

as for characterizing the isolated chlorophylls. The goal of these studies has been to provide structural information regarding the organization of the chlorophylls within the photosynthetic membrane. Such information elucidates the mechanistic role of these important pigments in the photosynthetic processes (i.e. light harvesting and electron-transfer steps). The results presented herein suggest that SERRS offers a viable approach for the study of intact photosynthetic preparations. Our previous studies of reaction centers<sup>44</sup> and chromatophore preparations<sup>45</sup> have already demonstrated that SERRS studies of designated membrane components are feasible. In addition to the fluorescence quenching advantage, SERRS provides extremely high sensitivity, thereby minimizing the amount of material required for spectral analysis. The distance sensitivity can be used to obtain information con-

cerning the spatial relationship of various components to the membrane surface. Finally, the ability to control the potential at an electrode surface suggests that SERRS may also be useful for determining spectra at fixed redox states of the reaction center.

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## Communications to the Editor

### Synthesis and X-ray Crystal Structure Determination of a Novel Chiral Heteropolyanion: The "3:1" Octadecatungstohexaphosphate<sup>1</sup>

Rafael Acerete\* and Juan Server-Carrió

Departamento de Química Inorgánica, Facultad de Farmacia  
Universitat de València, Blasco Ibáñez  
13. 46101 Valencia, Spain

Angel Vegas and Martín Martínez-Ripoll

U.E.I. de Cristalografía Instituto "Rocasolano"  
CSIC, Serrano 119, 28006 Madrid, Spain  
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Polyoxometalates<sup>2</sup> are well-known compounds, which over the past few years have received increasing attention, owed in part to the recognition of their potential in areas such as catalysis,<sup>3</sup> photochemistry,<sup>4</sup> and medicine,<sup>5</sup> among others. Polyoxotungstophosphates constitute by far the most fertile, rapidly expanding heteropoly system, which shows an amazing structural diversity not encountered in any other heteroatom system. Most polytungstophosphates characterized thus far are obtained from rather acidic solutions (pH < 5) or result from their partial decomposition to lacunary derivatives or condensations<sup>7</sup> of these lacunary species at appropriate pH. Yet, the bulk of polytungstophosphates present in weakly acidic (pH 5-7) aqueous solutions of WO<sub>4</sub><sup>2-</sup> and HPO<sub>4</sub><sup>2-</sup> remain relatively unexplored, even though their existence was reported more than a century ago.<sup>7,8</sup>

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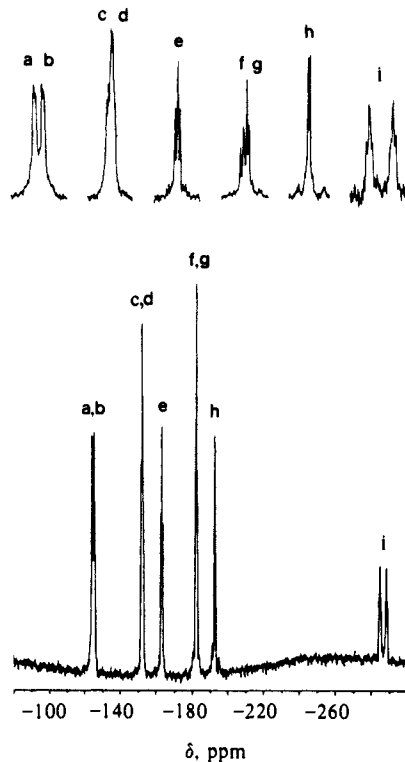


Figure 1. 200-MHz <sup>183</sup>W NMR spectrum of a 0.2 M solution of **1** (bottom) and expansion of peaks (top) in D<sub>2</sub>O (61 104 transients). Chemical shifts (in ppm) are referenced to saturated Na<sub>2</sub>WO<sub>4</sub>/D<sub>2</sub>O (substitution method) and negative to high field.

