Contribution from the Laboratoire de Physicochimie Inorganique,
Unité Associée au CNRS 419, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

A New Crown Heteropolyanion, $K_{28}Li_5H_7P_8W_{48}O_{184}{\cdot}92H_2O$: Synthesis, Structure, and Properties

Roland Contant and André Tézé*

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The heteropolyanion compound $K_{28}Li_5H_7P_8W_{48}O_{184}{\cdot}92H_2O$ is tetragonal with the space group $P4/m$ and $a = b = 24.200$ (8) Å, $c = 21.800$ (7) Å, $Z = 2$. The crystal contains discrete crown polyanions with nearly D_{4h} symmetry incorporating inner K^+ cations. The compound was prepared by condensation of the $[H_2P_2W_{12}O_{48}]^{12-}$ anion. An intermediate species has been isolated, and the condensation mechanism is discussed.

In recent years interest in large polyanions,[1,2] such as $[NaSb_9W_{21}O_{86}]^{18-}$ or $[\alpha s_4W_{40}O_{140}]^{28-}$, has increased especially because of their antiviral or antitumoral properties.[3] The former complex (known as HPA 23) has already been used for treatment of three patients with AIDS and one with prodrome.[4] Their anions were directly prepared by acidification of tungstate and antimony(III) chloride or arsenate(III). Until now the largest poly(tungstophosphate) was $[P_5W_{30}O_{110}]^{15-}$, whose structure has been recently determined.[5] It is a byproduct[6] in the preparation of $[P_2W_{18}O_{62}]^{6-}$.

A new route of synthesis of large polyanions is to condense basic lacunary polyoxometalates previously isolated. From $[H_2P_2W_{12}O_{48}]$,$^{12-}$ a lacunary polyanion[7] related to $[P_2W_{18}O_{62}]^{6-}$ and stable enough to react in such a way, was prepared a crown polyanion that is probably the largest discrete polyoxometalate known to date, $[H_7P_8W_{48}O_{184}]^{33-}$. We describe herein the synthesis, structure, and formation steps of this new polyanion, an oligomer of $[H_2P_2W_{12}O_{48}]^{12-}$.

Results and Discussion

Synthesis. The salt $K_{28}Li_5H_7P_8W_{48}O_{184}{\cdot}92H_2O$ spontaneously crystallizes from solutions of $K_{12}H_2P_2W_{12}O_{48}$ in lithium acetate–acetic acid buffer. It may be recalled that the latter salt has been obtained from $[P_2W_{18}O_{62}]^{6-}$ by alkaline degradation in the presence of amine, according to Scheme I. $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and $[H_7P_8W_{48}O_{184}]^{33-}$ are formed concurrently, and the yield is only about 50%.

The molecular weight determined by ultracentrifugation of an aqueous solution of the separated $[H_7P_8W_{48}O_{184}]^{33-}$ complex was 13 700 (theoretical, 12 024).

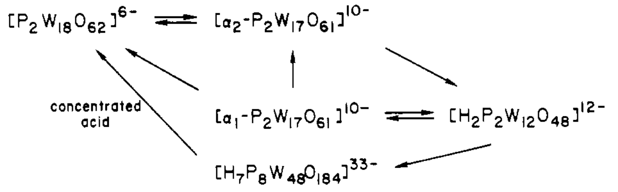
Characteristics. The ^{31}P NMR spectrum of $K_{28}Li_5H_7P_8W_{48}O_{184}$ in a lithium chloride aqueous solution exhibits a single sharp resonance at −6.6 ppm. For a freshly prepared solution of $K_{12}H_2P_2W_{12}O_{48}$ under the same conditions the chemical shift is −8.6 ppm.

The IR spectra of the two polyanions are similar, the P–O bands being split at 1140 and 1090 cm^{-1} for $K_{28}Li_5H_7P_8W_{48}O_{184}$ and at 1130 and 1075 cm^{-1} for $K_{12}H_2P_2W_{12}O_{48}$.

With Raman spectra, the differentiation is more appreciable because $K_{28}Li_5H_7P_8W_{48}O_{184}$ exhibits a broad band at 650 cm^{-1} (Figure 1).

The polarograms of $[P_8W_{48}O_{184}]^{40-}$ and $[H_2P_2W_{12}O_{48}]^{12-}$ are sufficiently different to allow identification. The larger difference was observed in weak alkaline medium. In molar tris(hydroxymethyl)aminomethane–tris(hydroxymethyl)methylammonium chloride buffer (abbreviated as "tris buffer") the waves of $[P_8W_{48}O_{184}]^{40-}$ are ill-defined. This particular behavior, characteristic of this anion, disappears in the presence of sufficiently concentrated lithium ions. In 0.2 M "tris buffer" and 0.8 M lithium chloride the half-wave potentials (V vs. SCE) are, respectively, as follows: for $[P_8W_{48}O_{184}]^{40-}$, −0.87 (8 e), −1.05 (8 e), and −1.25 (8 e); for $[H_2P_2W_{12}O_{48}]^{12-}$, −0.99 (4 e) and −1.29 (2 e).

Scheme I



Structure. Designation of atoms in a structure having an high pseudosymmetry and an important number of atoms may be made in two ways. Either atoms are designated with their symbol and a number, independant of their mutual relationships, or these relationships are taken into account by a more sophisticated designation rule with a more complex typography. The second way has been chosen, especially for oxygen atoms.

There are two independent anions in the tetragonal cell; one-eighth of each anion in the unit had to be determined. The numbering of tungsten atoms of the first anion is given in Figure 2; that for the atoms of the second anion is similar and is obtained by adding 6 in each case.

