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Yttrium Polyoxometalates. Synthesis and Characterization of a Carbonate-Encapsulated Sandwich-Type Complex

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Reaction of $\text{A-}\alpha\text{-PW}_9\text{O}_{34}{}^{9-}$ with YCl_3 in an aqueous Na_2CO_3 solution produces a dianion-encapsulated A-type sandwich polyoxometalate, $(\text{YOH}_2)_3(\text{CO}_3)(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2{}^{11-}$. The X-ray structure of this complex reveals that three Y(III) ions are sandwiched between two $\text{A-}\alpha\text{-PW}_9\text{O}_{34}{}^{9-}$ moieties and that a carbonate dianion is encapsulated in the same plane as the three Y(III) atoms. The oxygen atoms of the $\text{CO}_3{}^{2-}$ are sitting at the midpoints of the sides of the triangle formed by the three Y(III) ions. ^{31}P and ^{13}C NMR studies confirm that this complex is significantly more stable than the analogous A-type sandwich polyoxometalates containing divalent metals.

The synthesis and characterization of new transition-metal-substituted (d- and f-block) polyoxometalates (POMs) continues to be a focus of considerable ongoing research.[1−7] The highly tunable nature of these compounds, coupled with their chemically robust nature, has led to applications in catalysis, medicine, and molecular magnetism.[4,5] The POM of focus, $(\text{YOH}_2)_3(\text{CO}_3)(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2{}^{11-}$ (**1**), is related to the well-known and structurally similar trinuclear A-type sandwich complexes based on divalent d-block metals, $[\text{M}^{\text{II}}{}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{12-}$ (M = Mn, Fe, Co, Ni, Cu, and Zn).[8,9] This structural type was first reported by Knoth, and recently a Si-based analogue was reported by Hervé.[8−10] All of the divalent-metal-containing A-type sandwich complexes are unstable in solution and eventually isomerize into the B-type sandwich structures. However, a number of factors have been shown to significantly influence the stability of the A-type complexes, including pH, ionic strength, and temperature.[10−15] The trivalent oxidation state of the yttrium cations renders **1** more stable than the divalent-metal sandwich analogues, and it allows for the unusual stabilization of a carbonate anion, encapsulated within the sandwich-type structure.

Reaction of $\text{A-}\alpha\text{-PW}_9\text{O}_{34}{}^{9-}$ with Y(III) in an aqueous Na_2CO_3 solution produces **1** in modest yield (33%) and in high purity.[16] The synthesis of **1** requires the presence of $\text{CO}_3{}^{2-}$. Francesconi and co-workers have shown that, in the absence of $\text{CO}_3{}^{2-}$, the complex $[(\text{PY}_2\text{W}_{10}\text{O}_{38})_4(\text{W}_3\text{O}_{14})]^{30-}$ is formed instead.[17]

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(16) Synthesis of **1**: A 0.96 g (3.2 mmol) sample of $\text{YCl}_3\cdot 6\text{H}_2\text{O}$ is dissolved in 40 mL of deionized water, and 4 mL of 1 M Na_2CO_3 is slowly added to the solution with stirring. The slurry is heated to 80 °C, and then solid $\text{Na}_8\text{H}(\text{A-}\alpha\text{-PW}_9\text{O}_{34})$ (4.06 g, 1.6 mmol) is quickly added with vigorous stirring. The solution is maintained at 80 °C for 30 min and then cooled to room temperature. Any insoluble material present is removed by centrifugation. Solid KCl (6 g) is added to the solution, and a precipitate is formed. The solution is cooled in an ice water slurry to ensure the best yield of the product. The precipitate is filtered and washed twice with 2-mL aliquots of 5 °C water. The crude product is dissolved in a minimal amount (∼15 mL) of hot water and cooled to 5 °C. This procedure is repeated until a pure product is obtained (yield 33%). Diffraction-quality crystals are obtained by redissolving the pure compound in water at room temperature and adding NaClO_4. Elemental analyses and spectroscopic data are based on the bulk pure Na^+-free sample because yields of the diffraction-quality crystals are quite low. IR (2% in KBr pellet, 1500 to 600 cm^{-1}): 1491 (sh), 1480 (m), 1068 (s), 1014 (m), 943 (s), 916 (s), 830 (sh), 784 (s), and 708 (s). ^{31}P NMR (D_2O): −9.55 ppm. ^{13}C NMR (Li^+ salt in D_2O): 173.76 ppm. Anal. Calcd for $\text{K}_{11}(\text{YOH}_2)_3(\text{CO}_3)(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2\cdot 22\text{H}_2\text{O}$: C, 0.21; K, 7.59; Na, 0.0; P, 1.09; W, 58.4; and Y, 4.71. Found: C, 0.24; K, 7.56; Na, <0.1; P, 1.13; W, 58.1; and Y, 4.75.