The heteropolyanions present in such nearly neutral solutions generally have a relatively high phosphorus content (W/P < 4). Two of them, namely, the [P<sub>4</sub>W<sub>8</sub>O<sub>40</sub>]<sup>12-</sup> and [P<sub>4</sub>W<sub>14</sub>O<sub>58</sub>]<sup>12-</sup> heteropolyanions,<sup>9,10</sup> have only recently been fully characterized. There are old reports<sup>7,8</sup> on the existence of another phosphorus-rich heteropoly compound having a W/P ratio of 3:1, thus far formulated as [(PW<sub>3</sub>O<sub>13</sub>)<sub>x</sub>]<sup>3x-</sup>, but to our knowledge, nothing

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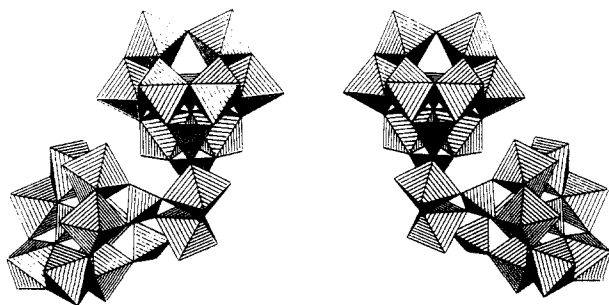


Figure 2. Coordination polyhedra representations of the chiral  $C_2$  structure for  $[P_6W_{18}O_{79}]^{20-}$  anion, showing one of the two enantiomer pairs per unit cell. Each vertex of a polyhedron locates the center of a close-packed oxygen atom. The heteroatom, P, is within each tetrahedra. Every octahedron contains a W atom.

had been definitely established concerning either its true composition, nor its characterization in modern terms.<sup>11</sup> We herein report the synthesis, complete structural characterization in the solid state (single-crystal X-ray diffraction) and in solution ( $^{31}P$  and  $^{183}W$  NMR), and experimental evidence of the chirality of a 1:3 phosphotungstate, namely, the sodium salt of the  $[P_6W_{18}O_{79}]^{20-}$  heteropolyanion (**1**).

The new heteropolyanion **1** is formed in a hot, slightly acidic (pH ca. 6) aqueous solution of approximate molar composition  $[HPO_4^{2-}]:[WO_4^{2-}] = 1:3$ . Slow addition of glacial acetic acid (8.4 mL) to a solution of 50 g of  $Na_2WO_4 \cdot 2H_2O$  and 3.5 mL of 85%  $H_3PO_4$  in 50 mL of water, followed by evaporation at 100 °C to a final volume of ca. 50 mL, gives upon cooling a good yield (better than 90% based on  $Na_2WO_4$ ) of **1** as a white crystalline precipitate, which, after recrystallization from water, was characterized by IR,<sup>12</sup>  $^{31}P$ ,<sup>13</sup> and  $^{183}W$  (Figure 1) NMR spectra.

An X-ray structure determination<sup>14</sup> of a single crystal of **1** reveals the dissymmetric structure shown in Figure 2. The unit cell contains four  $[P_6W_{18}O_{79}]^{20-}$  anions lying at sites of crystallographic point symmetry 2 ( $C_2$ ). The heteropolyanion of **1** consists of two  $\beta_3$ -A- $PW_8O_{33}$  units<sup>15</sup> linked by a central  $P_4W_2O_{21}$  moiety.<sup>16</sup> This central moiety is formed by corner-shared  $WO_6$  octahedra and four externally attached  $PO_4$  tetrahedra, which also share oxygens with one  $PW_8$  unit. The only symmetry element is a binary axis containing the oxygen corner-shared by the two central  $WO_6$  octahedra. Each  $\beta_3$ -A- $PW_8$  unit is formally derived from a  $\beta$ -A- $[PW_9O_{34}]^9$  anion by removal of a W and its terminal

oxygen from the "cap", edge-shared  $W_3O_{13}$  unit. The W-O, P-O, and W-W distances within each  $PW_8$  moiety agree well with the values reported for similar fragments in other heteropolytungstates.<sup>17</sup> Stabilization of incomplete Keggin fragments such as  $W_2O_{11}$  and  $\beta_3$ -A- $PW_8O_{33}$  by external heteroatoms ( $PO_4$ ) acting as junction between two subunits has been previously reported.<sup>10,18</sup> In our case, linkage by the  $P_4W_2O_{21}$  fragment results in a rotation of ca. 80° in the orientation of the (quasi-planar) ring of six "belt"  $WO_6$  octahedra within one  $PW_8$  unit relative to the other. Such twist between the two asymmetric units in the anion imparts the appearance of a *helical*, right-handed and left-handed, fragment to the structure of the heteropoly anion.

