at low temperature (ca. -45 to $-40\,^{\circ}$C) for 1 h, it was stirred at 0 °C for another hour. After the addition of water (0.20 mL) in THF (0.40 mL), the solution was stirred for 0.5 h at room temperature. The resultant suspension was filtered through celite, which was subsequently washed with Et_2O. The filtrate and Et_2O fractions were concentrated in vacuo to afford a crude oil. Purification by column chromatography (silica gel, hexane/ether 5/1) afforded **4c** (32 mg, 86 % yield) as a colorless oil. $[\alpha]_D^{27} = -0.65$ ($c = 0.46$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 3404, 3062, 2929, 1948, 1876, 1602, 1495, 1452, 976, 756, 701\ \mathrm{cm^{-1}}$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.15-7.32$ (m, 5H), 2.87 (dd, $J = 6.0$, 13 Hz, 1H), 2.43 – 2.66 (m, 2H), 1.82 (ddt, $J = 4.2$, 7.8, 12 Hz, 1H), 1.61 – 1.70 (m, 1H), 1.69 (s, 1H), 1.48 (dd, $J = 7.8$, 12 Hz, 1H), 1.37 (dt, $J = 9.0$, 4.2 Hz, 1H), 0.86 – 0.91 (m, 1H), 0.76 (dd, $J = 5.4$, 9.0 Hz, 1H), 0.67 (t, $J = 5.4$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.8$, 24.3, 25.3, 28.3, 37.9, 46.8, 67.1, 126.1, 128.6, 128.9, 141.7.

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Two New Isopolyoxotungstates(VI) with the Empirical Composition $Cs_2W_2O_7 \cdot 2\,H_2O$ and $Na_2W_2O_7 \cdot H_2O$: An Icosatetratungstate and a Polymeric Compound**

Irene Brüdgam, Joachim Fuchs, Hans Hartl,* and Rosemarie Palm

Dedicated to Professor Hartmut Bärnighausen on the occasion of his 65th birthday

Owing to their structural and electronic diversity, iso- and heteropolyoxometalates with different metal centers and varying oxidation states undergo an exceptionally wide variety of reactions, which have applications in many fields of chemistry (synthesis, analytical chemistry, catalysis, biochemistry).[1] The number of dissimilar polyoxometalates is enormous; however, certain structural units appear repeatedly, depending on the metal counterion and the synthesis conditions. These can serve as structural components of large, in some cases huge, polyoxometalates formed by conservative self-organizing processes.[2, 3] Examples of isopolytungstates (VI) include the dodecatungstates $H_2W_{12}O_{40}^{6-}$ (Keggin-type)[4] and $H_2W_{12}O_{42}^{10-}$ (paratungstate-Z),[5] the heptatungstate $W_7O_{24}^{6-}$,[6] and the hexatungstate $W_6O_{19}^{2-}$[7] as well as fragments of these anions, which act as isolated units or as components of high molecular aggregates. These groups are linked to each other either directly or through cations and heteroatoms.

Isopolyoxotungstates are produced in a similar manner as other polyoxometalates by acidification of aqueous solutions of monotungstates. In the present case, we used the oxide WO_3, which reacts in water like the hypothetical diprotic acid H_2WO_4, for the acidification. The molar ratio of H^+ introduced to WO_4^{2-} is defined as the degree of acidification of the metalate solution, the molar ratio of H^+ that reacted per WO_4^{2-} is the degree of protonation.[8] The title compounds $Cs_2W_2O_7 \cdot 2\,H_2O$ (**1**) and $Na_2W_2O_7 \cdot H_2O$ (**2**), which are formally prepared according to Equation (1), display a degree

$$2\,WO_4^{2-} + 2\,H^+ \rightleftharpoons W_2O_7^{2-} + H_2O \qquad (1)$$

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of protonation of 1. The degree of acidification of a tungstate solution is one of the most important factors in determining which polyoxometalate is formed. Other conditions, especially the type of cation present, also play a role. Alkali metal cations, for example, show a gradual change in coordination behavior dependent on the ion radius. When crystallized from the aqueous solution, the cations are normally coordinated by oxygen atoms of the polyoxometalate anions as well as by water molecules. In contrast to the Na^+ ion, the larger and softer Cs^+ ion prefers the polyanion ligands to the aqua ligands.[9] This difference in coordination behavior is expected to influence the condensation and crystallization processes through the formation of different cation–anion pairs in solution.

