Inorganic Chemistry

A Novel Zirconium Polyoxometalate Complex That Contains Both a Coordinated Saturated Anion, [PMo$_{12}$O$_{40}$]$^{3-}$, and a Coordinated Unsaturated Anion, [PMo$_{11}$O$_{39}$]$^{7-}$

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The novel 8-coordinate zirconium compound (NH$_4$)$_6$[Zr(PMo$_{12}$O$_{40}$)(PMo$_{11}$O$_{39}$)]·26H$_2$O (**1**) has been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, and vibrational and ^{31}P NMR spectroscopy. It is the first example of a metal complex containing both parent, [PMo$_{12}$O$_{40}$]$^{3-}$, and monovacant lacunary, [PMo$_{11}$O$_{39}$]$^{7-}$, anions. Furthermore, this is the first crystallographic determination of the [PMo$_{11}$O$_{39}$]$^{7-}$ anion.

Examples of structurally characterized zirconium complexes with polyoxometalates are rare. The reported crystal structures are of a zirconocene complex, [(PW$_{11}$NbO$_{40}$)$_2$ZrCp$_2$]$^{6-}$, the dimeric [{(MeO)ZrW$_5$O$_{18}$}$_2$]$^{6-}$ anion, and a sandwich complex, containing 6-coordinate zirconium ions, of formula [Zr$_3$(μ_2-OH)$_3$(β-SiW$_9$O$_{34}$)$_2$]$^{11-}$.[1] Increasing the understanding of the interactions of Zr^{4+} cations with polyoxoanions is of interest because of the presence of zirconium as a significant component in some nuclear wastes, arising from its use in fuel cladding,[2] and the potential use of polyoxometalates as sequestering/separation agents in nuclear waste remediation.[3] As well as interest in the properties of zirconium, the study of Zr^{4+} is also useful as a nonradioactive analogue of the tetravalent actinides, including Pu^{4+}.

The phosphomolybdate Keggin anion, [PMo$_{12}$O$_{40}$]$^{3-}$, is formed in acidic solutions of PO$_4^{3-}$ and MoO$_4^{2-}$. Careful raising of the pH results in loss of a {Mo=O}$^{4+}$ unit yielding the monovacant lacunary anion [PMo$_{11}$O$_{39}$]$^{7-}$, which has four unsaturated oxygen atoms available for coordination to a positive metal center. Despite several spectroscopic studies, [PMo$_{11}$O$_{39}$]$^{7-}$ has not been structurally characterized. First-row transition metal ions form 1:1 complexes in which the metal ion occupies the cavity in [XM$_{11}$O$_{39}$]$^{n-}$ anions.[4] The larger trivalent rare earth ions tend to form 1:2 sandwich complexes of general formula [RE^{III}(XM$_{11}$O$_{39}$)$_2$]$^{m-}$,[5] although [XW$_{11}$O$_{39}$]$^{n-}$ ions have also been shown to form 1:1 complexes, which give extended polymeric chains in the solid state.[6]

In the 1960s spectrophotometric methods were used to propose a 1:1 stoichiometry for the complexation of Zr^{4+} with [PMo$_{12}$O$_{40}$]$^{3-}$ at pH ~ 1 and 1:1.5 stoichiometry at pH ~ 4.[7] (NH$_4$)$_6$[Zr(PMo$_{12}$O$_{40}$)(PMo$_{11}$O$_{39}$)]·26H$_2$O (**1**) was synthesized from a reaction solution at a pH of 4.3 (the optimum acidity for degrading [PMo$_{12}$O$_{40}$]$^{3-}$ to [PMo$_{11}$O$_{39}$]$^{7-}$)[4a,8] containing a metal:phosphorus ratio of 1:2. The reaction yielded a yellow powder, which was then crystallized from an aqueous solution.[9]

Single-crystal X-ray diffraction[10] of **1** revealed the structure of the complex anion (Figure 1) to have the formula

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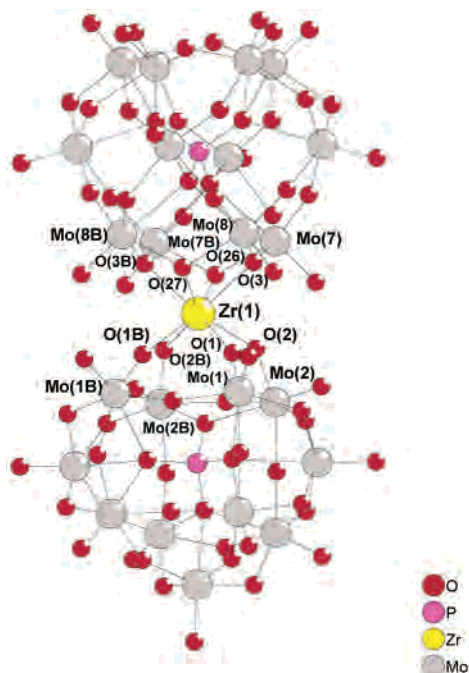(8) Himeno, S.; Hashimoto, M.; Ueda, T. *Inorg. Chim. Acta* **1999**, *284*, 237−245.

