Inorg. Chem. **1989**, *28*, 4297–4300

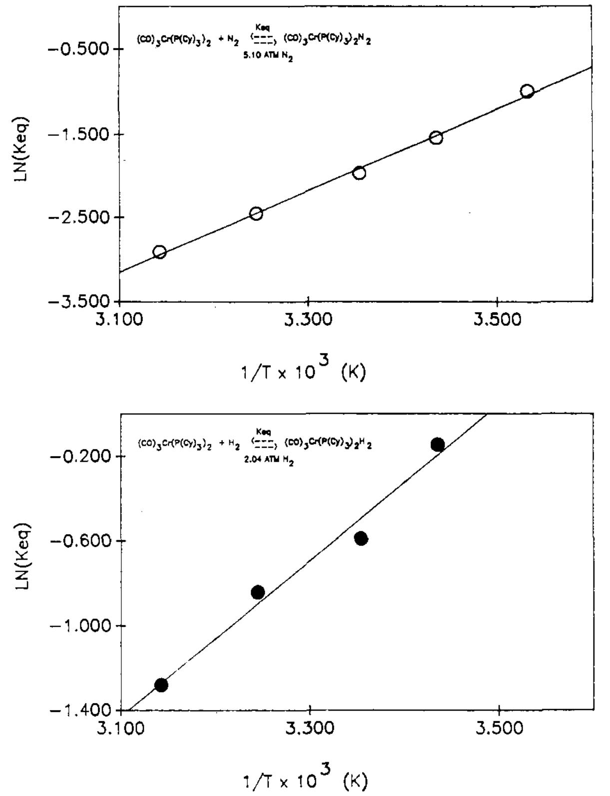

Figure 2. Plot of ln K_{eq} versus $1/T$ (K) for $(P(C_6H_{11})_3)_2Cr(CO)_3 + L \rightarrow (P(C_6H_{11})_3)_2Cr(CO)_3(L)$: (a, top) L = N_2; (b, bottom) L = H_2.

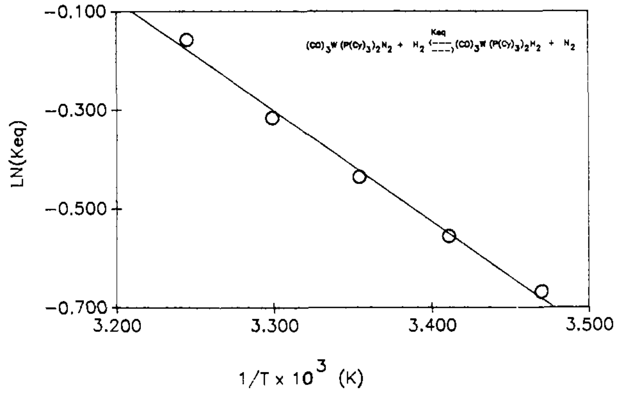

Figure 3. Plot of ln K_{eq} versus $1/T$ (K) for $(P(C_6H_{11})_3)_2W(CO)_3(N_2) + H_2 \rightarrow (C_6H_{11})_3)_2W(CO)_3(H_2) + N_2$.

The entropy of ligand binding for a gaseous ligand to a complex in solution reflects the difference in total entropies of the species involved:

$$ML_n(soln) + H_2(g) \rightarrow ML_n(H_2)(soln) \quad (4)$$

Binding a gaseous ligand to a metal increases the total entropy of the metal complex $ML_n(H_2)$ relative to ML_n but does so by a relatively minor amount compared to the entropy lost by the ligand.[6] On that basis the total entropy of exchange for general reaction 5 should depend primarily on the differences in absolute

$$ML_n(N_2)(soln) + H_2(g) \rightarrow ML_n(H_2)(soln) + N_2(g) \quad (5)$$

entropies for $N_2(g)$ and $H_2(g)$. The "third-law" entropies of the two gases can be calculated by using standard formulas of statistical thermodynamics.[7] At room temperature, the entropy is due exclusively to the translational and rotational components. Due to its lower mass and moment of inertia, the absolute entropy of H_2 (31.2 cal/(mol deg)) is 14.6 cal/(mol deg) lower than the absolute entropy of N_2 (45.8 cal/(mol deg)). If eq 5 is examined again, it is clear that if the total entropies of the complexes in solution exactly canceled, the predicted entropy change would be 14.6 cal/(mol deg). This is reasonably close to the value we obtain, 11 ± 4 cal/(mol deg) for the three complexes. The residue may be due to several factors,[6,7] including differences in vibrational partition functions for the complexes.