P(1) and P(2) belong to one molecule and P*(1) and P*(2) to the second one. Each phosphorus of the asymmetric unit is connected through an oxygen atom to three WO_6 octahedra. This set can be regarded as a one-fourth of a Keggin structure.[8] It may be recalled that in a Keggin anion, four types of oxygen atoms are considered: oxygens bridging tungsten atoms and the central P heteroatom (referred to as O_a); oxygens bridging two tungsten atoms (referred to as O_b when they belong to two different W_3O_{13} groups and referred to as O_c when they belong to the same W_3O_{13} group); oxygens linked to only one tungsten atom (terminal, referred to as O_d). The designation of the type of oxygen atoms of the title anion has been made in reference to the Keggin ion, the numbers in parentheses referring to the W atoms to which they are linked.

The atomic coordinates, vibrational parameters, and corresponding standard deviations are reported in Table I. Selected bond lengths are given in Table II.

The polyanion is a crown formed by linkage of four subunits $P_2W_{12}O_{48}$ (Figure 3). These subunits are derived from the well-known Dawson structure[9] of $[P_2W_{18}O_{62}]^{6-}$ by loss of six adjacent WO_6 octahedra, two from the cap and four from the belt polyhedra.

The polyanion has, approximately, point symmetry D_{4h}.

Octahedra W_xO_6 (x = 3–6 and 9–12) are very similar, the various W–O distances agreeing with those found in other Keggin-like structures.

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(1) Michelon, M.; Hervé, G.; Leyrie, M. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1583.
(2) Leyrie, M.; Hervé, G. *Nouv. J. Chim.* **1978**, *2*, 233.
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(7) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Synop.* **1977**, 222; *J. Chem. Res., Miniprint* **1977**, 2601.
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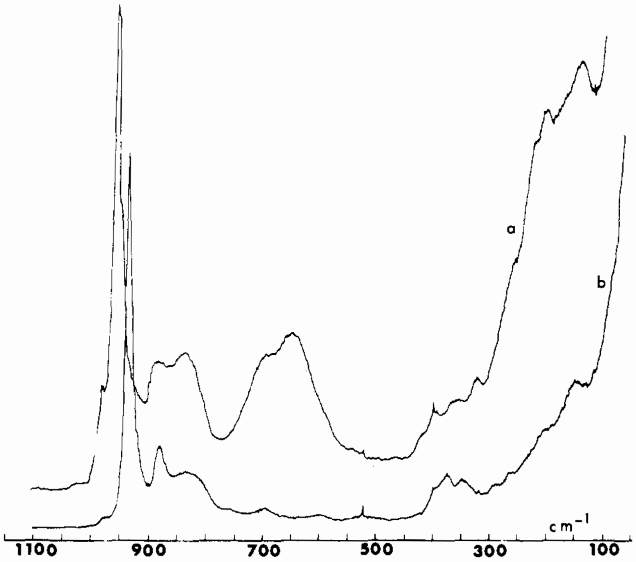

Figure 1. Raman spectra of (a) $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$ and (b) $K_{12}H_2P_2W_{12}O_{48}\cdot 24H_2O$.

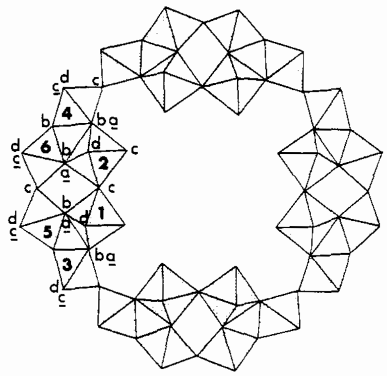

Figure 2. Polyhedral model of an anion (view along *c* axis) and tungsten numbering. Types a, b, c, or d of oxygen atoms are indicated. Atoms in the symmetry plane are underlined.

In W_xO_6 octahedra (x = 1, 2, 7, 8) the bonds between tungsten atoms and $O_c(x)$ or $O_d(x)$ oxygen atoms are partially multiple; their mean values—1.78 (4) or 1.73 (2) Å—are very close to W–O_d distances of other octahedra. The distance between the W atom and the O_b atom opposed to $O_c(x)$ is slightly enhanced. The other distances are in the usual range.

Two kinds of potassium atoms can be distinguished (Figure 3). The first one is comprised of K(1), K(2), K(3), and K(4), which are outside of the anions. They are in the neighborhood of external oxygens of both polyanions and establish ionic linkages between these anions, which are stacked, forming tubes. The second kind is formed by the K^+ ions inside the polyanion and thus inside the tubes. Atoms K(5) and K(6) give a problem: the symmetry planes lead to very short interatomic distances, 2.71 (3) and 2.62 (3) Å, respectively. Such short distances between alkali-metal cations have been already observed in Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$,[5] and were interpreted as a statistical distribution of one sodium atom between two sites. In our case, a statistical distribution of two cations between two sites that are improbably close for full occupancy does not agree with the potassium analysis and supposes that one potassium of the asymmetric unit is not found. It often occurs that, in structural determination of heteropolyanions, all cations are not found, and in the present work, most water molecules and Li^+ cations have not been located. Stereochemical considerations, which give a statistical occupation of site of 0.5 for K(5) and K(6), imply that one K^+ is also missing.

The K(7) and K(8) cations lie on the symmetry plane. The high value of B_{equ} may suggest a smaller atom, but Li would not have enough electrons and oxygen of a water molecule is most unlikely because of the proximity of O_a atoms. Because of the shapes of the thermal motion ellipsoids, K(7) or K(8) could be thought of as statistically distributed on either side of the symmetry plane, which would have no implication on the number of cations. Refinement according to this assumption did not give satisfactory results.