Figure 1. Ball and stick representation of the anionic complex of **1**.

[Zr(PMo$_{12}$O$_{40}$)(PMo$_{11}$O$_{39}$)]$^{6-}$ consisting of an 8-coordinate zirconium center, which is bonded to the four unsaturated oxygen atoms of [PMo$_{11}$O$_{39}$]$^{7-}$ and four bridging oxygen atoms of [PMo$_{12}$O$_{40}$]$^{3-}$. The four Zr−O bonds to the lacunary anion have an average distance of 2.183 Å, and the four

(9) H$_3$[PMo$_{12}$O$_{40}$]·xH$_2$O (78%, remainder moisture) (4.68 g, 2.00 mmol) was dissolved in H$_2$O (20 cm^3), the pH adjusted to 4.30 by addition of solid Li$_2$CO$_3$, and the solution stirred for 20 min. ZrCl$_4$ (0.233 g, 1.00 mmol) was added, with continuous magnetic stirring, resulting in a yellow precipitate, which was redissolved by gentle heating (∼30 °C) for 5 min. The pH of the solution dropped to 2.45 and so was readjusted to 4.30 by addition of Li$_2$CO$_3$. NH$_4$Cl (2 g, 37.4 mmol) was dissolved into the solution with magnetic stirring. The deep yellow colored solution was filtered under gravity, EtOH added until it was no longer immediately miscible with shaking, and the solution stored at 3 °C to give a yellow powder (2.53 g, 65% based on Zr) after 2 days. Crystals suitable for X-ray diffraction were grown by dissolving the powder in H$_2$O (10 cm^3) to yield yellow platelike crystals. Elemental anal. Calcd for **1**: Zr, 2.17; Mo, 52.53; P, 1.48; N, 2.00; H, 1.81; Cl, 0. Found: Zr, 2.22; Mo 51.86; P, 1.62; N, 3.36; H, 1.78; Cl, 0.60. IR: 1103, 1040, 1024 cm^{-1}. Raman: 976, 788 cm^{-1}. TGA: loss of H$_2$O, ∼25−100 °C (6.01%), ∼220−350 °C (5.47%), total of 26.9 H$_2$O molecules; loss of NH$_4^+$, ∼350−420 °C (2.49%), total of 5.8 NH$_4^+$ ions. The TGA data is consistent with the formula of **1**. The high N content in the elemental analysis may be explained by the presence of NH$_4$Cl and the possibility of the formation of some (NH$_4$)$_{10}$[Zr(PMo$_{11}$O$_{39}$)$_2$]·xH$_2$O which cannot be excluded from the spectroscopic data.

(10) The data were collected on a Bruker SMART CCD diffractometer at 100 K. The structure was solved by direct methods followed by Fourier syntheses, and refined on F^2. Data did not allow distinction between N and O atoms so initially all solvent atoms were modeled as O and in the latter stages of refinement the oxygen atoms with the highest thermal motion parameters were assigned as N atoms to account for the NH$_4^+$ cations which balance the charge of the anionic complex (solvent and cations are often disordered around polyoxoanions, and it is common for N and O atoms to be indistinguishable, see for example: Kim, K. C.; Pope, M. T. *J. Am. Chem. Soc.* **1999**, *121*, 8512). The Zr, W, P, and O atoms of the polyoxoanion complex were all refined anisotropically, except for O(6), and the solvent O atoms and the N atoms were refined isotropically. Crystal data for **1**: H$_{76}$N$_6$Mo$_{23}$O$_{105}$P$_2$Zr$_1$, M_r = 4200.45, monoclinic, space group $P2_1/c$, a = 12.743(3) Å, b = 19.827(4) Å, c = 18.791(4), β = 93.726(4)°, V = 4737.6(18) Å^3, Z = 2, crystal dimensions = 0.22 × 0.20 × 0.02 mm, final R ($I > 2\sigma(I)$), R1 = 0.0686, wR2 = 0.1987. Final R (all data), R1 = 0.0747, wR2 = 0.2041.
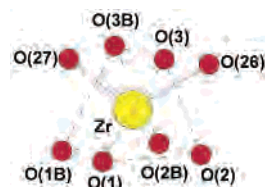
Figure 2. Representation of the coordination sphere and bicapped trigonal prismatic geometry of the Zr(IV) center of **1**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Zr(1)−O(1)	2.211(8)	Mo(1)−O(1)	1.772(8)
Zr(1)−O(2)	2.154(8)	Mo(2)−O(2)	1.770(8)
Zr(1)−O(3)	2.159(9)	Mo(7)−O(3)	2.046(10)
Zr(1)−O(26)	2.347(14)	Mo(8)−O(3)	2.030(9)
Zr(1)−O(27)	2.227(12)	Mo(8B)−O(3B)	2.030(9)
		Mo(7)−O(26)	1.998(6)
		Mo(8)−O(27)	2.031(6)
O(1)−Zr(1)−O(3B)	146.1(3)	O(1)−Zr(1)−O(27)	79.7(3)
O(1)−Zr(1)−O(26)	142.0(2)	O(2)−Zr(1)−O(3)	79.5(3)
O(2)−Zr(1)−O(27)	141.2(3)	O(2)−Zr(1)−O(2B)	77.5(4)
O(2)−Zr(1)−O(3B)	137.7(3)	O(1)−Zr(1)−O(2)	76.0(3)
O(2)−Zr(1)−O(1B)	119.9(3)	O(1)−Zr(1)−O(1B)	72.6(4)
O(26)−Zr(1)−O(27)	114.9(5)	O(2)−Zr(1)−O(26)	71.6(3)
O(3)−Zr(1)−O(3B)	95.0(5)	O(3)−Zr(1)−O(27)	69.7(3)
O(1)−Zr(1)−O(3)	87.5(3)	O(3)−Zr(1)−O(26)	67.7(3)