Recently we reported two new isopolytungstates $Na_5H_3W_6O_{22}\cdot 18H_2O$ (**3**)[10] and $K_7HW_5O_{19}\cdot 10H_2O$ (**4**);[11] both were synthesized from weakly alkaline solutions under the same conditions. The only difference between the two was that in the first case we used Na^+, and in the second K^+, as cation. Compounds **3** and **4** display certain structural similarities in that their anions represent fragments of the heptatungstate ion $W_7O_{24}^{6-}$ (Figure 1).[6] In the course of isolating **3**,[10] a colorless microcrystalline substance could be separated from the filtrate after the solution was left standing for months. The use of IR and Raman spectroscopy enabled us to identify the compound as $Na_2W_2O_7\cdot 4H_2O$. A sodium ditungstate that contains water has recently been described by Simons[12]; however, this was a pentahydrate. The tetrahydrate can be obtained in higher yields by starting with a solution of $WO_3\cdot H_2O$ and $Na_2WO_4\cdot 2H_2O$ in a ratio of 1:3 instead of 1:7. After thermal degradation, the monohydrate **2** is produced in microcrystalline form. Single crystals of **2** were obtained from the solution in a hydrolysis autoclave at 150–180 °C. The identity of these two substances, synthesized by different methods, was determined by IR and Raman spectroscopy. The nearly water insoluble **2** is the first known structure of a high polymeric oxotungstate to contain water.[13]

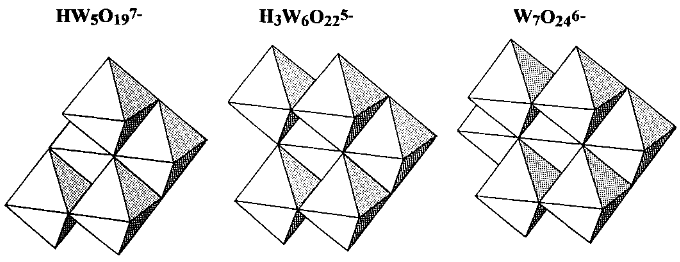

Figure 1. Polyhedra representation of the anions $HW_5O_{19}^{7-}$, $H_3W_6O_{22}^{5-}$, and $W_7O_{24}^{6-}$.

The basic structural components of **2** are planar W_4O_{16} units, which consist of edge-sharing WO_6 octahedra in a rhomboidal arrangement (Figure 2). The W_4O_{16} units are linked to the anions $H_3W_6O_{22}^{5-}$ and $HW_5O_{19}^{7-}$ since they are fragments of these anions (as well as of the heptatungstate $W_7O_{24}^{6-}$).[5] In **2**, the $W_4O_{16}^{8-}$ units share common vertices, leading to $^1_\infty[W_4O_{14}^{4-}]$ chains. The Na^+ ions bridge the chains of polytungstates, which are arranged in a rod packing parallel to the *b* axis. The molecule of crystal water is shared by the two crystallographically independent Na^+ ions, which are coordinated by five (Na1) and six oxygen atoms (Na2, Figure 3). The octahedral NaO_6 groups are linked through diagonally arranged edges, forming an isometric chain structure parallel to the polytungstate chains. The resulting gaps are filled with quadratic NaO_5 pyramids, which share common edges with three NaO_6 octahedra. The $W_4O_{16}^{8-}$ structural unit is already known as a component of $Li_2WO_4\cdot 4/7\,H_2O$.[14] However, the four WO_6 octahedra are not connected in a rhombic planar fashion in this compound, but compactly as tetrahedra.