The observation of nine resonance signals, each corresponding to two equivalent W atoms, one on each asymmetric unit, in the  $^{183}W$  NMR spectrum (Figure 1) of an aqueous solution of **1** confirms that the anion retains its  $C_2$  symmetry in solution. Thus, **1** should be *chiral*. Very few cases of chirality have been previously reported in heteropoly chemistry. With only two exceptions,<sup>19</sup> chirality in polyoxometalates results from only subtle metal atom displacements leading to alternating, short and long, M-O bond lengths (M = Mo or W), generally giving rise to labile chirality observed by a Pfeiffer (Cotton) effect.<sup>11,20</sup> The origin of chirality in our case is fundamentally *novel*, associated with the primary structure of the heteropolyanion, i.e., based on its effective (apparent) symmetry, both in the solid and in solution. Since it does not depend on just small differences in bond lengths, but on the actual bonding sequence, it probably corresponds to an *inert* type of *chirality*. The space group indicates the formation of racemic crystals, with the unit cell containing two pairs of enantiomers (Figure 2). A  $^{31}P$  NMR investigation using *l*-lysine monohydrochloride as resolving agent<sup>13</sup> shows the doubling of all  $^{31}P$  signals, indicating no racemization of the compound on the NMR time scale. This is the first case of a polytungstate for which chirality has been experimentally confirmed. Efforts to resolve the racemate by classical methods<sup>19b,d</sup> are currently in progress.

The herein reported heteropoly compound constitutes the first example of *true* structural chirality in polyoxotungstate chemistry. It should be noted that its *helical chirality* mimics, to a limited extent, the topology of the helical domains in proteins and other biomolecules. This could turn out to be important in view of the well-documented biological activity (as antiviral and antitumoral agents)<sup>5</sup> of many large polyanions. Biological activity is expected to depend on the chiral configuration (*R* vs *S*) as a result of enantioselective molecular recognition of biomolecules. Compound **1**, if resolved, could also have potentially important applications as an enantioselective catalyst (*chiral agent*).<sup>21</sup> In addition, this report should contribute to development of a more clear picture of the chemical equilibria in which polytungstophosphates are involved, as well as to the mechanisms of interconversion between different structural types.

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**Supplementary Material Available:** IR and  $^{31}P$  NMR spectra, figure indicating numbering schemes, and tables of crystal data, atomic positional parameters, isotropic and anisotropic thermal parameters, interatomic distances, and bond angles (10 pages); listing of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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(12) IR (KBr) for **1**:  $\nu(PO)$  1106 s, 1071 s, 1041 s, 1016 s;  $\nu(WO)$  929 vs, 900 sh, 886 s, 840 s, 770 sh, 737  $cm^{-1}$ .

(13)  $^{31}P$  NMR (200 MHz) for **1** (0.09 M in  $H_2O$ ):  $\delta$  (ppm) 3.69 (2 P, s); 1.16 (2 P, s); -5.42 (2 P, s).  $^{31}P$  NMR for *l*/L-lysine: 1:10  $\delta$  (ppm) 3.63 (2 P, s); 3.56 (2 P, s); 1.01 (2 P, s); 0.86 (2 P, s); -5.55 (2 P, s); -5.59 (2 P, s); 85%  $H_3PO_4$  external reference. The low-field resonances around 3.6 ppm reveal fine structure consisting in two satellite lines owed to coupling with one low-abundance  $^{183}W$  isotope (14.4%,  $S = 1/2$ ,  $^2J_{W-P} = 30$  Hz) from the central  $P_4W_2$  bridging fragment.

(14) Crystallographic data for **1**:  $Na_{14}H_6P_6W_{18}O_{79} \cdot 37.5H_2O$ , MW = 5762.62; monoclinic, space group  $C_2/c$ ;  $a = 16.754$  (8) Å,  $b = 18.762$  (9) Å,  $c = 35.898$  (12) Å,  $\beta = 99.80$  (3)°;  $V = 11120$  (5) Å<sup>3</sup>;  $Z = 4$ ;  $d_{calc} = 3.44$  g  $cm^{-3}$ ;  $\lambda(Mo K\alpha)$  (graphite-oriented monochromator). An empirical absorption correction was applied. The intensities of 10233 reflections were measured on an Enraf-Nonius CAD-4 diffractometer at room temperature. Scan range  $\theta = 2$ –25°. The structure was solved by direct methods (SIR 88; Cascarano, G.; Giacovazzo, C.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R.; Viterbo, D. University of Bari, 1988) and refined by full-matrix least-squares methods using 7382 unique reflections [ $F_o \geq 2\sigma(F_o)$ ]. GOF = 6959, data/parameter = 17.5. Largest residual peak =  $4.2 e \text{ \AA}^{-3}$  (next to a W atom).  $R = 0.043$ ,  $R_w = 0.055$ . Further details of the structure refinement are given in the supplementary material.

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