It is clear that the large entropy of ligand exchange is due to the fact that H_2 has the smallest absolute entropy of any diatomic gas. In the absence of unusual vibrational frequency changes upon complexation, this should be general for molecular hydrogen and nitrogen complexes. The net result is that, at higher temperatures, molecular hydrogen will be more competitive relative to dinitrogen. This could have important implications for catalysis. Additional work on the thermodynamics and kinetics of binding nitrogen, hydrogen, and nitrogen hydrides is in progress for these and related complexes.

Experimental Section

The complexes $(P(C_6H_{11})_3)_2M(CO)_3$ were prepared by published procedures for M = Cr,[1] Mo,[2] and W.[2] All manipulations were carried out in a glovebox or by using standard Schlenk techniques. The solvents THF and toluene were freshly distilled from sodium benzophenone ketyl under an argon atmosphere. Vibrational spectra were run on a Perkin-Elmer 1850 FTIR instrument. High-pressure spectra were run in a special CaF_2 cell obtained from Harrick Scientific, Ossining, NY. The cell was attached via Swagelok fittings to a 40-mL high-pressure bomb in such a way that, by rotation of the entire apparatus, fresh solution could be taken from the bomb into the infrared cell. A calibrated platinum resistance thermometer obtained from Omega Engineering, Stamford, CT, was inserted via a high-pressure fitting directly into the bulk of the solution and allowed direct reading of temperatures. The entire apparatus was placed inside a "water-bag" constructed from an old glovebox glove. A constant-temperature alcohol/water bath was circulated around the entire apparatus through holes cut in the glove and secured by hose clamps to metal tubing. The entire apparatus was placed in an optical bench/glovebox that will be described in detail elsewhere.[9] Measurements were made at a given temperature until no further change occurred in the spectra on three successive runs. Spectroscopic equilibrium constants[5] were measured at at least three different total pressures, and reported values represent an average of these determinations.

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(6) Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449.

(7) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley and Sons: New York, 1969.

(8) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl.* **1982**, *11*, No. 2.

(9) Gonzalez, A. A.; Kai, Z.; Hoff, C. D. Manuscript in preparation.

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New and General Route to the Synthesis of Oxopolymetalates via Peroxometalates in Aqueous Medium: Synthesis and Crystal and Molecular Structure of $(PPN)_2[W_6O_{19}]$ (PPN = Bis(triphenylphosphine)nitrogen(1+) Cation)

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Effective methods of synthesis of oxopolymetalates have been found to vary with the specific identity of the metal. The preparation[2] of $Mo_6O_{19}^{2-}$ and $M_6O_{19}^{8-}$ (M = Nb, Ta)[3] is achieved in a conventional manner by the treatment of alkaline MO_4^{2-} so-

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(1) (a) Jadavpur University. (b) Okalhoma State University.

(2) Fuchs, J.; Jahr, K. F. *Z. Naturforsch., B* **1968**, *23*, 1380.

(3) Nelson, W. M.; Tobias, R. S. *Inorg. Chem.* **1963**, *2*, 985.

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lutions with H^+; however, this approach does not yield $W_6O_{19}^{2-}$. The identification[4–6] of $W_6O_{19}^{2-}$ as the product of the hydrolysis of $WO(OCH_3)_4$ with tetra-*n*-butylammonium hydroxide in ethanol medium, as well as its subsequent synthesis[7,8] in other nonaqueous media, was unexpected and was believed to have been caused by the presence of water in the solvent.[7] The three methods[4,7,8] of $W_6O_{19}^{2-}$ synthesis are applicable to M = W only.

In pursuing our interest in the generation of oxo or peroxo analogues of polythiotungstates[9–11] or polynuclear perthiotungstates[12] or molybdates,[12–14] using H_2O_2 (and not polysulfide) in the synthetic process, we thought to have isolated polynuclear peroxotungstates[15] as Ph_4P (**1**) and PPN (**2**) salts, but on structural characterization, **2** (and thus **1** by inference) was found to be $(PPN)_2[W_6O_{19}]$. We have now found that the treatment of the appropriate oxometal species with H_2O_2 in aqueous solution can be applied, as a general method, to the production of hitherto unknown or uncommon oxopolymetalates.[16] In the present paper we report a synthesis (via peroxometalate intermediates) of $W_6O_{19}^{2-}$ as **1** and **2** from aqueous medium and the structural characterization of **2**. We also report here the isolation and characterization of the previously unknown $[WO(O_2)_2(L\text{-}L)]$ (L-L = 1,10-phenanthroline (phen; **3**) and 2,2′-bipyridine (bpy; **4**)), obtained in the process.

