The results described here thus experimentally demonstrated that diffused radical cations behave differently from geminate radical ion pairs and that the solvent polarity is remarkably important for reactions that proceed through EDA complexes. It is also of interest to note that the present observation of oxygenation in the dark is the first example of oxygenation through EDA complexes with TCNE and undoubtedly verified an electron-transfer mechanism for the thermal [3 + 2] cycloaddition of MCP with TCNE, which was previously explained by a simple concerted [2 + 2 + 2] cycloaddition mechanism.[13] Similar results which supplement the proposed mechanism have been obtained in the photoexcitations of the EDA complexes of three-membered compounds such as 1,1,2,2-tetraarylcyclopropanes, 2,3-diaryloxiranes, and 2,3-diarylaziridines with TCNE in oxygen-saturated solvents. Those detail results will be soon reported.

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Preparation of Triangular Tungsten(IV) Aqua Ion, $W_3S_4^{4+}$, and X-ray Structure of $(bpyH)_5[W_3S_4(NCS)_9]\cdot 3H_2O$

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Many reports have been made on the trinuclear tungsten compounds, in which tungsten atoms are bridged by several kinds of atoms or ligands, i.e., μ_3-O, μ_3-CMe, μ_3-O-*i*-Pr, μ_3-As, μ_3-NH, μ_3-Cl, μ_2-O, μ_2-O-*i*-Pr, and/or μ_2-O_2CR.[1] A molecular orbital treatment of the triangular compounds has also been published.[2] Quite recently preparation and characterization of a tungsten(IV) aqua ion, $W_3O_4^{4+}$, has been reported.[3] However, no report on triangular tungsten compounds with any sulfur bridge, including the triangular tungsten(IV) aqua ion, $W_3S_4^{4+}$, has been published previously.[4] Preparation and characterization of molybdenum(IV) aqua ions with and without sulfur bridge(s), $Mo_3O_4^{4+}$,[5] $Mo_3O_3S^{4+}$,[6] $Mo_3O_2S_2^{4+}$,[7] $Mo_3OS_3^{4+}$,[8] and $Mo_3S_4^{4+}$,[9] have been worked out[10] and the presence of incomplete cubane-type $Mo_3O_{4-n}S_n^{4+}$ core (n = 0–4) has been revealed by X-ray structure analyses of compounds derived from those aqua ions and appropriate ligands.[5-9] Detailed electrochemical studies of $Mo_3O_4^{4+}$ aqua ion have also been carried out.[11]

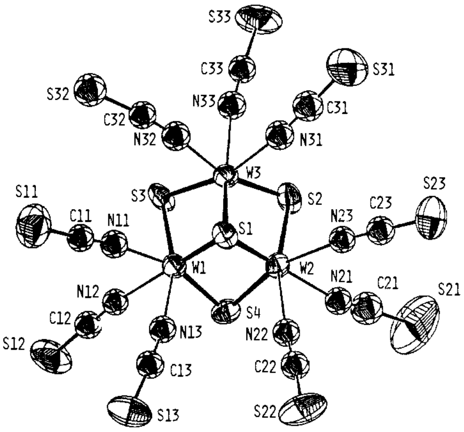

Figure 1. Perspective view of $[W_3S_4(NCS)_9]^{5-}$ with selected bond distances (Å): W1--W2, 2.767 (2); W1--W3, 2.766 (2); W2--W3, 2.761 (2); W1--S1, 2.355 (9); W2--S1, 2.384 (9); W3--S1, 2.354 (9); W1--S3, 2.320 (10); W1--S4, 2.313 (9); W2--S2, 2.313 (11); W2--S4, 2.310 (9); W3--S2, 2.304 (11); W3--S3, 2.289 (10); W--N, 2.154 (av).

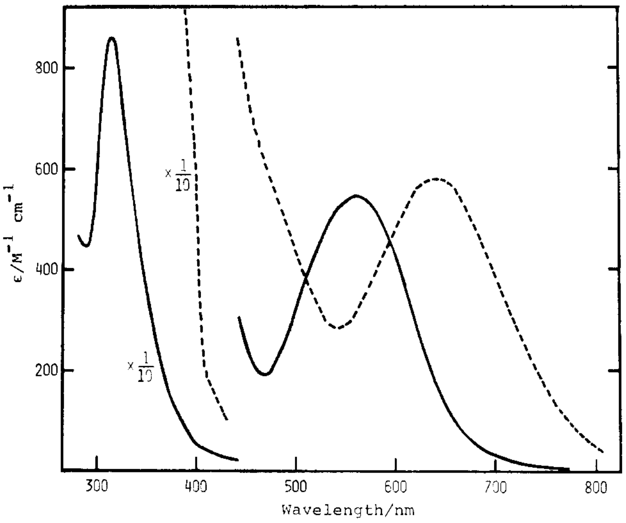

Figure 2. Electronic spectra: (—) $W_3S_4^{4+}$ in 2 M HPTS; (---) $[W_3S_4(NCS)_9]^{5-}$ in 1 M HCl containing 1 M KSCN.

