manganese porphyrins are the first example of the modification of the site of charge transfer for manganese porphyrins, and this is the first time this phenomenon has been observed for a high-valent metalloporphyrin.

Acknowledgment. Support of this research by the DHHS through Grant No. HL-33734-02 and by the NIH Biomedical Research Program at Georgia Tech is gratefully acknowledged. We wish to thank Professor Craig Hill for helpful discussions during the early stages of this work.

Registry No. (2,4,6-(MeO)$_3$-TPP)Mn(N), 113132-55-1; (2,6-(MeO)$_2$-TPP)Mn(N), 113132-56-2; (2,4-(MeO)$_2$-TPP)Mn(N), 113132-57-3; (2-MeO-TPP)Mn(N), 113132-58-4; (4-MeO-TPP)Mn(N), 83632-52-4; (2,4,6-Me$_3$-TPP)Mn(N), 84987-03-1; (4-Me-TPP)Mn(N), 84206-81-5; (TPP)Mn(N), 83632-54-6; (4-Cl-TPP)Mn(N), 113132-59-5; (2,6-Cl$_2$-TPP)Mn(N), 113132-60-8; (OEP)Mn(N), 84206-82-6.

Contribution from the Department of Chemistry
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A New Synthetic Entry to Tungsten–Sulfur Cluster Chemistry: Preparation and Structure of [$W_3S_4Cl_3(dmpe)_3$]$^+$

F. Albert Cotton* and Rosa Llusar

Received September 15, 1987

Although the chemistry of the trinuclear cluster compounds has developed in a similar way for both molybdenum and tungsten, that of molybdenum has always been in advance and is at present more highly developed. This is particularly true of the metal–sulfur clusters. Methods of obtaining derivatives of the $Mo_3S_4^{4+}$ cluster, as well as mixed species of the type $Mo_3O_{4-n}S_n^{4+}$, are numerous, whereas almost our entire knowledge of the analogous tungsten systems is covered by a few recent papers of Shibahara and coworkers.[1-4]

We recently developed a new type of synthetic entry to $Mo_3S_4^{4+}$ chemistry,[5] and we now wish to report that a similar type of chemistry exists for tungsten as well. Our approach, which is of an essentially nonaqueous nature, is perhaps of even greater interest for tungsten than for molybdenum because the entire body of $W_3O_{4-n}S_n^{4+}$ chemistry is still so limited.

Experimental Section

Materials. NaSH[6] and WCl$_4$[7] were prepared as described elsewhere. Dmpe was synthesized from commercially available $Cl_2PCH_2CH_2PCl_2$ (Aldrich Chemicals) according to the literature method.[8]

Physical Measurements. The electronic spectra were measured in methanol solutions with a Cary 17D spectrophotometer. Electrochemical measurements were performed with a Bioanalytical Systems, Inc., Model BAS 100 electrochemical analyzer in conjunction with a Houston Instruments Model DMP 40 digital plotter. Electrochemical data were obtained on acetone solutions of the BPh_4^- salt of the complex that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to an Ag/AgCl electrode at room temperature. A platinum disk (Model BAS MF 2032) was used as the working electrode.

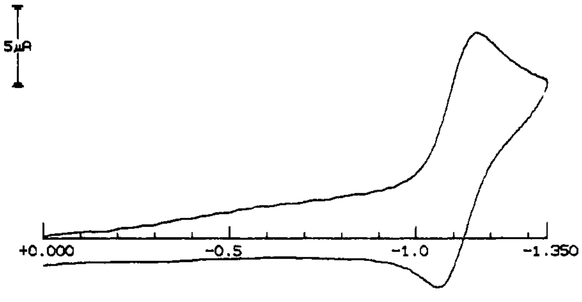

Figure 1. Cyclic voltammogram of [$W_3S_4Cl_3(dmpe)_3$]BPh_4 in acetone solution at a scan rate of 400 mV s^{-1} (reference: Ag/AgCl).