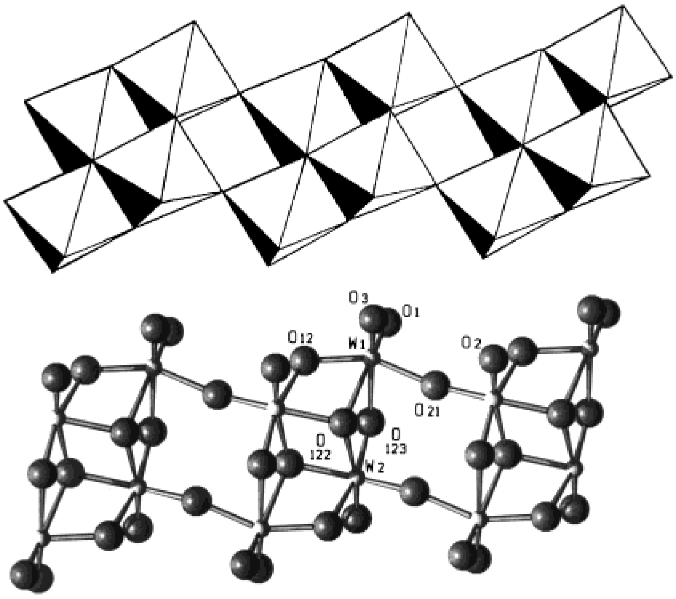

Figure 2. Polyhedra and ball-and-stick representation of the anion $^1_\infty[W_4O_{14}^{4-}]$. Selected bond lengths [Å]: W–O$_{\text{term.}}$ 1.71–1.75, W–μ_2-O 1.78–2.24, W–μ_3-O 2.23–2.27.

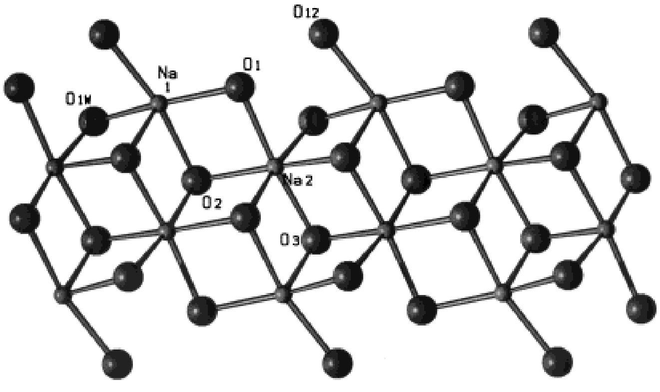

Figure 3. Ball-and-stick representation of the sodium–oxygen polyhedra chain of **2**.

An even better example, which demonstrates clearly how the type of cation present influences polyoxotungstate formation, is the cesium compound **1**, which was synthesized in the same manner as **3** and **4**. A crystal structure analysis[15] shows that the actual compound hiding behind the given empirical formula in the title has the formula $Cs_{24}W_{24}O_{84}\cdot 24H_2O$. The anion $W_{24}O_{84}^{24-}$ present in **1** (symmetry C_i) is the largest discrete isopolyoxotungstate known to date. It does not have any structural similarities to **2**–**4**. Not only is it made up of WO_6 octahedra, but it also contains WO_5 units, which are very rare. Six vertice-sharing WO_6 octahedra form an inner ring. Six W_3O_{13} groups are condensed to this ring, again through common octahedra vertices. The W_3O_{13} groups are made up of two vertice-sharing octahedra WO_6 and one quadratic pyramid WO_5, which is distorted in the direction of a trigonal bipyramid (Figures 4 and 5, top). The WO_5 pyramid shares two neighboring edges of its base (two μ_2-O atom and one μ_3-O atom) with the two WO_6 octahedra; one of the two terminal oxygen atoms is axial. All of the oxygen atoms of the six inner octahedra are involved in cross-linking, whereas the outer WO_6 octahedra and the WO_5 groups each bear two terminal oxygen atoms. The bond lengths between W and the asymmetrically bridging μ_2-O atoms alternate between short and long, a result of the distortion of the WO_6 octahedra commonly observed in polytungstates.[7b]

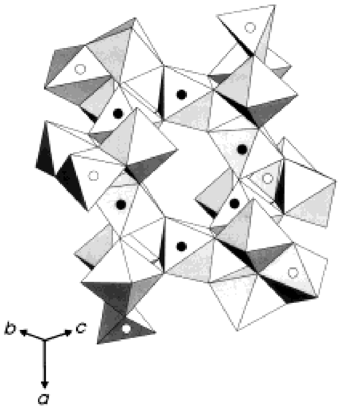

Figure 4. Polyhedra representation of the anion $W_{24}O_{84}^{24-}$. Black dots: inner ring of vertice-sharing WO_6 octahedra; white dots: WO_5 units, which together with two WO_6 octahedra make up the W_3O_{13} structural fragments. Selected bond lengths [Å]: W–O$_{ring}$ 1.75–2.13; WO_6 octahedra: W–O$_{term.}$ 1.71–1.78, W–μ_2-O 1.78–2.32, W–μ_3-O 2.03–2.14; WO_5 units: W–O$_{term.}$ 1.73–1.81, W–μ_2-O 1.88–1.97, W–μ_3-O 2.01–2.04.