Experimental Section

Materials. Sodium tungstate (AR) was obtained from BDH. Hydrogen peroxide (30% purified), 1,10-phenanthroline, and 2,2′-bipyridine were of GR (E. Merck) grade. Extrapure grade tetraphenylphosphonium chloride and bis(triphenylphosphine)nitrogen(1+) chloride were obtained from Schuchardt. Dichloromethane and acetonitrile (AR grade, E. Merck) were further purified by P_4O_{10} treatment followed by distillation until a fresh sample of P_4O_{10} (GR grade, E. Merck) was not stained yellow by the respective solvents. Triple-distilled water (all glass) was used throughout, and all other solvents used were of analytical grades (E. Merck) and were further purified by literature methods.[17]

Physical Measurements. Spectroscopic data were obtained by using the following instruments: IR spectra (KBr disk, 4000–200 cm^{-1}), Perkin-Elmer 597 spectrophotometer; electronic spectra (2600–200 nm), Hitachi Model U-3400 UV–vis–near-IR spectrophotometer; Raman spectra (solid powders) Spex Model 1403 double-monochromator spectrometer using an argon ion laser (5145-Å line). Scattered light at 90° was detected with the help of a cooled Spex Datamate R 928/115 photomultiplier tube and a photon-counting processing system. Solution conductances were measured with a Systronics Model 335 digital conductivity bridge. X-ray powder diffraction data for **3** and **4** were measured with a Philips Model PW 1730/PW 1710 XRD system. The 2θ range is from 10 to 45° with Cu Kα radiation (1.5418 Å). The elements C, H, and N were analyzed microanalytically by using a Perkin-Elmer 240 C elemental analyzer, and W and P were determined by conventional macro methods.[18]

Preparation of Compounds. HCl (6M) was added dropwise to a solution (40 mL) of $Na_2WO_4{\cdot}2H_2O$ (0.5 g; 1.5 mmol) dissolved in 40 mL of water until complete precipitation of $WO_3{\cdot}H_2O$ occurred. The precipitate was collected by filtration, washed thoroughly with water to remove all chloride ion, and dissolved in 30% H_2O_2 (20 mL) with stirring at room temperature.

Table I. Crystal Data for $(PPN)_2[W_6O_{19}]$

formula	$W_6O_{19}(NP_2C_{36}H_{30})_2$	V	3654 (3) $Å^3$
mol wt	2484.26	μ(Mo Kα)	97.66 cm^{-1}
a	10.526 (5) Å	λ(Mo Kα)	0.71069 Å
b	25.84 (1) Å	T	25 °C
c	15.216 (9) Å	D_{calc}, D_{obs}	2.258, 2.205 g cm^{-3}
α	90.0°	Z	2
β	118.00 (5)°	space group	$P2_1/c$ (No. 14)
γ	90.0°	R, R_w	6.3, 8.3%

$(Ph_4P)_2[W_6O_{19}]$ (1). Addition of an aqueous solution (20 mL) of Ph_4PCl (1.10 g, 3.0 mmol; Ph_4P = tetraphenylphosphonium) to a solution of $WO_3{\cdot}H_2O$ in aqueous H_2O_2, prepared as described above, gave a white precipitate with stirring. The solid was collected by filtration, washed successively with water, 95% ethanol, and diethyl ether, and then recrystallized from dichloromethane/ether/pentane. The colorless crystalline product was dried over $CaCl_2$ at reduced pressure; yield 0.32 g (≅10%). Anal. Calcd for $(Ph_4P)_2[W_6O_{19}]$: C, 27.6: H, 1.93; P, 2.97; W, 52.9. Found: C, 28.1; H, 1.96; P, 3.01; W, 52.4. IR: 1115 (s), 1000 (w), 980 (s), 815 (s), 750 (w), 720 (s), 695 (m), 590 (w), 520 (s), 440 (s), 360 (w) cm^{-1}.

$(PPN)_2[W_6O_{19}]$ (2). A solution of (PPN)Cl (PPN = bis(triphenylphosphine)nitrogen(1+); 1.7 g, 3.0 mmol) in aqueous ethanol (1:1) was added to a solution of $WO_3{\cdot}H_2O$ in aqueous H_2O_2 prepared as described above, giving a white precipitate, which was collected, washed, and recrystallized as for the Ph_4P analogue **1**, yielding colorless crystals (0.52 g, ≅14%). Anal. Calcd for $(PPN)[W_6O_{19}]$: C, 34.8; H, 2.41; N, 1.12; W, 44.4; P, 2.49. Found: C, 34.5; H, 2.36; N, 1.10; W, 44.1; P, 2.46. IR: 1120 (s), 1020 (w), 1000 (w), 980 (s), 900 (w), 870 (m), 820 (s), 750 (m), 730 (s), 700 (s), 595 (s), 530 (s), 500 (s), 440 (m), 365 (w) cm^{-1}.

