Anion Controlled Donor Alignment: Electrosynthesis and Crystal Structure of a Novel Cation Radical Salt Constructed from Porphyrin and Hexatungstate

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Elecrtochemical oxidation of tetrabutanoporphyrin free base with hexatungustate electrolyte produces a novel cation radical salt. X-ray crystallographic study showed that the crystal structure is constructed by C-H···O hydrogen bonds between the porphyrin and the inorganic counter anion.

In the past two decades, porphyrin-based cation radical salts have attracted much attention from the view points of conductivity and magnetism.[1] In all of the cases, size, shape and electronic states of inorganic counter anions strongly perturb the solid-state properties of the materials. However, the reported salts are constructed with commercially available simple small anions, *i.e.*, I_3^-, PF_6^-, BF_4^-, etc., and the role of anions is not clear by the limitation of examples. Oxopolymetalate clusters are large in size and have high electron-acceptor ability.[2] They are widely used as inorganic anions for TTF-based cation radical salts.[3] In this communication, we wish to report the electrosynthesis and X-ray crystallographic study of a porphyrin cation radical salt with hexatungstate cluster anion; $[H_2TBuP]^{+\bullet}{}_2[W_6O_{19}]^{2-}[TCE]_2$ (H_2TBuP = 2,3:7,8:12,13: --15,17-tetrabutanoporphyrin free-base, TCE = 1,1,2-trichloroethane).

The porphyrin free-base, H_2TBuP,[4] and supporting electrolyte, $[N(n\text{-}C_4H_9)_4]^+{}_2[W_6O_{19}]^{2-}$,[5] were prepared by the reported methods. The title complex has been obtained after three weeks on a platinum wire electrode as dark red needles by constant current oxidation (0.5 μA) of the porphyrin in a saturated electrolyte solution in TCE. Figure 1 and 2 show the molecular and crystal structures of the complex, respectively.[6] The anion has the typical shape of Lindquist-type polyoxoanion.[2] Although this anion has the possibility to take two different reduction states, 2^- and 3^-,[5] the bond lengths and angles are nearly identical to the reported values for the 2^- anion.[7-10] The finger print region of IR spectra for the anion, 977, 809, and 588 cm^{-1}, also supports the valence states of 2^-.[7] Only small differences were observed in the bond distances for the porphyrin compared with the reported values for the neutral state. However, the oxidation state of the porphyrin is expected to be a cation radical on the basis of the stoichiometry of the complex.

The central oxygen atom of the hexatungstate anion is located at the origin of the lattice. This huge anion is regarded as an octahedron and the resulted primitive lattice produces a specific periodical potentials. Short C-H···O contacts were found between the oxygen atoms of the anion and protons of the porphyrin as seen in TTF-based cation radical salts.[3,11] Thus, observed C···O distances are in the range of 3.19-3.55 Å and are comparable to those of hydrogen-bonded cases, indicating that hydrogen bondings are operating in the present crystals. Not only axial, but also equatorial hydrogen atoms at benzylic positions act as a hydrogen donor. The both types of oxygen atoms in the anions, *i.e.*, carbonyl and ether type, participate in hydrogen bonding. These hydrogen bonds distort the porphyrin nucleus and the largest deviation from the least squares plane is 0.281 Å for C(17).

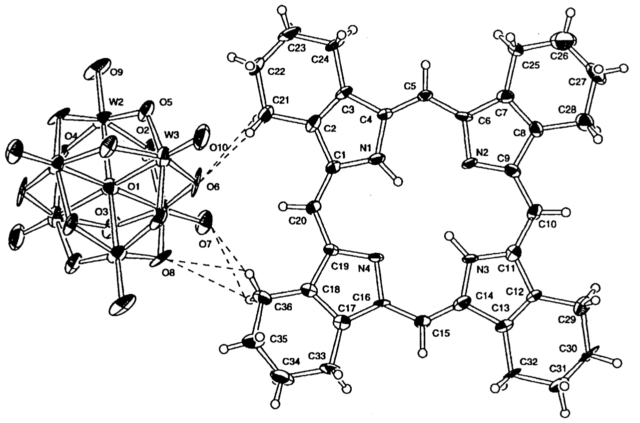

Figure 1. ORTEP drawing of the title salts. Thermal ellipsoids are at the 30% probability level. The crystallographically unique atoms are labeled. The CH-O hydrogen bonds are indicated by the dotted lines.