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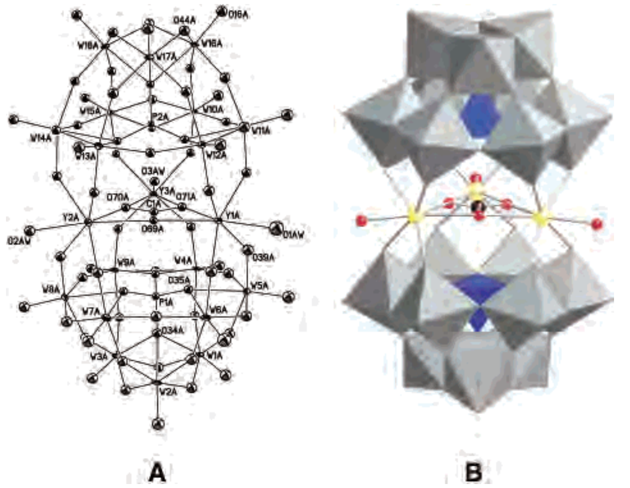

Figure 1. (A) Thermal ellipsoid plot of $(YOH_2)_3(CO_3)(A\text{-}\alpha\text{-}PW_9O_{34})_2^{11-}$ (**1**) set at the 50% probability level. (B) Combination ball-and-stick/polyhedral representation of **1**. The W, P, Y, C, and O atoms are shown in gray, blue, yellow, black, and red, respectively.

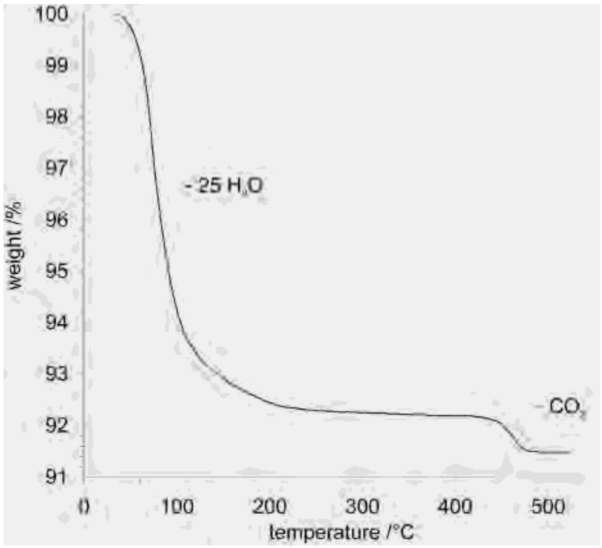

Figure 2. Thermogravimetric curve showing the loss of crystalline water molecules (from 30 to 200 °C) and CO_2 (from 440 to 480 °C) in complex **1**.

The X-ray structure of **1** reveals that three yttrium ions are sandwiched between two $A\text{-}\alpha\text{-}PW_9O_{34}^{9-}$ moieties (Figure 1).[18] The compound crystallizes in the triclinic space group $P\bar{1}$, with two complete sandwich structures in the asymmetric unit linked by Na^+ and K^+ cations. Bond valence sum calculations of **1** yield an average oxidation state of 3.2 ± 0.1 for Y.[19] The three Y(III) ions reside in approximate YO_7 capped trigonal prism coordination polyhedra. They form an approximate equilateral triangle with sides ranging from 4.78(1) to 4.92(1) Å and angles from 58.6(3)° to 61.5(3)°. These slight differences in bond lengths and angles reduce the overall symmetry of the molecule from D_{3h} to C_s (with the mirror plane containing the central Y^{III}_3 unit). The CO_3^{2-} is encapsulated in the Y^{III}_3 plane and ligated by its oxygen atoms at the midpoints of the sides of the triangle formed by the Y(III) ions. There are many metallocarbonate complexes in which the carbonato ligand(s) is either unidentate or bidentate, but only one in which the carbonate is in a six-coordinate tridentate environment as in **1**, the Gd macrocyclic amino carboxylate complex of Chang et al.[20]