[a] Symmetry transformations used to generate equivalent B atoms: x, $-y + \frac{1}{2}$, z.

Zr−O bonds to the Keggin anion have a slightly longer average distance of 2.223 Å, probably reflecting the decreased negative charge on [PMo$_{12}$O$_{40}$]$^{3-}$ vs [PMo$_{11}$O$_{39}$]$^{7-}$. The gap between the 17th and 18th lowest O−Zr−O bond angles is 19.9°, which means that following criteria devised by Haigh[11] the geometry of the zirconium center is best described as bicapped trigonal prismatic (Figure 2), although there is some distortion. See Table 1 for selected bond parameters for **1**.

The structure of **1** was unexpected because a sandwich complex analogous to [RE^{III}(XMo$_{11}$O$_{39}$)$_2$]$^{11-}$ (1:2 complex) was anticipated from the reaction conditions. One possible reason for the formation of **1** is the large pH decrease of the solution upon addition of ZrCl$_4$, which could have caused partial conversion of the lacunary to the Keggin anion. This would result in insufficient [PMo$_{11}$O$_{39}$]$^{7-}$ anions being present in solution to form 1:2 complexes, so instead Zr^{4+} coordinates to one [PMo$_{11}$O$_{39}$]$^{7-}$ and one [PMo$_{12}$O$_{40}$]$^{3-}$ anion. The readjustment of the pH back to 4.3 would be expected to degrade any [PMo$_{12}$O$_{40}$]$^{3-}$ anions to [PMo$_{11}$O$_{39}$]$^{7-}$. However, this does not appear to happen and is probably caused by stabilization of [PMo$_{12}$O$_{40}$]$^{3-}$ when complexed with Zr^{4+}. Another factor to be considered is the gentle heating (∼30 °C) of the solution, which could lead to conversion of [PMo$_{11}$O$_{39}$]$^{7-}$ to [PMo$_{12}$O$_{40}$]$^{3-}$.

The most informative bands in the solid-state IR spectrum of **1** belong to the four P−O stretching vibrations at 1109, 1066, 1042, and 1026 cm^{-1}. The bands at 1066 and 1042 cm^{-1} are assigned to the P−O stretches for the [PMo$_{12}$O$_{40}$]$^{3-}$ anion of **1**, compared to a typical value of approximately 1067 cm^{-1} for the Keggin anion.[12] This shift and splitting of the band is because of the effect of coordination of Zr^{4+}.

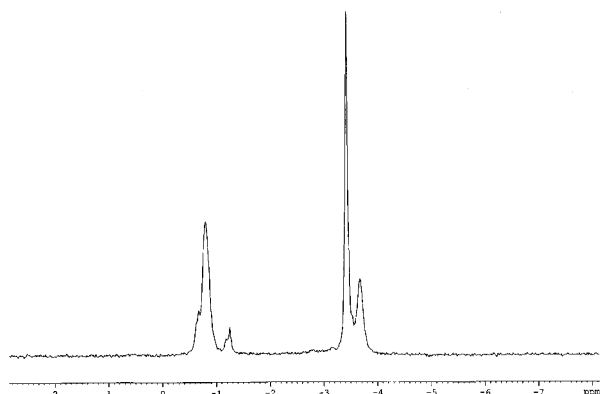(11) Haigh, C. W. *Polyhedron* **1995**, *14*, 2871.