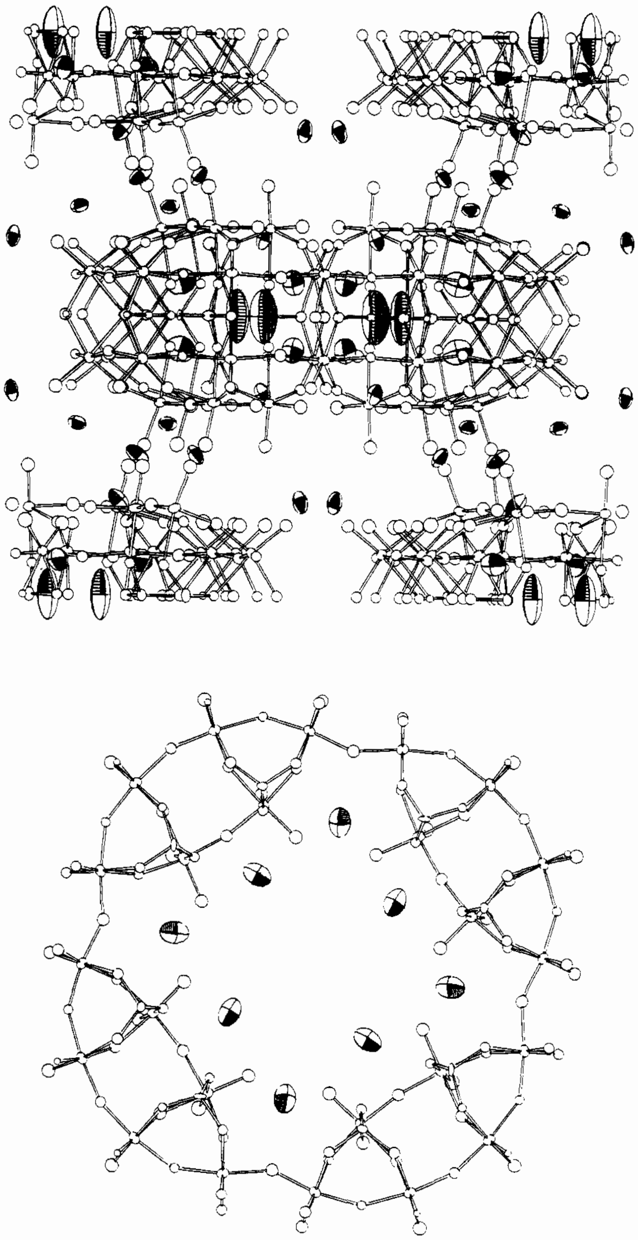

Figure 3. ORTEP drawings of an unit cell projected along the *b* and the *c* axes. In this latter case (bottom) only one anion is represented with its inner K^+ cations. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Principal ellipses and axes with envelope and octant shading are drawn for the cations.

The vicinity of the inner oxygen atoms of the polyanion and the K^+ (5, 6, 7, or 8) cations can be noticed. The atom K(5) or K(6) is close to four inner oxygen atoms (K–O distances in the range 2.74–3.08 Å). In the same way K(7) or K(8) is close to $O_a(1)$ and $O_a(2)$ or $O_a(7)$ and $O_a(8)$ mean value 2.86 (4) Å).

The K^+ ions inside the crown decrease the centrifugal repulsions between the negative charges on the inner surface of the polyanion and therefore, play a key role in its stability.

The structure of the $[P_8W_{48}O_{184}]^{40-}$ anion confirms the previously[10] proposed structure of $[H_2P_2W_{12}O_{48}]^{12-}$, corresponding to a one-fourth of the crown.

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[10] Contant, R.; Ciabrini, J. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1525.

Table I. Fractional Atomic Coordinates and Thermal Parameters[a]

atom	x/a	y/b	z/c	B(equiv), Å^2	atom	x/a	y/b	z/c	B(equiv), Å^2
W(1)	0.29000 (5)	0.33075 (5)	0.15468 (6)	1.64 (3)	W(7)	0.03376 (5)	0.26909 (5)	0.34469 (6)	1.62 (3)
W(2)	0.41934 (5)	0.24310 (5)	0.15536 (6)	1.38 (3)	W(8)	0.17670 (5)	0.20626 (6)	0.34544 (6)	1.88 (3)
W(3)	0.15556 (5)	0.35794 (5)	0.07674 (6)	1.47 (3)	W(9)	0.37088 (5)	0.05647 (5)	0.42333 (6)	1.47 (3)
W(4)	0.49185 (5)	0.12700 (5)	0.07668 (6)	1.42 (3)	W(10)	0.31460 (5)	0.19888 (5)	0.42324 (6)	1.59 (3)
W(5)	0.21105 (5)	0.21481 (5)	0.07713 (6)	1.62 (3)	W(11)	0.09596 (5)	0.39465 (5)	0.42284 (6)	1.54 (3)
W(6)	0.33855 (5)	0.12828 (5)	0.07723 (6)	1.52 (3)	W(12)	0.23704 (5)	0.33082 (5)	0.42319 (7)	1.78 (3)
P(1)	0.2731 (4)	0.3203 (5)	0.0000	1.4 (3)	P*(1)	0.0343 (5)	0.2886 (5)	0.5000	1.6 (3)
P(2)	0.4164 (5)	0.2232 (4)	0.0000	1.0 (2)	P*(2)	0.1914 (4)	0.2168 (5)	0.5000	1.3 (3)
K(1)	0.1103 (4)	0.2562 (4)	0.1933 (4)	3.8 (2)	K(2)	0.3022 (4)	0.2081 (5)	0.2489 (5)	4.8 (3)
K(3)	0.4721 (4)	0.1786 (4)	0.3314 (5)	5.0 (3)	K(4)	0.4092 (4)	0.0032 (3)	0.1378 (5)	3.8 (2)
K(5)	0.2138 (6)	0.0815 (5)	0.4379 (6)	6.7 (4)	K(6)	0.2756 (7)	0.4578 (6)	0.0601 (8)	8.4 (5)
K(7)	0.409 (1)	0.367 (1)	0.0000	17.4 (20)	K(8)	0.0652 (9)	0.1503 (9)	0.5000	14.2 (16)