We describe here the preparation and characterization of the incomplete cubane-type $W_3S_4^{4+}$ aqua ion and X-ray structure analysis of a derivative complex $(bpyH)_5[W_3S_4(NCS)_9]\cdot 3H_2O$ (bpy; 2,2′-bipyridine).

Sodium borohydride (3 g in 20 mL of H_2O) and HCl (6 M, 20 mL) were pipetted alternately into a yellow solution of $(NH_4)_2WS_4$[12] (3 g in 500 mL of H_2O) at room temperature. Another quantity of HCl (6 M, 80 mL) was added to the resultant dark brown solution, through which air was passed at ca. 80 °C for 12 h. One molar HCl was added occasionally to the solution during air oxidation, in order to keep the volume of the solution at ca. 200 mL. After it was cooled to room temperature, the solution was filtered and Sephadex G-15 column chromatography was applied (1 M HCl). The third blue-violet band (λ_{max} = 570 nm in 1 M HCl)[13] obtained by the procedure was purified by use

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[2] Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. C. *Inorg. Chem.* **1982**, *21*, 302–307.

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[4] The presence of dinuclear[4a] and linear trinuclear[4b] tungsten compounds with sulfur bridges has been known: (a) Pan, W. H.; Chandler, T.; Enemark, J. H.; Stiefel, E. I. *Inorg. Chem.* **1984**, *23*, 4265–4269. Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946–2950. (b) Muller, A.; Bhattacharyya, R. G.; Koniger-Ahlborn, E.; Sharma, R. C.; Rittner, W.; Neumann, A.; Henkel, G.; Krebs, B. *Inorg. Chim. Acta* **1979**, *37*, L493–L494. Koniger-Ahlborn, E.; Muller, A. *Angew. Chem.* **1975**, *87*, 598–598.

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[12] McDonald, J. M.; Frisen, G. D.; Rosenheim, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205–210.

[13] First and second bands are of purple (λ_{max} = 540 nm) and yellow (λ_{max} = 430 nm) in 1 M HCl.

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of a Dowex 50W-X4 cation exchanger (2 M HCl). The resultant solution was analyzed to give S/W = 1.29 + 0.05 (four determinations).[14] The yield was ca. 17% based on tungsten. An HPTS (*p*-toluenesulfonic acid) solution was obtained as described elsewhere.[6]

The charge of the ion was estimated to be 4+ on the basis of its behavior, similar to that of the $Mo_3S_4^{4+}$ aqua ion on the ion exchanger.

The W/S ratio and the electronic spectrum of the purple solution ($\lambda_{max,nm}$ (ϵ/M^{-1} cm^{-1} per trimer) 315 (8650) and 560 (546) in 2 M HPTS) indicate the probable existence of a $W_3S_4^{4+}$ aqua ion. The aqua ion in 2 M HPTS is stable toward air oxidation as can be expected from the preparative method. X-ray structure analysis[15] of $(bpyH)_5[W_3S_4(NCS)_9]\cdot 3H_2O$[16] prepared from the aqua ion revealed the presence of an incomplete cubane-type trinuclear tungsten core structure, $W_3S_4^{4+}$, in the $[W_3S_4(NCS)_9]^{5-}$ anion (Figure 1).

The W–W distance is distinctly longer than those of compounds with a W_3O_4[17] or Mo_3O_4[18] core and similar to those of compounds with a Mo_3S_4[19] or bi-oxo-capped-Mo_3O_2[20] or -W_3O_2[21] core. The X-ray structure analysis supports the existence of a $W_3S_4^{4+}$ ion (probably $[W_3S_4(H_2O)_9]^{4+}$) in solution.

The electronic spectra of the $W_3S_4^{4+}$ aqua ion and $[W_3S_4(NCS)_9]^{5-}$ are shown in Figure 2. The maximal peak position of the aqua ion in the visible region is red-shifted by ca. 100 nm as compared to that of $W_3O_4^{4+}$ (λ_{max} = 455 nm), and this is similar to the case of $Mo_3S_4^{4+}$ (λ_{max} = 602 nm) compared to that of $Mo_3O_4^{4+}$ (λ_{max} = 505 nm).[22]

A cyclic voltammogram of the aqua ion (0.05 M in 2 M HPTS) shows no appreciable peak in the 0.7 to –0.7 V region (vs. SCE). The reactivity of the aqua ion with Hg is very low in contrast to the case of the $Mo_3S_4^{4+}$ aqua ion.[9b] The $W_3S_4^{4+}$ aqua ion in 2 M HCl reacts rapidly with reductants (e.g., $NaBH_4$, Sn, and $W_2Cl_9^{3-}$) to give an orange solution which comes back to the former blue-violet solution on exposure to air; the reactivity of the aqua ion in HPTS with the above-metnioned reductants is very low. Characterization of these reactions is in progress.

Registry No. $(bpyH)_5[W_3S_4(NCS)_9]\cdot 3H_2O$, 101652-56-6; $(NH_4)_2WS_4$, 13862-78-7.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances, and bond angles (2 pages). Ordering information is given on any current masthead page.