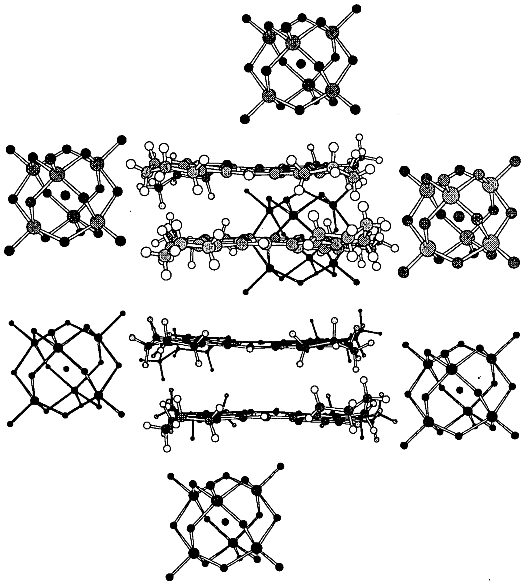

Figure 2. The packing structure of the title salt. For clarity, TCE and the front W_6O_{19} units are omitted.

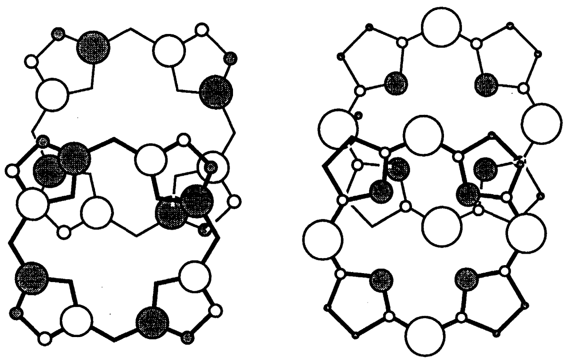

Figure 3. Overlap between a_{1u} (left side) and a_{2u} (right side) molecular orbitals.

These interactions also perturb the alignment of the porphyrins strongly and prevent to form one dimensional uniform chain structure as usually seen in the reported salts.[1] Dimerized porphyrins (interplanar distance: 3.59 Å) stack each other with 3.70 Å separation in a slipped fashion along *b*-axis to form a column as shown in Figure 2. The observed two interplanar distances are remarkably longer than those of reported cation radicals (3.26 Å for phthalocyanine free-base[12] and 3.31 Å for zinc octaethylporphyrinato[13]). The overlapping mode between the dimers are summarized in Figure 3. The interaction between the highest occupied molecular orbitals, a_{1u} and a_{2u}, is smaller than that of highly conducting phthalocyanine-based conductors.[14] Observed hydrogen bonded pinnings are regarded as a motivation force for this unique crystal structure. Such kind of interaction between organic cation radicals and inorganic anions will be applicable to the design of molecular based advanced materials.

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6 Crystal data for $[H_2TBuP]_2[W_6O_{19}][TCE]_2$: 0.63 X 0.01 X 0.10 mm, $C_{76}H_{82}Cl_6N_8O_{19}W_6$, $M = 2593.94$, triclinic, $P\bar{1}$(#2), $a = 13.741(9)$, $b = 13.74(2)$, $c = 11.982(9)$ Å, $\alpha = 97.02(8)$, $\beta = 104.91(5)$, and $\gamma = 105.04(7)°$, $V = 2067(3)$Å^3, $Z = 1$, $D_{calc} = 2.191$ gcm^{-3}, $\mu = 85.90$ cm^{-1}, $F_{(000)} = 1292.00$, λ(Mo-Kα) = 0.71069 Å. Rigaku AFC5R diffractometer. The data were collected at room temperature using the ω–2θ scan technique to a maximum 2θ value of 55.0°. 9472 Independent reflections were observed. The data were corrected for Lorentz and polarization effects. 4873 Absorption corrected data with $I \geq 4\sigma(I)$ were obtained. The structure was solved by Patterson Methods. Full matrix least squares refinement was used (non-hydrogens anisotropic, hydrogen in idealized positions not refined); 520 variables, weight $w = (4Fo^2)(\sigma^2 Fo^2)^{-1}$, $R = 0.078$, $Rw = 0.091$. C-H···O hydrogen bonds: O(3)-C(10) 3.25(2), O(4)-C(29) 3.44(2), O(7)-C(36) 3.33(3), O(8)-C(36) 3.41(3), O(9)-C(32) 3.33(3) and O(10)-C(28) 3.19(3) Å.

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