atom	x/a	y/b	z/c	B(iso), Å^2	atom	x/a	y/b	z/c	B(iso), Å^2
Oa(1)	0.3075 (7)	0.3353 (7)	0.0566 (9)	1.2 (3)	Oa(7)	0.0398 (8)	0.2522 (8)	0.4456 (9)	1.4 (3)
Oa(2)	0.4186 (8)	0.2589 (7)	0.0554 (9)	1.4 (3)	Oa(8)	0.1615 (8)	0.1976 (8)	0.4430 (9)	1.4 (3)
Oa(3)	0.219 (1)	0.358 (1)	0.0000	1.3 (5)	Oa(9)	0.316 (1)	0.024 (1)	0.5000	0.7 (4)
Oa(4)	0.469 (1)	0.186 (1)	0.0000	1.5 (5)	Oa(10)	0.250 (1)	0.191 (1)	0.5000	1.6 (5)
Oa(5)	0.255 (1)	0.259 (1)	0.0000	0.0 (4)	Oa(11)	0.081 (1)	0.334 (1)	0.5000	1.2 (5)
Oa(6)	0.364 (1)	0.186 (1)	0.0000	1.6 (5)	Oa(12)	0.198 (1)	0.280 (1)	0.5000	1.8 (5)
Ob(1–3)	0.2171 (8)	0.3587 (7)	0.1294 (9)	1.2 (3)	Ob(7–11)	0.0805 (8)	0.3376 (8)	0.372 (1)	1.9 (4)
Ob(1–5)	0.2554 (8)	0.2557 (8)	0.129 (1)	1.9 (4)	Ob(7–9)	0.316 (1)	0.028 (1)	0.369 (1)	2.8 (5)
Ob(2–4)	0.4704 (8)	0.1845 (8)	0.1296 (9)	1.4 (3)	Ob(8–10)	0.2527 (9)	0.1915 (9)	0.369 (1)	1.0 (4)
Ob(2–6)	0.3612 (8)	0.1823 (8)	0.1289 (9)	1.6 (4)	Ob(8–12)	0.1987 (8)	0.2841 (8)	0.3690 (9)	1.5 (3)
Ob(3–5)	0.1630 (7)	0.2794 (7)	0.0729 (9)	1.1 (3)	Ob(9–11)	0.0130 (7)	0.4029 (7)	0.4288 (9)	1.3 (3)
Ob(4–6)	0.4162 (7)	0.1055 (7)	0.0711 (9)	1.1 (3)	Ob(10–12)	0.2944 (8)	0.2769 (8)	0.429 (1)	2.0 (4)
Oc(1–2)	0.3587 (8)	0.2923 (8)	0.159 (1)	1.8 (4)	Oc(7–8)	0.1048 (9)	0.2314 (9)	0.339 (1)	2.4 (4)
Oc(3–4)	0.1608 (8)	0.4378 (8)	0.069 (1)	1.9 (4)	Oc(9–10)	0.3212 (8)	0.1212 (8)	0.432 (1)	1.6 (3)
Oc(5–6)	0.2672 (8)	0.1592 (7)	0.0653 (9)	1.5 (3)	Oc(11–12)	0.1707 (8)	0.3741 (8)	0.432 (1)	1.6 (3)
Oc(3–3)	0.116 (1)	0.357 (1)	0.0000	1.4 (5)	Oc(9–9)	0.404 (1)	0.080 (1)	0.5000	1.3 (5)
Oc(4–4)	0.089 (1)	0.493 (1)	0.0000	1.7 (5)	Oc(10–10)	0.353 (1)	0.210 (1)	0.5000	1.4 (5)
Oc(5–5)	0.180 (1)	0.188 (1)	0.0000	0.6 (4)	Oc(11–11)	0.098 (1)	0.435 (1)	0.5000	1.5 (5)
Oc(6–6)	0.327 (1)	0.089 (1)	0.0000	0.6 (4)	Oc(12–12)	0.262 (1)	0.365 (1)	0.5000	1.6 (5)
Oc(1)	0.3203 (8)	0.3985 (8)	0.159 (1)	2.1 (4)	Oc(7)	0.2084 (9)	0.0064 (9)	0.341 (1)	2.2 (4)
Oc(2)	0.4705 (9)	0.2932 (9)	0.161 (1)	2.3 (4)	Oc(8)	0.1594 (8)	0.1327 (8)	0.344 (1)	1.0 (4)
Od(1)	0.2720 (9)	0.318 (1)	0.230 (1)	2.7 (5)	Od(7)	0.0316 (9)	0.2939 (9)	0.270 (1)	2.3 (4)
Od(2)	0.4149 (9)	0.2191 (9)	0.231 (1)	2.2 (4)	Od(8)	0.1939 (9)	0.2166 (9)	0.270 (1)	2.6 (4)
Od(3)	0.1003 (8)	0.3575 (8)	0.1261 (9)	1.4 (3)	Od(9)	0.4160 (9)	0.0874 (9)	0.373 (1)	2.4 (4)
Od(4)	0.0748 (8)	0.4878 (8)	0.127 (1)	1.9 (4)	Od(10)	0.3660 (9)	0.2086 (9)	0.372 (1)	2.3 (4)
Od(5)	0.1703 (9)	0.1780 (9)	0.129 (1)	2.2 (4)	Od(11)	0.1044 (9)	0.4497 (9)	0.373 (1)	1.0 (4)
Od(6)	0.3215 (9)	0.0748 (9)	0.128 (1)	2.3 (4)	Od(12)	0.2693 (9)	0.3749 (9)	0.374 (1)	2.5 (4)
Ow(1)	0.006 (2)	0.417 (2)	0.0000	4.3 (9)	Ow(7)	0.439 (2))	0.089 (2)	0.239 (2)	8.1 (11)
Ow(2)	0.019 (2)	0.296 (2)	0.0000	6.6 (13)	Ow(8)	0.178 (3)	0.448 (3)	0.232 (3)	12.8 (18)
Ow(3)	0.069 (3)	0.173 (3)	0.0000	8.5 (16)	Ow(9)	0.200 (3)	0.092 (3)	0.221 (4)	15.9 (22)
Ow(4)	0.045 (1)	0.407 (1)	0.249 (2)	5.9 (8)	Ow(10)	0.161 (1)	0.342 (1)	0.263 (1)	3.3 (5)
Ow(5)	0.196 (3)	0.068 (3)	0.0000	9.2 (18)	Ow(11)	0.240 (2)	−0.008 (2)	0.126 (2)	6.8 (9)
Ow(6)	0.316 (2)	0.096 (2)	0.259 (2)	8.5 (11)					