$[WO(O_2)_2(phen)]$ (3). An ethanolic solution (10 mL) of phen (0.30 g, 1.5 mmol) was added with stirring to the filtrate of **1** or **2**, when a white solid precipitated. The solid was filtered off and washed with water, 95% ethanol, and ether and dried as usual. The yield was 0.48 g (≅72%). Anal. Calcd for $[WO(O_2)_2(phen)]$: C, 32.5; H, 1.81; N, 6.30; W, 41.4. Found: C, 32.1; H, 1.78; N, 6.26: W, 41.0. IR: 1630 (m), 1600 (m), 1510 (s), 1430 (s), 1220 (w), 1200 (vw), 1140 (w), 1110 (vw), 960 (s), 840 (s), 760 (m), 740 (s), 720 (m), 650 (m), 540 (s) cm^{-1}. Raman: 1452 (s), 1427 (s), 1315 (m), 953 (s), 854 (s), 744 (s), 561 (s), 541 (m), 432 (s), 310 (s) cm^{-1}. UV–vis (Nujol mull): 357 nm. *d* spacings: 7.83 (s), 5.44 (s), 4.74 (w), 4.46 (m), 3.92 (m), 3.48 (m), 3.17 (w), 3.03 (vw), 2.75 (vw), 2.24 (vw) Å.

$[WO(O_2)_2(bpy)]$ (4). Instead of phen, bpy (0.23 g, 1.5 mmol) was added by following the procedure described above. The yield was 0.44 g (≅70%). Anal. Calcd for $[WO(O_2)_2(bpy)]$: C, 28.6; H, 1.90; N, 6.67; W, 43.8. found: C, 28.3; H, 1.91; N, 6.64; W, 43.2. IR: 3080 (w), 1615 (m), 1610 (s), 1580 (m), 1560 (w), 1500 (w), 1480 (m), 1450 (s), 1420 (m), 1320 (m), 1250 (w), 1180 (w), 1160 (w), 1040 (m), 950 (s), 880 (w), 840 (s), 780 (s), 730 (m), 650 (m), 580 (w), 540 (s) cm^{-1}. Raman: 1601 (s), 1573 (w), 1565 (m), 1498 (s), 1318 (s), 1275 (w), 1035 (s), 944 (s), 852 (s), 766 (s), 550 (s), 313 (s) cm^{-1}. UV–vis (Nujol mull): 340 nm. *d* spacings: 6.92 (s), 5.75 (s), 4.65 (w), 4.31 (s), 3.74 (m), 3.44 (m), 3.31 (w), 3.20 (vw), 2.67 (w), 2.21 (vw) Å.

X-ray Crystallography. Well-formed crystals of $(PPN)_2[W_6O_{19}]$ were obtained by slow diffusion of a 1:1 mixture of pentane and diethyl ether into a dichloromethane solution of $(PPN)_2[W_6O_{19}]$. A crystal of suitable dimensions was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data (4652 points) were collected at room temperature with use of a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2Θ value of 45.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. After removal of space-group-forbidden and redundant data, 3011 observed data ($I > 3.0\sigma(I)$) were used for solution and refinement. The structure was solved for heavy-atom positions by using direct methods.[19] The remainder of the atoms were located with

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(4) Jahr, K. F.; Fuchs, J.; Oberhauser, R. *Chem. Ber.* **1968**, *101*, 477.

(5) Henning, G.; Hullen, A. *Z. Kristallogr.* **1969**, *130*, 162.

(6) Fuchs, J.; Freiwald, W.; Hartl, H. *Acta Crystallogr.* **1978**, *B34*, 1764.

(7) Kirillova, N. I.; Kolomuikov, I. S.; Zolstarev, Yu. A.; Lysyak, T. V.; Struchkov, Yu. T. *Russ. J. Coord. Chem.* (*Engl. Transl.*) **1977**, *3*, 1488. This work describes the synthesis of $(Me_2NH_2)_2[W_6O_{19}]$ from $W(CO)_6$ and HCOOH in a dimethylformamide medium under an argon atmosphere.

(8) Larue, A.; Lin, A. T.; Felippo, J. A. *Inorg. Chem.* **1980**, *19*, 315.

(9) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657.

(10) Koniger-Ahlborn, E.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 574.

(11) Müller, A.; Bhattacharyya, R. G.; Koniger-Ahlborn, E.; Rittner, A.; Newman, A.; Henkel, G.; Krebs, B.; Sharma, R. C. *Inorg. Chim. Acta* **1979**, *37*, L493.

(12) Müller, A.; Jastes, R.; Eltznew, W.; Shinie, C.; Diemann, E.; Bögge, H.; Zimmerman, M.; Dartmann, M.; Reinsch-Vogell, U.; Che, S.; Cyvin, B. N. *Inorg. Chem.* **1985**, *24*, 2872.

(13) Müller, A.; Dartmann, M.; Romer, C.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1060.