Figure 3. ^{31}P NMR spectrum of **1** dissolved in D_2O.

The bands at 1109 and 1026 cm^{-1} are assigned to the P–O stretching vibrations of the $[PMo_{11}O_{39}]^{7-}$ part of **1**. The P–O stretch of $[PMo_{11}O_{39}]^{7-}$ is always split into two bands because of the lower symmetry than the T_d Keggin parent anion. The magnitude of the splitting is 83 cm^{-1}, which is larger than the values for the 1:2 trivalent lanthanide sandwich complexes,[13] probably reflecting the +4 charge of the zirconium ion and the fact that it is coordinated to only one $[PMo_{11}O_{39}]^{7-}$ anion instead of being shared with two.

A ^{31}P NMR spectrum (Figure 3) of **1**, dissolved in D_2O, would be expected to show two peaks of equal intensity, corresponding to the P atoms in the lacunary and in the Keggin anions, if the complex remains intact in solution. The recorded spectrum shows three major peaks at −3.67, −3.41, and −0.79 ppm and a smaller peak at −1.25 ppm with shoulders also visible on some of the peaks. The peak at −3.41 ppm is assigned to uncoordinated $[PMo_{12}O_{40}]^{3-}$ and probably arises from dissociation of the Keggin anion from Zr^{4+} in solution. The peak at −3.67 ppm is most likely attributed to $[PMo_{12}O_{40}]^{3-}$ with Zr^{4+} coordinated to four of its bridging oxygen atoms, as in **1**. Both peaks at −1.25 and −0.79 ppm fall within or near the observed range (−0.7 to −1.2 ppm) for uncomplexed $[PMo_{11}O_{39}]^{7-}$ in solution,[4a,14] but complexes with diamagnetic ions have also been observed at similar values.[4a,13] Therefore, the large peak at −0.79 ppm is assigned to $[PMo_{11}O_{39}]^{7-}$ coordinated to Zr^{4+} because it is unlikely that zirconium would decomplex given the large charge differences and the known stability, in solution, of $[PMo_{11}O_{39}]^{7-}$ complexes with other metal ions.[4a,13] It is possible that the peak in the NMR spectrum at −1.25 ppm is due to the formation of a 1:2 $[Zr(PMo_{11}O_{39})_2]^{10-}$ complex. In summary the ^{31}P NMR spectrum indicates that **1** is not stable upon dissolution in D_2O and is converted into a range of Zr/phosphomolybdate products. We are currently carrying out further solution studies to gain a fuller understanding of the Zr^{4+}/$[PMo_{12}O_{40}]^{3-}$/$[PMo_{11}O_{39}]^{7-}$ system in aqueous solution.

To the best of our knowledge there are no previously reported polyoxometalate complexes that contain both the saturated parent anion and one of its lacunary degradation products, making the presence of $[PMo_{12}O_{40}]^{3-}$ and $[PMo_{11}O_{39}]^{7-}$ in **1** a completely new observation. The closest related examples of other "hybrid" complexes are sandwich compounds which consist of two distinct anions, such as $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce^{3+} and Eu^{3+}),[15] where both of the coordinating anions are lacunaries. In **1** it is the bridging oxygen atoms of $[PMo_{12}O_{40}]^{3-}$ that coordinate to Zr^{4+}; often complexes and derivatives of saturated polyoxoanions are formed through coordination to terminal oxygen atoms.[16] Examples of bridging oxygen atoms bonded to a metal ion are the hydrothermally synthesized sandwich complexes in which transition metal ions are coordinated to two $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ anions to give octahedral geometry at the metal centers[17] and $[Mn^{IV}(Nb_6O_{19})_2]^{12-}$ in which Mn^{4+} is coordinated to three bridging oxygen atoms of each $[Nb_6O_{19}]^{8-}$ anion.[18] In addition, there are examples of Keggin ions coordinated to metal centers through four bridging oxygens, e.g., $[PV_{14}O_{42}]^{9-}$, which is formally a phosphovanadate Keggin anion, $[PV_{12}O_{40}]^{15-}$, capped by two VO^{3+} units.[19] In the case of **1**, the four bridging oxygen atoms appear to lie in suitable positions to allow zirconium to acquire its preference for high coordination numbers. The less common bicapped trigonal prismatic geometry may be rationalized by the flexible nature of zirconium with respect to accommodating different coordination numbers and geometries.[20]

In conclusion, we have communicated the X-ray crystal structure and spectroscopic characterization of the new 8-coordinate zirconium centered polyoxometalate complex, $(NH_4)_6[Zr(PMo_{12}O_{40})(PMo_{11}O_{39})]\cdot26H_2O$, that uniquely contains both the parent Keggin anion and its monovacant lacunary derivative.

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