Complex **1** is the first example of a structure containing a dianion encapsulated in a sandwich-type POM. Knoth reported nitrate, a monoanion, encapsulated in the A-type sandwich complex, $(Cu)_3(NO_3)(A\text{-}\alpha\text{-}PW_9O_{34})_2^{13-}$ (**2**), a POM that is structurally similar to **1**.[9] The stability of both **1** and **2** likely derives in part from the localized positive charge resulting from the three chelated Y(III) or Cu(II) atoms. Pope and Müller define these anion-encapsulated sandwich-type structures as *cryptates* since they have well-defined bonding interactions.[2] In contrast, there are also a large class of reduced polyoxovanadates that have been referred to as *clathrates* in which the host−guest interactions are significantly weaker. In these compounds, a variety of anions (including Cl^-, Br^-, I^-, and CO_3^{2-}) can act as templates for the induced self-assembly of the cluster shell.[21]

The thermal stability and decomposition characteristics of **1** in the solid state were assessed by thermogravimetric analysis (Figure 2). Two distinct mass loss regions are observed below 500 °C. First, there is a weight loss of approximately 7.7% between 30 and 200 °C that is associated with the loss of 25 water molecules (both crystalline lattice solvent molecules and coordinated aqua ligands) per molecule of **1** in the bulk pure sample.[22] In addition, there is a weight loss of approximately 0.8% from 440 to 480 °C, corresponding to the loss of 1 equiv of CO_2 per molecule of **1** from the decomposition of CO_3^{2-}.[22] This decomposition was confirmed by heating a solid sample of **1** to 500 °C and observing the loss of the ν_3 stretching frequencies characteristic of CO_3^{2-} by FT-IR. Differential scanning calorimetry (DSC) data suggest that decomposition of the POM itself is also observed upon loss of CO_3^{2-}.

The infrared spectrum of **1** shows bands assignable to CO_3^{2-} at 1491 and 1480 cm^{-1}, with a small splitting of the doubly degenerate ν_3 vibrational mode (11 cm^{-1}) due to the

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(18) Single-crystal X-ray data for **1** was collected on a Bruker D8 SMART APEX CCD area detector system at 100(2) K. Structure solution and refinement were carried out by using the SHELXTL V6.12 program. A colorless rod of dimensions 0.61 × 0.14 × 0.07 mm^3 was used. Crystal data for **1**: $CH_{50}K_{6.5}Na_{4.5}O_{96}P_2W_{18}Y_3$, MW = 5593.98, triclinic, space group $P\bar{1}$, $a = 19.385(1)$ Å, $b = 22.845(2)$ Å, $c = 23.638(2)$ Å, $\alpha = 77.886(1)°$, $\beta = 70.969(1)°$, $\gamma = 65.504(1)°$, $Z = 4$, $V = 8970.9(10)$ Å^3, $2\theta = 66.28°$, $\rho_{calcd} = 4.142$ Mg m^{-3}. The structure was refined on F^2 and converged on 63485 unique reflections and 1384 parameters to give $R1 = 0.0591$, $wR2 = 0.1415$, and a goodness-of-fit = 1.032.

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(22) The theoretical values for the loss of 25 water molecules and one CO_2 from $K_{11}(YOH_2)_3(CO_3)(A\text{-}\alpha\text{-}PW_9O_{34})_2\cdot 22H_2O$ are 7.9% and 0.8%, respectively.