Table I. Crystal Data for [$W_3S_4Cl_3(dmpe)_3$]$PF_6 \cdot H_2O$

formula	$W_3S_4Cl_3P_7F_6OC_{18}H_{50}$
fw	1399.57
space group	$R3c$
systematic absences	$(hkil)$: $-h + k + l \neq 3n$ $(h\bar{h}0l)$: $h + l \neq 3n$, $l \neq 2n$ $(000l)$: $l \neq 6n$
a, Å	15.269 (2)
c, Å	30.620 (6)
V, Å^3	6182 (3)
Z	6
d_{calcd}, g/cm^3	2.25
crystal size, mm	0.3 × 0.3 × 0.4
μ(Mo Kα), cm^{-1}	92.4
data col instrument	Syntex P3
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflcns: no., range (2θ)	24, 20–30
temp, °C	11
scan method	ω–2θ
data col range, 2θ, deg	4–45
total no. of unique data	1031
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	907
no. of params refined	125
trans factors: max, min	0.99, 0.59
R^a	0.0324
$R_w{}^b$	0.0458
quality-of-fit indicator^c	1.228
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	1.3

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2 / (N_{observns} - N_{params})]^{1/2}$.

Synthesis of [$W_3S_4Cl_3(dmpe)_3$]$PF_6 \cdot H_2O$. NaSH (86 mg, 1.54 mmol) was added to a suspension of WCl$_4$ (374 mg, 1.15 mmol) in 15 mL of THF. Addition of 10 mL of methanol (to dissolve the NaSH) produced an instantaneous color change to green. Dmpe (190 μL, 1.15 mmol) was introduced and the reaction mixture refluxed for 2 h. After the mixture was cooled to room temperature, a brown precipitate was separated from a dark blue solution by filtration under argon. This blue solution is air stable and was absorbed onto a silica gel column. After the column was washed with acetone, the blue band that remained on the top was eluted with methanol. This resulting blue solution was treated with NH$_4$PF$_6$, and the mixture was allowed to evaporate slowly in air to give black crystals suitable for X-ray diffraction studies. Yield: ca. 20%. These crystals were characterized as [$W_3S_4Cl_3(dmpe)_3$]$PF_6 \cdot H_2O$. The BPh_4^- salt could also be obtained by addition of NaBPh$_4$ to the blue eluate. The UV–vis spectrum of this compound shows two bands at 560 and 300 nm.

Electrochemistry. The cyclic voltammogram of a solution of [$W_3S_4Cl_3(dmpe)_3$]BPh_4 in 0.1 M TBAH–acetone showed the presence of a quasi-reversible couple which corresponds to a reduction ($E_{1/2}$ = 1.11 V vs. Ag/AgCl). The separation between the "coupled" anodic and cathodic peaks (ΔE_p) was 100 mV at 300 mV/s and the $i_{p,c}/i_{p,a}$ ratios were in the range 0.5–0.55 depending on the scan speed. The ratio approached 1 as the scan speed increased. This is indicative of a reversible reaction at fast scan speeds, with some chemical event that follows the electrochemical process. The voltammogram obtained at 400 mV/s is shown in Figure 1.

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Table II. Positional Parameters and Their Estimated Standard Deviations for $[W_3S_4Cl_3(dmpe)_3]PF_6{\cdot}H_2O$

atom	*x*	*y*	*z*	$B,^a$ Å^2
W(1)	0.08486 (3)	−0.03140 (3)	0.000	1.74 (1)
Cl(1)	0.0844 (3)	−0.1549 (2)	0.0531 (1)	2.92 (8)
S(1)	0.000	0.000	0.0579 (2)	2.20 (9)
S(2)	−0.0421 (2)	−0.1477 (3)	−0.0456 (1)	2.49 (8)
P(1)	0.2581 (3)	0.0676 (2)	0.0393 (1)	2.58 (8)
P(2)	0.1907 (2)	−0.0871 (3)	−0.0418 (1)	2.33 (7)
C(1)	0.345 (1)	0.1952 (9)	0.0214 (8)	3.8 (4)
C(2)	0.260 (1)	0.078 (1)	0.0992 (6)	3.2 (3)
C(3)	0.330 (1)	−0.002 (1)	0.0269 (5)	2.9 (3)
C(4)	0.325 (1)	−0.016 (1)	−0.0225 (7)	4.8 (5)
C(5)	0.203 (1)	−0.068 (1)	−0.1004 (5)	4.0 (5)
C(6)	0.152 (1)	−0.221 (1)	−0.0355 (7)	4.1 (4)
P(4)	1.000	0.000	−0.2842 (4)	5.6 (2)
F(1)	1.059 (2)	0.096 (1)	−0.2523 (9)	8.5 (6)
F(2)	0.973 (2)	0.066 (2)	−0.3137 (8)	15.8 (7)
O(1)	1.000	0.000	−0.149 (2)	12 (1)*