Of the twelve cesium cations in the asymmetrical unit, one is situated above and one below the center of symmetry in the middle of the anion. These fit perfectly into the cavities formed by the oxygen atoms of the anion and have an unusually high coordination number of 15, if one takes into account Cs–O distances up to 3.6 Å; only oxygen atoms of the anion are in the sphere of coordination. The other cesium atoms have a seven- to elevenfold coordination by oxygen atoms of the polyanion and crystal water molecules. The anion and all of the cesium atoms (minus the water molecules) are shown in a space-filling model in the bottom part of Figure 5. The fit of the cesium atoms in the oxygen atom packing, and the fact that this bulky anion could not be isolated with other alkaline cations, suggests that the large cesium cations promote its formation through a type of template effect.

Experimental Section

1: Cs_2WO_4 (1 g, 1.9 mmol), synthesized by melting $WO_3 \cdot H_2O$ (pure, Merck) and Cs_2CO_3 (Fluka) at 1000 °C in a porcelain crucible, is stirred under argon (CO_2 exclusion) in a Cautex beaker with $WO_3 \cdot H_2O$ (0.07 g, 0.28 mmol) in 1.5 mL of H_2O at 20 °C for 2 h (degree of acidification: 0.294 based on $WO_3 \cdot H_2O/Cs_2WO_4$). The solution is separated from a very fine solid substance by filtration (possibly more than once). After letting the solution stand for several hours (pH ≈ 8), **1** crystallizes in the form of flat, trapezoidal columns. The compound is soluble in water, but cannot be recrystallized in aqueous solution.

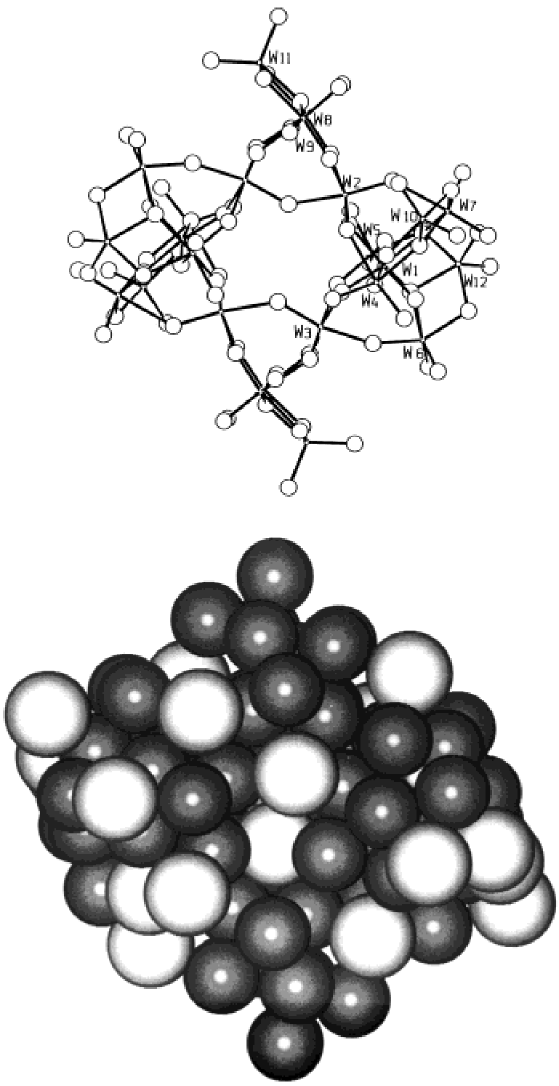

Figure 5. Ball-and-stick (top) and space-filling representation (bottom) of the anion $W_{24}O_{84}^{24-}$. The light balls in the bottom part represent the Cs^+ ions built in to the oxygen packing.