[a] Esd's in parentheses refer to the last significant digit.

It is noteworthy that the same PW_6O_{26} subunit appears in our anion and in $[P_5W_{30}O_{110}]^{15-}$.[5] This entity that has never been isolated may be a precursor in the simultaneous synthesis[6] of $[P_2W_{18}O_{62}]^{6-}$ and $[P_5W_{30}O_{110}]^{15-}$.

Mechanism of Formation and Properties. The resolution of the structure of $K_{28}Li_5H_7P_8W_{48}O_{184}$ has given evidence of potential sites of coordination and therefore $[H_mP_8W_{48}O_{184}]^{(40-m)-}$ (shortened as P_8W_{48}[11]) can be considered as a lacunar species. However its stability and inertness are noteworthy.

P_8W_{48} reacts with tungstate or molybdate only in concentrated acidic medium; the crown is broken and $[P_2W_{18}O_{62}]^{6-}$ or $[P_2W_{12}Mo_6O_{62}]^{6-}$ are respectively formed.

In aqueous solution P_8W_{48} is stable in a large pH range (1–8). All alkaline cations are exchangeable by acidic resin, and solutions of the acid $H_{40}P_8W_{48}O_{184}$ were obtained. Actually, with polyanions of this size the precision of experimental results leads to uncertainties in the determination of the number of protons. However the 40 protons found by potentiometric titration by lithium hydroxyde agree with the charge showing up from structural results. Among these 40 acidities about 24 are weak with pK_a in the range 2–7 in 0.1 M LiCl (pK_a values for such compounds largely depend on the nature and concentration of the counterion[12]). The eight weakest acidities are close together and are separated from the others by a distinct pH jump. The solution of the salt $K_{28}Li_5H_7P_8W_{48}O_{184}$ needs 1–1.2 proton/mol to reach this pH jump corresponding to $[H_8P_8W_{48}O_{184}]^{32-}$, and 6.8–7 OH^-/mol to reach the final pH jump. The salt $K_{28}Li_5H_7P_8W_{48}O_{184}$ crystallizes from solutions of the $[H_8P_8W_{48}O_{184}]^{32-}$ anion whereas the salts of the $[P_8W_{48}O_{184}]^{40-}$ anion are not sufficiently soluble to give suitable crystals.

Unlike P_8W_{48}, P_2W_{12} instantaneously react on tungstate or molybdate[10] below pH 7 and has no stability range. From more concentrated solutions a new salt has been isolated; its composition and molar mass (7400) correspond to $K_{16}Li_2H_6P_4W_{24}O_{94}$.

It reacts with tungstate or molybdate solutions like P_2W_{12}, but only by heating. In 1 M lithium chloride it gives after some days crystals of $K_{28}Li_5H_7P_8W_{48}O_{184}$ and the $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ anion.

^{31}P NMR spectrum of $K_{16}Li_2H_6P_4W_{24}O_{94}$ in lithium chloride aqueous solution exhibits two peaks at −6.94 and −8.3 ppm. It corresponds to a new species with inequivalent phosphorus atoms or even to several new species. Nevertheless it is the first step of the condensation of P_2W_{12}, as shown by the spectrum of an

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(11) Such a P_xW_y abbreviation always refers to species whose protonation is variable or unknown.

(12) Contant, R. *J. Chem. Res., Synop.* **1984**, 120; *J. Chem. Res., Miniprint* **1984**, 1063.