(14) Müller, A.; Reinsch-Vogell, U.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 796.

(15) Our experience of obtaining $[MoO_2(8\text{-quinolinol})_2]$ from $[MoO(O_2)(8\text{-quinolinol})_2]$ during crystallization from acetone, however, raised the possibility of getting an oxo derivative rather than a peroxo one.

(16) To be submitted for publication.

(17) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1966.

(18) Vogel, I. A. *A Textbook of Quantitative Inorganic Analysis*; The English Language Book Society and Longmans: London, 1968.

(19) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. "MULTAN78", University of York, York, England, 1980.

Table II. Positional Parameters for $(PPN)_2[W_6O_{19}]$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)	U_{equiv}, Å^2
W1	0.4421 (1)	0.01125 (4)	0.3334 (1)	30.7 (7)
W2	0.2564 (1)	−0.00611 (5)	0.4560 (1)	32.3 (8)
W3	0.4902 (1)	0.08853 (4)	0.5184 (1)	32.3 (7)
P1	0.8599 (7)	0.2910 (3)	0.4850 (5)	25 (4)
P2	0.6226 (7)	0.3727 (3)	0.4822 (5)	27 (4)
O1	0.4067 (23)	0.0202 (8)	0.2163 (16)	56 (14)
O2	0.0762 (18)	−0.0110 (9)	0.4212 (18)	61 (15)
O3	0.4838 (20)	0.1541 (7)	0.5271 (13)	38 (12)
O4	0.2613 (18)	0.0019 (7)	0.3352 (16)	42 (12)
O5	0.2973 (18)	0.0668 (7)	0.4785 (14)	38 (11)
O6	0.4535 (19)	0.0802 (6)	0.3817 (14)	37 (12)
O7	0.4609 (19)	−0.0622 (7)	0.3487 (13)	37 (11)
O8	0.3492 (18)	−0.0144 (7)	0.5949 (14)	35 (11)
O9	0.6905 (20)	0.0760 (8)	0.5481 (14)	42 (12)
O10	0.5000	0.0000	0.5000	14 (12)
N1	0.7019 (19)	0.3041 (8)	0.4647 (14)	20 (12)
C111	0.997 (3)	0.298 (1)	0.613 (2)	28 (16)
C112	1.052 (3)	0.347 (1)	0.648 (2)	40 (18)
C113	1.152 (3)	0.349 (1)	0.749 (2)	52 (21)
C114	1.196 (3)	0.304 (2)	0.811 (2)	53 (21)
C115	1.124 (4)	0.260 (2)	0.775 (2)	70 (26)
C116	1.033 (3)	0.254 (1)	0.675 (2)	43 (19)
C121	0.916 (3)	0.326 (1)	0.409 (2)	36 (16)
C122	1.057 (3)	0.340 (1)	0.441 (2)	49 (20)
C123	1.093 (3)	0.364 (1)	0.377 (3)	59 (23)
C124	0.987 (3)	0.385 (1)	0.275 (2)	62 (22)
C125	0.856 (4)	0.359 (2)	0.244 (3)	92 (31)
C126	0.816 (3)	0.338 (2)	0.310 (2)	58 (23)
C131	0.867 (3)	0.223 (1)	0.454 (2)	19 (14)
C132	0.984 (3)	0.202 (1)	0.457 (2)	30 (16)
C133	0.989 (3)	0.151 (1)	0.437 (2)	41 (18)
C134	0.870 (4)	0.120 (1)	0.410 (3)	85 (29)
C135	0.745 (4)	0.142 (1)	0.402 (2)	50 (20)
C136	0.741 (3)	0.195 (1)	0.424 (2)	47 (19)
C211	0.478 (2)	0.374 (1)	0.364 (2)	29 (15)
C212	0.419 (3)	0.424 (1)	0.352 (2)	39 (17)
C213	0.306 (3)	0.438 (1)	0.262 (2)	50 (20)
C214	0.247 (3)	0.404 (1)	0.187 (2)	37 (18)
C215	0.304 (3)	0.353 (2)	0.198 (2)	50 (21)
C216	0.416 (3)	0.340 (1)	0.285 (2)	46 (14)
C221	0.546 (3)	0.335 (1)	0.558 (2)	33 (16)
C222	0.780 (3)	0.368 (1)	0.596 (2)	46 (18)
C223	0.419 (3)	0.350 (1)	0.652 (2)	44 (19)
C224	0.416 (3)	0.296 (1)	0.666 (2)	60 (23)
C225	0.473 (3)	0.264 (1)	0.631 (3)	61 (23)
C226	0.529 (4)	0.280 (1)	0.571 (2)	64 (23)
C231	0.732 (3)	0.409 (1)	0.539 (2)	34 (17)
C232	0.761 (3)	0.444 (1)	0.485 (2)	51 (21)
C233	0.852 (4)	0.484 (2)	0.530 (3)	73 (28)
C234	0.920 (4)	0.487 (1)	0.631 (4)	85 (34)
C235	0.896 (4)	0.453 (1)	0.685 (2)	46 (21)
C236	0.803 (3)	0.413 (1)	0.645 (2)	34 (16)