[a] Starred value indicate atom was refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Bond Distances (Å) for $[W_3S_4Cl_3(dmpe)_3]PF_6{\cdot}H_2O^a$

W(1)–W(1)′	2.755 (1)	P(1)–C(1)	1.810 (13)
W(1)–Cl(1)	2.488 (4)	P(1)–C(2)	1.84 (2)
W(1)–S(1)	2.382 (5)	P(1)–C(3)	1.91 (2)
W(1)–S(2)	2.327 (3)	P(2)–C(4)	1.88 (2)
W(1)–S(2)″	2.288 (5)	P(2)–C(5)	1.81 (2)
W(1)–P(1)	2.595 (3)	P(2)–C(6)	1.83 (2)
W(1)–P(2)	2.520 (4)	C(3)–C(4)	1.52 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

X-ray Diffraction Studies.[9,10] A black crystal was mounted on the top of a glass fiber with epoxy cement. Table I summarizes the data collection and refinement procedures. Three reflections monitored throughout the data collection displayed no significant change in intensity. Unit cell parameters were obtained by applying the autoindexing routine to 24 centered reflections; they were then confirmed, together with the Laue class, by axial photographs. Lorentz, polarization, and empirical absorption corrections (ψ scans) were applied to the measured intensities.

The compound is isostructural with the analogous Mo compound, and consequently the positional parameters of the previous structure[5] (without including C and O atoms) were used to initiate the refinement. The carbon and oxygen atoms were located by alternating difference Fourier maps and least-squares cycles. All the atoms in the cluster and the anion were refined anisotropically. After location of the cluster and the anion, one peak in a special position remained in the difference Fourier map. This peak was assigned to the oxygen atom of an H_2O molecule, since the solvent used was wet methanol; it was refined with isotropic thermal parameters. With 907 reflections having $I > 3\sigma(I)$ considered observed and used to refine (full-matrix least squares) the structure, the final residuals were $R = 0.0324$ and $R_w = 0.0458$. The residual values for refinement of the alternative enantiomer were $R = 0.0362$ and $R_w = 0.0527$, thus indicating that the correct enantiomer had been chosen the first time.

Results and Discussion

Table IV. Selected Bond Angles (deg) for $[W_3S_4Cl_3(dmpe)_3]PF_6{\cdot}H_2O^a$

W(1)″–W(1)′–W(1)	60.00	Cl(1)–W(1)–S(2)″	158.9 (1)
W(1)″–W(1)–Cl(1)	136.9 (1)	Cl(1)–W(1)–P(1)	75.7 (1)
W(1)″–W(1)–S(1)	54.66 (8)	Cl(1)–W(1)–P(2)	80.6 (1)
W(1)″–W(1)–S(2)	98.6 (1)	S(1)–W(1)–S(2)	105.7 (1)
W(1)″–W(1)–S(2)″	54.00 (8)	S(1)–W(1)–S(2)″	107.0 (1)
W(1)″–W(1)–P(1)	98.99 (9)	S(1)–W(1)–P(1)	92.1 (1)
W(1)″–W(1)–P(2)	141.15 (9)	S(1)–W(1)–P(2)	162.1 (1)
W(1)′–W(1)–Cl(1)	101.25 (8)	S(2)–W(1)–S(2)″	98.1 (2)
W(1)′–W(1)–S(1)	54.67 (8)	S(2)–W(1)–P(1)	160.1 (2)
W(1)′–W(1)–S(2)	52.7 (1)	S(2)–W(1)–P(2)	82.4 (1)
W(1)′–W(1)–S(2)″	99.58 (8)	S(2)″–W(1)–P(1)	84.9 (1)
W(1)′–W(1)–P(1)	146.4 (1)	S(2)″–W(1)–P(2)	87.3 (1)
W(1)′–W(1)–P(2)	135.07 (7)	P(1)–W(1)–P(2)	78.1 (1)
Cl(1)–W(1)–S(1)	82.5 (1)	W(1)–S(1)–W(1)″	70.7 (2)
Cl(1)–W(1)–S(2)	97.4 (1)	W(1)–S(2)–W(1)′	73.3 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Comparison of Bond Lengths (Å)[a]

dist	$[Mo_3S_4Cl_3(dmpe)_3]^+$	$[W_3S_4Cl_3(dmpe)_3]^{4+}$	$[W_3S_4(NCS)_9]^{5-}$	$W_3S_4{}^{4+}$(aq)
M–M	2.766 (4)	2.755 (1)	2.765 [2]	2.724 [10]
M–(μ_3-S)	2.360 (9)	2.382 (5)	2.364 [10]	2.345 [5]
M–(μ_2-S)	2.336 (7)	2.327 (3)		
	2.290 (7)	2.288 (5)		
M–(μ_2-S) av	2.313 [15]	2.308 [14]	2.308 [14]	2.283 [4]
M–Cl	2.473 (7)	2.488 (4)		
M–P(1)	2.605 (8)	2.595 (3)		
M–P(2)	2.534 (8)	2.520 (4)		

[a] Average values for the last two compounds, taken from ref 1 and 2, respectively. Figures in [ ] are esd's from the mean.