Table II. Selected Interatomic Distances (Å) and Average Values of Bond Lengths

W(1)-O_a(1)	2.18 (2)	W(7)-O_a(7)	2.24 (2)	2.20 (3)
W(2)-O_a(2)	2.21 (2)	W(8)-O_a(8)	2.17 (2)	
W(3)-O_a(3)	2.28 (2)	W(9)-O_a(9)	2.27 (2)	2.27 (1)
W(4)-O_a(4)	2.26 (2)	W(10)-O_a(10)	2.29 (2)	
W(5)-O_a(5)	2.26 (2)	W(11)-O_a(11)	2.27 (2)	
W(6)-O_a(6)	2.27 (2)	W(12)-O_a(12)	2.28 (2)	
W(1)-O_b(1-5)	2.08 (2)	W(7)-O_b(7-11)	2.09 (2)	2.08 (4)
W(2)-O_b(2-6)	2.12 (2)	W(8)-O_b(8-12)	2.02 (2)	
W(1)-O_b(1-3)	1.96 (2)	W(7)-O_b(7-9)	1.95 (2)	1.96 (1)
W(2)-O_b(2-4)	1.96 (2)	W(8)-O_b(8-10)	1.94 (2)	
W(3)-O_b(1-3)	1.88 (2)	W(9)-O_b(7-9)	1.91 (2)	1.90 (6)
W(3)-O_b(3-5)	1.91 (2)	W(9)-O_b(9-11)	1.85 (2)	
W(4)-O_b(2-4)	1.88 (2)	W(10)-O_b(8-10)	1.92 (2)	
W(4)-O_b(4-6)	1.91 (2)	W(10)-O_b(10-12)	1.95 (2)	
W(5)-O_b(1-5)	1.85 (2)	W(11)-O_b(7-11)	1.81 (2)	
W(5)-O_b(3-5)	1.95 (2)	W(11)-O_b(9-11)	2.02 (2)	
W(6)-O_b(2-6)	1.81 (2)	W(12)-O_b(8-12)	1.88 (2)	
W(6)-O_b(4-6)	1.96 (2)	W(12)-O_b(10-12)	1.91 (2)	
W(1)-O_c(1)	1.80 (2)	W(7)-O_c(7)	1.76 (2)	1.78 (4)
W(2)-O_c(2)	1.74 (2)	W(8)-O_c(8)	1.83 (2)	
W(1)-O_c(1-2)	1.91 (2)	W(7)-O_c(7-8)	1.95 (2)	1.93 (3)
W(2)-O_c(1-2)	1.89 (2)	W(8)-O_c(7-8)	1.85 (2)	
W(3)-O_c(3-4)	1.94 (2)	W(9)-O_c(9-10)	1.98 (2)	
W(3)-O_c(3-3)	1.93 (1)	W(9)-O_c(9-9)	1.94 (1)	
W(4)-O_c(3-4)	1.90 (2)	W(10)-O_c(9-10)	1.90 (2)	
W(4)-O_c(4-4)	1.95 (1)	W(10)-O_c(10-10)	1.94 (1)	
W(5)-O_c(5-6)	1.93 (2)	W(11)-O_c(11-12)	1.89 (2)	
W(5)-O_c(5-5)	1.96 (1)	W(11)-O_c(11-11)	1.95 (1)	
W(6)-O_c(5-6)	1.90 (2)	W(12)-O_c(11-12)	1.93 (2)	
W(6)-O_c(6-6)	1.95 (1)	W(12)-O_c(12-12)	1.97 (2)	
W(1)-O_d(1)	1.73 (2)	W(7)-O_d(7)	1.74 (2)	1.73 (2)
W(2)-O_d(2)	1.76 (2)	W(8)-O_d(8)	1.71 (2)	
W(3)-O_d(3)	1.72 (2)	W(9)-O_d(9)	1.72 (2)	1.72 (2)
W(4)-O_d(4)	1.74 (2)	W(10)-O_d(10)	1.69 (2)	
W(5)-O_d(5)	1.74 (2)	W(11)-O_d(11)	1.73 (2)	
W(6)-O_d(6)	1.75 (2)	W(12)-O_d(12)	1.70 (2)	
P(1)-O_a(1)	1.53 (2)	P*(1)-O_a(7)	1.48 (2)	
P(1)-O_a(3)	1.59 (3)	P*(1)-O_a(9)	1.56 (3)	
P(1)-O_a(5)	1.54 (3)	P*(1)-O_a(11)	1.56 (3)	
P(2)-O_a(2)	1.49 (2)	P*(2)-O_a(8)	1.51 (2)	
P(2)-O_a(4)	1.57 (3)	P*(2)-O_a(10)	1.55 (3)	
P(2)-O_a(6)	1.55 (3)	P*(2)-O_a(12)	1.54 (3)	
K(7)-O_a(1)	2.86 (3)	K(8)-O_a(7)	2.80 (3)	
K(7)-O_a(2)	2.89 (3)	K(8)-O_a(8)	2.88 (3)	

acidified solution of P_2W_{12} evolving during about 1 h (Figure 4).

It is notable that P_2W_{12} and P_4W_{24} cannot be deprotonated beyond $[H_2P_2W_{12}O_{48}]^{12-}$ and $[H_2P_4W_{24}O_{94}]^{22-}$, respectively, whereas the wholly deprotonated species $[P_8W_{48}O_{184}]^{40-}$ is stable. This difference can be explained by considering that the two untitrable protons are bound to the oxygens atoms of the W_2O_{10} groups located at the extremities of the polyanion. The oxygen atoms are those actually involved when acidified P_2W_{12} polymerizes or binds tungsten atoms and are the most reactive because of their stronger basicity. Thus, condensation occurs from the extremities of the polyanion, and addition of tungstate leads to an $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, in which the two extremity sites are occupied,[10] although in the more stable isomer $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ the lacuna is in an extremity site.

P_4W_{24} would then correspond to two P_2W_{12} entities linked by their extremities. Two terminal W_2O_{10} groups stay free and fix one proton each. There are two possibilities for such a P_4W_{24} structure: (i) the two P_2W_{12} entities are orthogonally linked (C_{2v} symmetry), leading to P_8W_{48} if potassium ions are present; (ii) the two P_2W_{12} entities are approximately linearly linked (C_{2h}), which would give a chain polymer.