Table III. Bond Distances (Å) and Angles (deg) for $W_6O_{19}[(Ph_3P)_2N]_2$

W1–O1	1.66 (2)	W2–O8	1.89 (2)
W1–O4	1.93 (2)	W2–O9	1.90 (2)
W1–O6	1.91 (2)	W2–O10	2.33 (3)
W1–O7	1.91 (2)	W3–O3	1.70 (2)
W1–O8	1.94 (2)	W3–O5	1.91 (2)
W1–O10	2.33 (3)	W3–O6	1.94 (2)
W2–O2	1.72 (2)	W3–O7	1.96 (2)
W2–O4	1.88 (3)	W3–O9	1.96 (2)
W2–O5	1.93 (2)	W3–O10	2.31 (3)
O1–W1–O4	108 (1)	O8–W2–O9	85.6 (8)
O1–W1–O6	103.0 (9)	O8–W2–O10	76 (7)
O1–W1–O7	103.1 (9)	O9–W2–O10	77 (8)
O1–W1–O8	103 (1)	O3–W3–O5	104.0 (9)
O1–W1–O10	178 (8)	O3–W3–O6	101.4 (8)
O4–W1–O6	90 (1)	O3–W3–O7	105.4 (8)
O4–W1–O7	85.5 (8)	O3–W3–O9	103.0 (9)
O4–W1–O8	149.3 (9)	O3–W3–O10	177 (8)
O4–W1–O10	74 (8)	O5–W3–O6	88.8 (9)
O6–W1–O7	153.6 (8)	O5–W3–O7	87.2 (8)
O6–W1–O8	83.9 (8)	O5–W3–O9	152.9 (8)
O6–W1–O10	76 (8)	O5–W3–O10	77 (8)
O7–W1–O8	87.0 (7)	O6–W3–O7	153.0 (7)
O7–W1–O10	77 (8)	O6–W3–O9	83.1 (8)
O8–W1–O10	75 (8)	O6–W3–O10	76 (7)
O2–W2–O4	104 (1)	O7–W3–O9	88.4 (8)
O2–W2–O5	87.6 (9)	O7–W3–O10	77 (6)
O2–W2–O8	104.7 (9)	O9–W3–O10	76 (8)
O2–W2–O10	179 (7)	W1–O10–W2	90 (7)
O4–W2–O5	87.6 (9)	W2–O10–W3	89 (1)
O4–W2–O8	151.2 (8)	W3–O10–W1	90 (2)
O4–W2–O10	75 (6)	W1–O8–W2	119 (1)
O5–W2–O8	87.6 (7)	W2–O9–W3	117 (1)
O5–W2–O9	152.9 (8)	W3–O7–W1	116 (1)
O5–W2–O10	76 (8)		

use of successive cycles of least-squares refinement followed by difference Fourier syntheses. Least-squares refinement[20] converged with anisotropic thermal parameters. Hydrogen atom positions were calculated by using the appropriate geometry and a C–H distance of 0.97 Å. Hydrogen positions were included in the final cycles of refinement with isotropic thermal parameters but held invariant. A final difference Fourier synthesis revealed no electron density of interpretable level. Anomalous dispersion corrections were made for tungsten. Scattering factors were taken from Cromer and Mann.[21] The final cycle of refinement (function minimized $\sum(|F_o| - |F_c|)^2$) led to the final agreement factor R = 6.3% ($R = 100(\sum||F_o| - |F_c||/\sum|F_o|)$). Unit weights were used until the final cycles of refinement, when weights equal to $1/\sigma(F)^2$ were introduced. R_w = 8.3%. Final positional parameters are shown in Table II. Bond angles and distances for the hexatungstate anion are given in Table III.

Results and Discussion

The geometry of the W_6O_{19} unit resembles that seen in the tetra-*n*-butyl[5,6] and $[W(t\text{-}C_4H_9NC)_7]^{2+}$ salts,[8] each of which shows a similar arrangement of six tungsten atoms about a μ_6-oxo atom with 12 μ_2-oxo atoms and six terminal oxo groups. The W_6O_{19} unit of **2** may be viewed as comprised of six distorted WO_6 octahedra bonded via shared edges with one O atom common to each of the six (Figure 1). The oxygen atom in common is located on a crystallographic inversion center and is equidistant from the six tungsten atoms. Each WO_6 octahedron is irregular due to the displacement of the metal toward the terminal or unshared oxygen atom. The W–O_t, W–O_b, and W_6–O distances of our PPN salt average 1.69, 1.92, and 2.32 Å, respectively, in close agreement with previous structure determinations[5,6,8] of this hexatungstate.