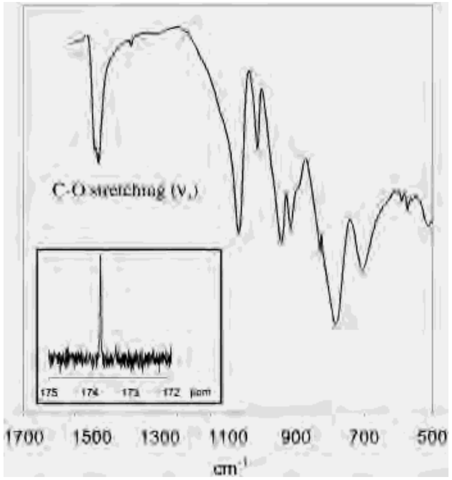

Figure 3. Infrared spectra of $(YOH_2)_3(CO_3)(A\text{-}\alpha\text{-}PW_9O_{34})_2^{11-}$ (**1**) (2% POM in KBr pellet) and ^{13}C NMR spectrum of **1** (inset) obtained on a lithiated sample (exchanged by addition of $LiClO_4$ followed by precipitation and removal of $KClO_4$).

distortion of the CO_3^{2-} group (Figure 3). This splitting is commonly observed in carbonate complexes.[23] The vibrational frequencies of the other two infrared active modes, ν_2 and ν_4, overlap with the W−O stretching bands, thus preventing any reliable assignment.[24] The characteristic ν_3 vibrational modes of the PO_4 unit (1068 and 1014 cm^{-1}) also show splitting, implying that there is a loss of local symmetry as expected for the A-type trivacant Keggin unit.[25] In addition, the terminal W−O and bridging W−O−W stretches characteristic of all heteropolytungstates are present.

The ^{31}P NMR spectrum of **1** consists of one peak corresponding to the two symmetry-equivalent P atoms in each $A\text{-}\alpha\text{-}PW_9O_{34}^{9-}$ unit (−9.55 ppm).[26] Unlike the A-type sandwiches based on divalent d-block metals, the data suggest that complex **1** is stable in unbuffered H_2O for several hours. In addition, ^{13}C NMR was used to observe the encapsulated CO_3^{2-} group (Figure 3).[26] The low solubility of the K^+ salt of **1** made it necessary to conduct a K^+/Li^+ exchange (via $LiClO_4$) in order to achieve concentrations sufficiently high for a good spectrum. The results show one peak attributable to the coordinated CO_3^{2-} anion at 173.76 ppm. Due to the long acquisition time (∼10 h), a small peak at 173.38 ppm appears after several hours which is attributable to decomposition of the POM. Decomposition is also observed by ^{31}P NMR as two additional peaks at −9.85 and −7.97 ppm also appear after several hours at 25 °C. Because the decomposition from CO_3^{2-} to CO_2 is unlikely to occur in a pH-neutral aqueous solution under ambient conditions, and no free CO_3^{2-} ($\delta = \sim 169.4$ ppm) is observed in the product solution by NMR, it is likely that the species giving rise to the growing peak at 173.38 ppm in the Figure 3 inset is a new CO_3^{2-}-containing complex.[27]

In summary, a carbonate-encapsulated A-type sandwich POM of Y(III) ions has been synthesized and characterized. Preliminary studies suggest that the divalent first-row transition-metal A-type sandwiches do not complex carbonate. However, $A\text{-}\alpha\text{-}PW_9O_{34}^{9-}$ and some of the late-group lanthanides (such as Yb(III)) do appear to form carbonate-encapsulated complexes.

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Supporting Information Available: Structure determination parameters, crystal and structure refinement data, atomic coordinates, and isotropic displacement parameters for **1** (in CIF form). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The ^{13}C NMR data were collected at 150.8 MHz on a Varian Unity 600 MHz instrument with chloroform as the external standard. The concentration of **1** (for the lithiated sample) was 0.05 mM. The ^{31}P NMR data were collected at 161.9 MHz on a Varian INOVA 400 MHz instrument with chemical shifts reported relative to 85% phosphoric acid.

(27) Solution IR, solid state ^{13}C NMR, or ^{183}W NMR may provide additional support for solution speciation.