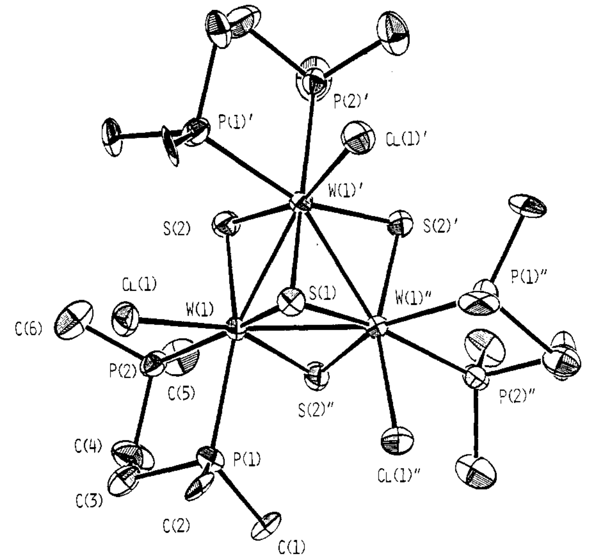

Figure 2. ORTEP drawing of the cation in $[W_3S_4Cl_3(dmpe)_3]PF_6{\cdot}H_2O$. Crystallographic C_3 symmetry is imposed. All atoms were refined anisotropically, and each one is represented by its ellipsoid of thermal displacement drawn at the 30% probability level.

The atomic positional parameters are listed in Table II along with the equivalent isotropic thermal displacement parameters. The *z* coordinate of the tungsten atom was assigned as zero in order to fix the origin. The molecule is required to have $C_3(3)$ symmetry. Tables III and IV list the most important bond distances and angles, respectively. These were obtained from the enantiomorph that refined to the lowest residuals.

The $[W_3S_4Cl_3(dmpe)_3]^+$ ion is depicted in Figure 2. Its structure is virtually identical with that of its molybdenum homologue, as shown by the comparison of bond lengths in Table V. Deviations of the W_3S_4 core from its (presumably) preferred C_{3v} symmetry are again seen and are attributable to the dissymmetric arrangement of the Cl and dmpe ligands.

It was previously shown[5] that the $Mo_3S_4{}^{4+}$ core in $[Mo_3S_4Cl_3(dmpe)_3]^+$ is generally very similar to those in other compounds containing that moiety, and the same sort of similarities are found between the present $W_3S_4{}^{4+}$ core and the two that have previously been described,[1,2] as also shown in Table V. We also note that the appearance of two bands at 560 and 300 nm in the

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(9) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with a VAX-SDP software package.

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UV-visible spectrum is in accord with the spectra reported[1] for the other $W_3S_4^{4+}$ species.

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Registry No. $[W_3S_4Cl_3(dmpe)_3]PF_6{\cdot}H_2O$, 113353-42-7; $[W_3S_4Cl_3(dmpe)_3]BPh_4$, 113471-51-5.

Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic thermal parameters (3 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Specific Syntheses of the Unsaturated Phosphorus-Nitrogen-Sulfur Rings $R_2PN_3S_2$, 1,5-$(R_2P)_2N_4S_2$, and $R_2PN_5S_3$ (R = Ph, Me)

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Stephen W. Liblong, and Trenton Parks

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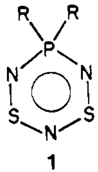
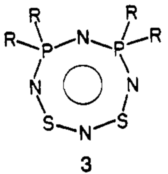
The cyclophosphathiazenes **1**-**3**[1] are aggregates of R_2PN and SN units that can be considered as hybrids of the well-known phosphazene and thiazene ring systems. The first example, **1**



1



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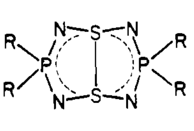