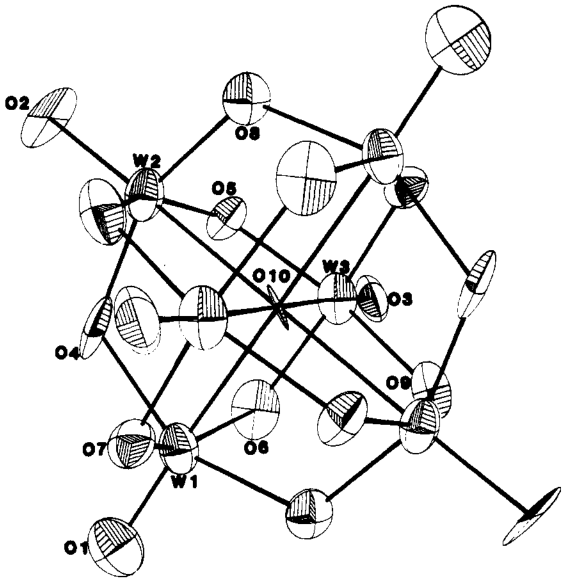

Figure 1. Projection view of the $[W_6O_{19}]^{2-}$ anion.

Both polymetalates and peroxo derivatives coexist in solution. Peroxometalates **3** and **4**, alone, may be isolated from a solution of WO_3 in H_2O_2. The polynuclear peroxometalate apparently serves as an intermediate in the production of polymetalate. While $[W_6O_{19}]^{2-}$ is apparently formed too rapidly to allow isolation of the intermediate,[22] the polymolybdate[16] $[Mo_2O_7(H_2O)_2]^{2-}$ is clearly

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(20) Stewart, J. M., Ed. "The XRAY system of 1980"; Technical Report TR 446; Computer Center, University of Maryland: College Park, Md, 1980.

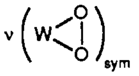
(21) Cromer, D. T.; Mann, I. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(22) Otherwise a high-yield synthesis would have been made possible.

formed[23] via a binuclear oxo-bridged peroxo intermediate.[24]

Oxopolytungstates **1** and **2** behave as 2:1 elecrolytes (250 and 240 Ω^{-1} cm^2 M^{-1}) in acetonitrile.[25] The IR band at 980 cm^{-1} in the spectra of **1** and **2** can be assigned to the $\nu(\mathrm{W{=}O})_{\mathrm{asym}}$ vibration, while those at 815 cm^{-1} (**1**) and 820 cm^{-1} (**2**) are attributable to the $\nu(\mathrm{W{-}O{-}W})_{\mathrm{asym}}$ vibration in the polytungstate unit. The corresponding symmetric band appears at 440 cm^{-1}. The $\nu(\mathrm{W_6{-}O})$ vibration involving each of the six tungsten atoms about O(10) appears at 360 cm^{-1} for **1** and at 365 cm^{-1} for **2**. The two species also show identical UV–vis absorption spectra; 295 nm (ϵ = 1120 for **1** and 970 for **2**), assigned to the $\mathrm{O_{p\pi}} \rightarrow \mathrm{W_{d\pi}}$ LMCT transition.

Peroxometalates **3** and **4**, previously unknown, show $\nu(\mathrm{W{=}O})_{\mathrm{asym}}$ vibrations at 960 and 950 cm^{-1}, respectively. The band at 840 cm^{-1} in **3** and **4** is attributable to the $\nu(\mathrm{O{-}O})_{\mathrm{asym}}$ vibration, which, however, appears at 854 and 852 cm^{-1}, respectively, in their Raman spectra. The Raman spectra show that the $\nu(\mathrm{W{=}O})_{\mathrm{asym}}$ vibration is found at 953 cm^{-1} for **3** and at 944 cm^{-1} for **4**. The strong IR band at 540 cm^{-1} in both compounds may be attributed to



vibration. In the Raman spectra this vibration appears at 561 cm^{-1} in **3** and 550 cm^{-1} in **4**. UV–vis spectra (Nujol mull) show a single absorption band for both: at 357 nm for **3** and 340 nm for **4**. This band can be attributed to a $\mathrm{O_2^{2-}}\ \pi^* \rightarrow \mathrm{W_{d\pi}}$ LMCT transition.[26] The X-ray powder diffraction patterns of **3** and **4** indicate that they are possibly isostructural.

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Registry No. **1**, 65599-15-7; **2**, 67316-62-5; **3**, 25464-03-3; **4**, 23273-38-3; $\mathrm{Na_2WO_4}$, 13472-45-2.

