(2)–O(4)	2.071(8)	
Co(3)–O(19)	2.067(8)	
Mean	2.063(10)	2.102(20)
	Co–OW	
Co(1)–O(1C1)	2.096(8)	2.113(17)
Co(1)–O(2C1)	2.070(9)	2.090(16)
Co(2)–O(1C2)	2.055(11)	2.10(2)
Co(2)–O(2C2)	2.087(10)	2.109(16)
Co(3)–O(1C3)	2.100(9)	2.085(17)
Co(3)–O(2C3)	2.072(9)	2.109(16)
Co(4)–O(1C4)	2.24(2)	2.09(2)
Co(4)–O(2C4)	2.11(2)	2.077(19)
Co(4)–O(3C4)	2.50(4)	2.125(18)
Co(4)–O(4C4)	2.15(3)	2.083(19)
Co(4)–O(5C4)	1.90(5)	2.099(17)
Mean	2.13(2)	2.10(2)
Na–O(1)	2.529(8)	
Na–O(1NA)	2.306(10)	
Na–O(2NA)	2.335(10)	
Mean	2.302(20)	

Symmetry code: #1 $0.5-x$, $0.5-y$, $-z$

significant spread of individual values in each group, as witnessed by large e.s.d.'s of the mean values.

The Co–O–tungsten distances (mean 2.06(10) (I), 2.10(20) Å (II)) are in agreement with values found in other compounds containing Co–OX species, as in $(Me_4N)_2Na_2[Na_2Co_2H_2W_{12}O_{42}(H_2O)_{12}].16H_2O$ (2.04(2) Å) and $Na_3[NaCo_3H_2W_{12}O_{42}(H_2O)_{16}].22H_2O$ (2.07(1) Å [9], and also $CoSO_4.4H_2O$ ($Co–OSO_3$ 2.102(7) Å) [10] and $CoSO_4.H_2O$ ($Co–OSO_3$ 2.053(2) Å) [11].

The Co–OW distances (2.13(2) Å in I, 2.10(2) Å in II) agree with those found in $(Me_4N)_2Na_2[Na_2Co_2H_2W_{12}O_{42}(H_2O)_{12}].16H_2O$ (2.13(2) Å) and $Na_3[NaCo_3H_2W_{12}O_{42}(H_2O)_{16}].22H_2O$ (2.10(3) Å) [9], $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}].14H_2O$ (2.10(?) Å) [8], and $CoSO_4.xH_2O$, $x=1$, 4, 6 (2.05(?)–2.175(?) Å) [10–12], except the Co4–OW in (I). Due to its disorder the distances range from 1.90 to 2.5 Å. Important interatomic distances are in Table 4.

A fairly octahedral environment of the Na cation in (I) is achieved by two O atoms from two symmetry related anions in the axial positions (Na . . . O–tungsten 2.529(8) Å) and four water molecules in the equatorial positions (Na–OW 2.306(10), 2.335(10) Å). These values correspond with those found in other sodium paradodecatungstates, e.g. $Na_{10}[H_2W_{12}O_{42}].20H_2O$ (mean values 2.534(120), 2.385(80) Å) [7], $Na_{10}[H_2W_{12}O_{42}].28H_2O$ (mean values 2.550(150), 2.388(110) Å) [13], $(Me_4N)_2Na_2[Na_2Co_2H_2W_{12}O_{42}(H_2O)_{12}].16H_2O$ (mean values 2.56(3) Å, 2.88(25) Å), and $Na_3[NaCo_3H_2W_{12}O_{42}(H_2O)_{16}].22H_2O$ (2.58(1) Å, 2.38(2) Å) [9].

The structure of (II) is one of the very few examples of a paradodecatungstate containing transition metal cations only. Syntheses of isostructural cubic compounds $M_7(MW_{12}O_{42})(OH)_4(H_2O)_8$, M=Mn, Fe, Co, Ni, Mg, were reported [14] but the actual structure was determined only for Mg compound.

4. Supplementary material

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@FIZ-BKarlsruhe.de) on quoting the depository number CSD-408791 (I) and CSD-408792 (II), respectively.

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