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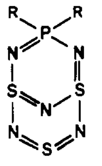
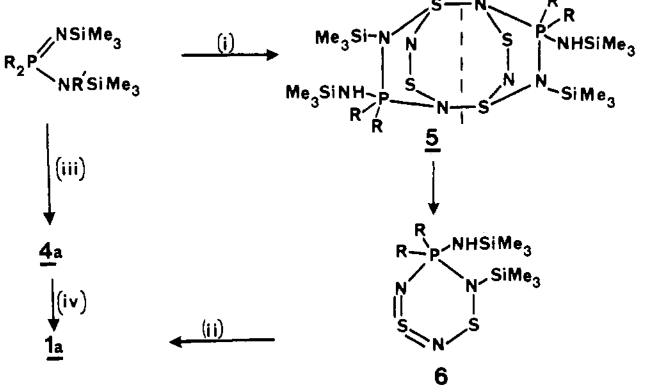


4

(R = Me_3SiNH), was prepared in 1976 by the reaction of S_4N_4 with $(Me_3Si)_2NP(NSiMe_3)_2$.[4,5] Subsequently, we obtained two other phosphadithiatriazines, **1a** (R = Ph) and **1b** (R = Me), from the reaction of S_4N_4 with R_2PPR_2.[6] Compound **1b** decomposes at room temperature to give the eight-membered ring **2b** (R = Me).[7] Further investigations of the reaction of R_2PPR_2 (or Ph_2PH) with S_4N_4 led to the isolation of both 1,3- and 1,5-diphosphadithiatetrazocines, **2a** and **3a** (R = Ph) and **2b** and **3b** (R = Me).[8] The yields of **2a** and **2b** are very low, however, and the separation and purification procedures for **1** and **3** are time-consuming. The rings **1** (R = CF_3, C_2F_5) have also been obtained in low yields (<20%) from the reaction of $R_2PN(SiMe_3)_2$ with $S_3N_2Cl_2$ and found to decompose at room temperature to give **3** (R = CF_3).[9]

Scheme I. Synthetic routes to **1a** from the reagents $R_2P(NR'SiMe_3)(NSiMe_3)$ (R = H, $SiMe_3$)[a]



[a] Key: (i) R = H'; S_4N_4, toluene reflux; (ii) R = Ph; $-(Me_3Si)_2NH$; (iii) R = Ph, R' = $SiMe_3$; $(NSCl)_3$, CH_2Cl_2, 0 °C; (iv) toluene, 100 °C.

Some aspects of the chemistry of **1**-**3** have been described,[6,10-12] but these investigations have been hampered by the lack of good preparative routes for individual ring systems. The synthesis of organic analogues of **1** and **2**, in which R_2P groups are replaced by RC, via cyclocondensation reactions of $RC(NR)(NR_2)$ (R = H, $SiMe_3$) with SCl_2[13] or $(NSCl)_3$,[14] suggested that a similar approach might be successful for the preparation of **1** and **2**. We have, therefore, investigated the synthesis of these PNS rings from the readily available reagents $Ph_2P(NR)(NRR')$ (R = Me_3Si; R' = H, $SiMe_3$). The direct synthesis of the bicyclic compounds **4a** and **4b** using these reagents is also described.

Experimental Section

Reagents and General Procedures. All solvents were dried and freshly distilled before use: toluene (Na), acetonitrile (CaH_2 and P_2O_5), methylene dichloride (P_2O_5), chloroform (P_2O_5). All reactions and the manipulation of moisture-sensitive reagents were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox (oxygen scavenger, Fisher), P_2O_5, and silica gel.

Diphenylphosphine, chlorodiphenylphosphine, trimethylsilyl azide, and sulfur dichloride (all from Aldrich) were distilled before use. $Ph_2P(NHSiMe_3)(NSiMe_3)$ was prepared by heating a neat mixture of trimethylsilyl azide and diphenylphosphine (2:1 molar ratio) until nitrogen evolution ceased.[15] Literature procedures were used for the preparation of S_4N_4,[16] $(NSCl)_3$,[17] $Me_2PN(SiMe_3)_2$,[18] and $Me_2P(NSiMe_3)[N$-

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(1) The term cyclophosphathiazene refers here to unsaturated P-N-S rings containing two-coordinate sulfur in the formal oxidation state of +3. Related hybrid ring systems containing either three-coordinate sulfur in the +4 oxidation state[2] or four-coordinate sulfur in the +6 oxidation state[3] are known and are sometimes also referred to as cyclophosphathiazenes.

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