The simultaneous presence of the two isomers would explain both the ^{31}P NMR band broadening and the partial formation of P_8W_{48}.

Solutions of P_2W_{12} or P_4W_{24} from which potassium ions have been removed by lithium perchlorate never give P_8W_{48} but possibly partly give some other chain oligomer. Indeed even after dilution they react less easily with tungstate.

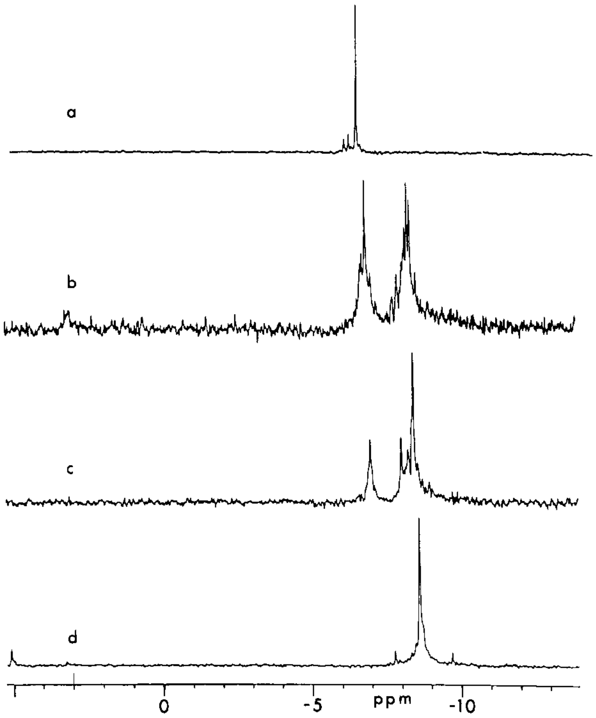
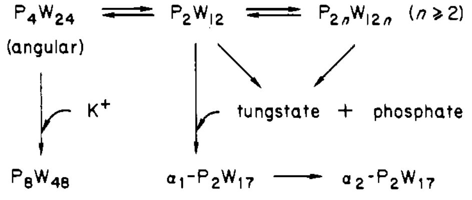


Figure 4. ^{31}P NMR spectra in lithium chloride H_2O/D_2O solutions of (a) $K_{28}Li_5H_7P_8W_{48}O_{184}$, (b) $K_{16}Li_2H_6P_4W_{24}O_{94}$, (c) acidified $K_{12}H_2P_2W_{12}O_{48}$, and (d) $K_{12}H_2P_2W_{12}O_{48}$.

Scheme II



Relations between the different species are summarized in Scheme II.

The ^{183}W NMR spectrum of a solution of $[H_8P_8W_{48}O_{184}]^{32-}$ in lithium perchlorate shows three equal peaks at −203.7, −204.4, and −216.6 ppm. This agrees with the crystal structure, which has three different types of tungsten atoms. Under the same experimental conditions the ^{183}W NMR spectrum of P_2W_{12} solutions cannot be obtained, as has already been noticed by Acerete et al.[13] This may be due to the presence in such a concentrated solution of several species differing in condensation and structure. Besides, the solutions change during the relatively long accumulation time.

Unlike most lacunar heteropolyanions, P_2W_{12} and P_8W_{48} do not give complexes with divalent or trivalent transition-metal ions. With the basic species $[P_8W_{48}O_{184}]^{40-}$ and $[H_2P_2W_{12}O_{48}]^{12-}$ insoluble precipitates are formed. In more acidic solutions, the progressive addition of cobalt(II), for instance, shows no absorption break corresponding to a defined stable compound but a only weak change of the electronic spectra of the ligands and the metal ion. The charge-transfer band of the polyanion and the ν_3 band at 19.4 × 10^3 cm^{-1} of the cobalt hexaaquo ion are slightly enhanced. For the first equivalent cobalt added this feature is more appreciable with P_8W_{48} (ϵ = 25 M^{-1} cm^{-1} at 19.3 × 10^3 cm^{-1}) than with P_2W_{12} (ϵ = 10 M^{-1} cm^{-1} at 19.4 × 10^3 cm^{-1}). Nevertheless the behavior of both polyanions agrees better with the formation of ion aggregates or outer-sphere complexes than with formation of in-

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(13) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem.* **1984**, *23*, 1478.

Table III. Summary of Crystal and Experimental Data

formula	$K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$
fw	14 809
cryst face (dist from center, mm)	001, 00$\bar{1}$ (0.089) 011, 0$\bar{1}$1, 01$\bar{1}$, 0$\bar{1}\bar{1}$ (0.162) 101, $\bar{1}$01, 10$\bar{1}$, $\bar{1}$0$\bar{1}$ (0.016)
μ, cm^{-1}	212.5
space group	$P4/m$
a = b, Å	24.200 (8)
c, Å	21.800 (7)
V,	12 767
Z	2
d(calcd), g cm^{-3}	3.87
d(obsd), g cm^{-3}	3.85
scan type	θ–2θ
2θ max, deg	50
scan speed, deg s^{-1}	0.02
scan width, deg	$\Delta\theta = 0.90 + 0.30 \tan \theta$
std reflcns	3 measd every 2 h; no decay in intens obsd
no. of reflcns collcd	11 108
no. of reflcns used in refinement with $I > 3\sigma(I)$	5477
no. of params refined	439
final R^a	0.042
final $R_w{}^a$	0.050
w	1.0

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

ner-sphere complexes like other lacunar heteropolyanions.