2: An aqueous solution of 1 M sodium monotungstate (10 mL) is heated to 150–180 °C with tungstic acid (0.7 g, 2.8 mmol) in a hydrolysis autoclave (pressure hydrolysis system II, Berghof) in a PTFE insert (degree of acidification: 0.56 based on $WO_3 \cdot H_2O/Na_2WO_4$). Compound **2** crystallizes along with a white powder after about three weeks. The powder can be separated from the product by repeatedly decanting in water in a ultrasound bath. The purity of the product can be verified with IR and Raman spectroscopy. Data on the yields of **1** and **2** is difficult to obtain because of a fluctuation in yields depending on the quality of the mechanical separation process (filtering, decanting) of the solid-state products, which all precipitate out of the solution simultaneously.

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[15] Crystal structure analysis of **1**:[16] $M_r = 9378.9$, monoclinic, space group $P2_1/n$, $Z = 2$, $a = 17.548(3)$, $b = 20.351(3)$, $c = 19.401(3)$ Å, $\beta = 90.98(2)$, $V = 6927.42$ Å^3, $\rho_{calcd} = 4.49$ g cm^{-3}, $\mu_{Mo} = 274.2$ cm^{-1}, crystal size $0.3 \times 0.3 \times 0.2$ mm^3, $2\theta_{max} = 50^\circ$, $Mo_{K\alpha}$ radiation, Nonius-CAD4 four-circle diffractometer, graphite monochromator, $\omega/2\theta$ scanning, $T = 293$ K, 15367 measured reflections, 12030 symmetry-independent reflections, 8358 reflections $> 2\sigma(I)$, absorption correction (psi scan, max./min. transmission 99.9/53.9%), isotropic extinction correction, 437 refined parameters (W, Cs anisotropic; O isotropic; no H atoms), residual electron density < 6.9 e Å^{-3}, structure solution with direct methods (SHELXS-86) and difference Fourier techniques (XTAL 3.5), weighting $1/\sigma^2(F)$, $R = 0.076$ ($I > 2\sigma I$), $Rw = 0.05$.

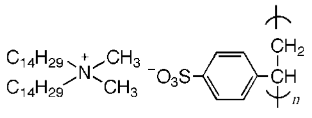
[16] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408188 (**1**) and CSD-408189 (**2**).

A Fullerene/Lipid Electrode Device: Reversible Electron Transfer Reaction of C_{60} Embedded in a Cast Film of an Artificial Ammonium Lipid on an Electrode in Aqueous Solution**

Naotoshi Nakashima,* Takeshi Tokunaga, Yuko Nonaka, Takashi Nakanishi, Hiroto Murakami, and Takamasa Sagara

The development of lipid bilayer modified electrodes whose structures mimic those of biomembranes is highly attractive, because such a study would produce a methodology for novel surface modification and functionalization. We and other have focused on the combination of fullerene chemistry and the chemistry of lipid bilayer membranes.[1] The goal in this study is to design and construct a system showing fast electron transfer reactions of fullerenes using lipid films as an electrode modifier. Fullerenes form multiply charged anions because of their high degrees of degeneracy of the LUMO, which lead to a variety of unique properties;[2, 3] however, the electrochemistry of fullerene thin films is rather complicated.[3, 4]

We describe here for the first time the discovery that C_{60} embedded in a cast film of an artificial lipid with multiple ion pair interactions (poly(ion-complexed) lipid)—namely, dimethylditetradecylammonium poly(styrene sulfonate) (**1**)—on an electrode undergoes two reversible electron transfer reactions with the underlying electrode in an aqueous solution. Furthermore, the generated radical monoanion and the dianion are very stable. To our knowledge, no report has been published thus far describing reversible electron transfer reactions of fullerene thin films on electrodes in an aqueous solution.[5] The poly(ion-complexed) lipid **1** used in this study is insoluble in water, but possesses fundamental characteristics of dispersed lipid bilayer membranes in an aqueous solution.[6] We also used cast films of the biological lipid dimyristoylphosphatidyl choline (**2**) as matrix films for comparison with **1**.



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Compound **1** was synthesized according to the previously described method[7] and analyzed by IR and NMR spectroscopy as well as elemental analysis. This compound is readily soluble in benzene and can be used to form, by the conventional solvent evaporation method, multibilayer films. Lipid **2** was purchased from Sigma and used as received. Production

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