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(14) Sulfur was determined gravimetrically as $BaSO_4$ and tungsten by the thiocyanate photometric method (*ASTM E* 146-64).

(15) Crystal data: triclinic system, space group $P\bar{1}$, a = 12.611 (5) Å, b = 24.927 (8) Å, c = 12.138 (4) Å, α = 93.05 (3)°, β = 91.06 (3)°, γ = 77.36 (3)°, V = 3718 (2) Å^3, Z = 2, Intensity data were collected on an automated four-circle diffractomer by use of graphite-monochromated Mo Kα radiation on the $4 \leq 2\theta \leq 45$ range. The coordinates of W's were determined by means of MULTAN, and the remaining non-hydrogen atoms were located from difference maps. The current R value is 0.102 for 7009 reflections ($F_o \geq 3\sigma(F_o)$).

(16) Excess KSCN (15 g) was added to the aqua ion (100 mL, 0.002 M per trimer in 1 M HCl). The color of the solution turned immediately from blue-violet to green. The solution was heated at 50 °C for 90 min to promote the reaction and allowed to stand overnight at room temperature. After filtration, 2,2′-bipyridine in 2 M HCl was added to the solution. On standing at room temperature, dark green crystals deposited. Anal. Found (calcd): N, 13.01 (13.01); C, 33.92 (34.67); H, 2.35 (2.52)%. Infrared spectrum of the complex shows absorption bands at 484, 466, 443, and 346 cm^{-1} due to W–S stretching.

(17) $[W_3O_4(NCS)_9]^{5-}$ (2.534 Å)[3] and $[W_3O_4F_9]^{5-}$ (2.514 Å: Matter, R.; Mennemann, K. *Z. Anorg. Allg. Chem.* **1977**, *437*, 175–182).

(18) For example, $[Mo_3O_4(mida)_3]^{2-}$ (2.495 Å)[5b] and $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ (2.486 Å).[5a]

(19) For example, $[Mo_3S_4(ida)_3]^{2-}$ (2.754 Å)[9b] and $[Mo_3S_4(CN)_9]^{5-}$ (2.765 Å: Howlader, N. C.; Haight, G. P., Jr.; Hambley, T. W.; Lawrance, G. A.; Rahomoller, G. A.; Snow, M. R. *Aust. J. Chem.* **1983**, *36*, 377–383).

(20) For example, $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ (2.759 Å: Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 3104–3106).

(21) For example, $[W_3O_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (2.742 Å: Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 4728–4742).

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Stereocontrolled Access to the Octosyl Acids: Total Synthesis of Octosyl Acid A

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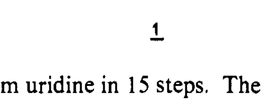
The octosyl acids, isolated from culture filtrates of *Streptomyces cacaoi* var. asoerisis,[1] have been shown to be anhydrooctose uronic acid nucleosides[2] consisting of an unusual trans- or cis-fused bicyclic perhydrofuropyran-type (dioxahydrindane) structure.[3] Related compounds can be found in the ezomycin complex[4] of nucleosides which have antifungal and antibiotic properties. Previous studies in our laboratories were concerned with developing methodology to construct the bicyclic ring systems found in such compounds[3,5] as well as in quantamycin, a computer-derived model for ribosomal binding.[6]

We now report on the first total synthesis of octosyl acid A (**1**) from uridine in 15 steps. The synthetic challenge was heightened by the presence of a number of stereochemically demanding features, not the least of which was the presence of a strained bicyclic system. An expedient route, unlike those already published,[3,6,7] was therefore developed, based on an assembly strategy that utilized uridine as a template, and subsequently built the tetrahydropyran ring (with its appendages) in a stereocontrolled fashion. The readily available aldehyde **2**[8] was treated with allylmagnesium bromide to give the desired chain-extended crystalline nucleoside derivative **3**, mp 155–157 °C, $[\alpha]^{25}_D$ –3.5° (c 1.0, AcOEt), as the major isomer (16:1)[9,10] (Scheme I). Sequential protection and hydrolysis of the acetonide function gave derivative **5**, $[\alpha]^{25}_D$ +3.1° (c 1.07, CH_2Cl_2).



OCTOSYL ACID A

1

The ring-closure strategy was based on an alkoxymercuration–oxidation sequence, which had precedence albeit in sterically and stereochemically less demanding systems.[11,12] Clearly the adąptatation of this sequence to our polyfunctional substrate was crucial to the successful completion of the synthesis. Toward this end, treatment of the O,N-protected diol **5** with mercuric acetate, followed by oxidative removal of the intermediate C_8' alkylmercurial bromide gave the expected bicyclic nucleoside **6**, $[\alpha]^{25}_D$ +52.3° (c 0.95, AcOEt) in 54% overall yield from **5**. The stereochemistry of the ring junction was unambiguously established by 400-MHz ^1H NMR spectroscopic analysis of **6** as

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