Experimental Section

Preparations. $K_{12}H_2P_2W_{12}O_{48}\cdot 24H_2O$ was prepared as reported previously.[7]

$K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$. A 28-mg sample of $K_{12}H_2P_2W_{12}O_{48}\cdot 24H_2O$ was dissolved in 1 L of a mixture of lithium chloride (0.5 mol), lithium acetate (0.5 mol), and acetic acid (0.5 mol) in water. The solution was left in a closed flask. After 1 day fine white radiating needles appeared, and crystallization continued for several days. When 1 week had passed the crystals were filtered off and dried in air.

Anal. Calcd for $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$: P, 1.67; W, 59.6; K, 7.39; Li, 0.23; H_2O, 11.61. Found: P, 1.66; W, 59.4; K, 7.26; Li, 0.25; H_2O, 11.56.

Thermogravimetric analysis has shown that 92 mol of water are removed below 250 °C and 3.5 mol above 300 °C.

$K_{16}Li_2H_6P_4W_{24}O_{94}\cdot 33H_2O$. An 8-g sample of $K_{12}H_2P_2W_{12}O_{48}\cdot 24H_2O$ was dissolved in 250 mL of 1 M lithium chloride acidified by 0.7 mL of glacial acetic acid. The solutions was left for 4 h at room temperature and then 50 mL of saturated potassium chloride was added. The white precipitate was filtered off and washed once with potassium chloride solution and twice with ethanol. The white powder was air-dried. Anal. Calcd for $K_{16}Li_2H_6P_4W_{24}O_{94}\cdot 33H_2O$: P, 1.70; W, 60.6; K, 8.59; Li, 0.190; H_2O, 8.90. Found: P, 1.70; W, 60.9; K, 8.52; Li, 0.173; H_2O, 8.81.

This compound can be characterized by polarography in tris buffer (0.2 M) and lithium chloride (0.8 M). It exhibits three equal waves (4 e), whose $E_{1/2}$ are respectively at −0.92, −1.03, and −1.27 (V vs. SCE).

Physical Measurements. Polarograms were recorded on a PO_4 Radiometer instrument with a dropping-mercury electrode.

Molecular weights were estimated with a Beckman Type E centrifuge provided with a Schlieren optical system. Measurements were carried out in 0.1 M LiCl solution (0.032 M in tungsten). The rotation speed was 3000 rpm. Results were discussed according to Archibald's method modified by Trautman.

Optical spectra were recorded on a Perkin-Elmer 555 spectrophotometer (UV), a Perkin-Elmer 283 instrument (IR), and a Coderg PHO instrument using the 514.5-nm line of a Spectra Physics argon laser (Raman).

NMR spectra were obtained by using 10-mm-o.d. sample tubes on a Bruker WM 250 instrument at 101 MHz for ^{31}P and at 10.4 MHz for ^{183}W. ^{31}P chemical shifts were referenced to external 85% H_3PO_4 and ^{183}W chemical shifts to external 2 M Na_2WO_4 in alkalinized D_2O.

^{31}P NMR sample solutions were obtained by respectively dissolving 0.506 g of $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$, 0.55 g of $K_{12}H_2P_2W_{12}O_{48}\cdot 24H_2O$, or 0.25 g of $K_{16}Li_2H_6P_4W_{24}O_{94}\cdot 33H_2O$, in a mixture of 10 mL of aqueous 1 M LiCl and 1 mL of D_2O.

The solution of acidified P_2W_{12} was obtained by dissolution of 0.28 g of $K_{12}H_2P_2W_{12}O_{48}\cdot 24H_2O$ in a mixture of 10 mL of aqueous 1 M LiCl, 0.25 mL of 1 M hydrochloric acid, and 1 mL of D_2O. ^{183}W NMR solutions was obtained by addition of 5 g of $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$ in 10 mL of 3 M $LiClO_4$. After the filtration of potassium perchlorate, 1 mL of D_2O was added.

Structure Determination. The crystallographic study was carried out on $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$. The compound is sensitive to air, and a crystal was sealed in a Lindeman capillary. Preliminary oscillation and Weissenberg photographs indicated a tetragonal lattice and narrowed the choice of space group to one of three, $P4$, $P\bar{4}$, or $P4/m$. Statistics of normalized structure factors led to centrosymmetric $P4/m$ group. The intensities were collected at room temperature on a Phillips PW 1100 four-circle diffractometer (Mo Kα radiation, graphite monochromator and scintillation counter) in the θ–2θ scan mode up to $2\theta_{max} = 50°$ (background measurement in fixed position before and after every scan for a time equal to one-half of the scan time). Crystal data are given in Table III. The intensities were corrected for the Lorentz and polarization factors and absorption (μ = 212.5 cm^{-1}).

The structure was solved by direct methods with the MULTAN[14] program. The 16 highest peaks on the E map correspond to the W and P atoms. These atoms were introduced in a full-matrix least-squares refinement, which gave a R factor of 0.21.

The potassium cations and oxygen atoms of the polyanion were located from alternate difference Fourier synthesis and least-squares refinement. Eleven other peaks were attributed to the water molecules. All calculations were carried out on the IRIS 80 computer of the Université Pierre et Marie Curie with the SHELX program.[15]

Acknowledgment. We thank Dr. R. Thouvenot for NMR spectral measurements and fruitful discussions.

Registry No. $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot 92H_2O$, 99397-48-5; $K_{12}H_2P_2W_{12}O_{48}$, 63950-53-8; $K_{16}Li_2H_6P_4W_{24}O_{94}$, 99397-47-4.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters of W, P, and K atoms (27 pages). Ordering information is given on any current masthead page.

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