Supplementary Material Available: Listings of all crystal data and details of the refinement, anisotropic thermal parameters for non-hydrogen atoms, and bond angles and distances for the PPN cation (3 pages); a listing of structure factor amplitudes (38 pages). Ordering information is given on any current masthead page.

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(23) Bhattacharyya, R. G.; Biswas, S. Unpublished results.

(24) Jacobson, S. E.; Mares, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055.

(25) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(26) Djordjevic, C.; Puryear, B. C.; Vuletic, N.; Abelt, C. J.; Sheffield, S. J. *Inorg. Chem.* **1988**, *27*, 2926.

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Synthesis and Structures of (2,9-Dimethyl-1,10-phenanthroline)(acetonitrile)copper(I) Perchlorate and Hexafluorophosphate. A Correlation between Bond Angles and Bond Distances in T- and Y-Shaped Three-Coordinate Copper(I) Complexes

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Coordination number 3 is a rare coordination number in transition-metal complexes, because the metal atom can usually serve as an acceptor to stronger Lewis bases.[1] Such a metal atom is coordinatively unsaturated. The copper(I) in $\mathrm{Na_2[Cu(CN)_3]\cdot 3H_2O}$[2] is a typical example of regular trigonal-planar geometry with the angles of 120°. Several other examples of three-coordination, $\mathrm{[Cu(Me_3PS)Cl]_3}$,[3a] $\mathrm{[Cu(Br)(PPh_3)_2]}$,[3b]$\mathrm{[Cu(SPh)_3]PPh_4}$,[3c]$\mathrm{[Cu(etu)_3]BF_4}$ (etu = ethylenethiourea),[3d] $\mathrm{[Cu(tmtu)_3]BF_4}$[3d] (tmtu = tetramethylthiourea), $\mathrm{[Cu(SPMe_3)_3]ClO_4}$,[3e]$\mathrm{[Cu(tpt)_2Cl]}$[3f] (tpt = tetrahydro-1*H*-pyrimidine-2-thione), $\mathrm{[Cu_2I_2(tmpip)_2]}$[3g] (tmpip = 2,2,6,6-tetramethylpiperidine) and $\mathrm{[Cu(2\text{-}Me\text{-}py)_3]ClO_4}$,[4] have been verified by X-ray studies. In all examples, the geometry approximates an equilateral triangle with the copper atom at the center as expected for sp^2 hybridization. Recently, three-coordinate T-shaped copper(I) complexes in which one of the bond angles around copper(I) is remarkably larger than 120° have been synthesized.[5,6] The most striking feature of this geometry is that the middle Cu–donor atom distance is quite a bit longer than the terminal bond distances. In contrast to the T-shaped geometry, we have synthesized three-coordinate Y-shaped copper(I) complexes $\mathrm{[Cu(dmp)(CH_3CN)]ClO_4}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) and $\mathrm{[Cu(dmp)(CH_3CN)]PF_6}$ in which one of the bond angles about the copper atom is remarkably smaller than 120°. The structure of the Y-shaped complex in this paper has been determined by a single-crystal structure analysis, and the relationship between the bond distance and the bond angle has been discussed.

Table I. Crystallographic Details for **1** and **2**

	1	**2**
formula	$\mathrm{CuClC_{16}H_{15}O_4N_3}$	$\mathrm{CuPF_6C_{16}H_{15}N_3}$
fw	412.3	457.8
space group	$P2_1/c$	$P1$
a, Å	11.9101 (9)	11.305 (4)
b, Å	19.987 (1)	12.479 (5)
c, Å	7.636 (1)	7.669 (4)
α, deg		87.91 (5)
β, deg	108.159 (9)	106.42 (4)
γ, deg		117.69 (3)
Z	4	2
temp, K	296	296
λ, Å	0.710 69 (Mo Kα)	1.541 78 (Cu Kα)
ρ_{cal}, g/cm^3	1.585	1.665
μ, cm^{-1}	14.46	31.29
$F(000)$	840	460
R^a	0.051	0.077
$R_w{}^b$	0.056	0.105

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_c|^2]^{1/2}$.

Experimental Section

$\mathrm{[Cu(dmp)(CH_3CN)]ClO_4}$ (1). A solution of 2,9-dimethyl-1,10-phenanthroline (dmp) (50 μmol, 10.4 mg) and 1,5-cyclooctadiene (1.5 mmol, 0.18 mL) in methanol (5 mL) was added to tetrakis (acetonitrile)copper(I) perchlorate (50 μmol, 16.4 mg) under argon. Then, ca. 1 mL of the solution was sealed in a glass tube and left at −10 °C. After

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(1) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper: New York, 1978; pp 427–428.

(2) Kappenstein, C.; Hugel, R. P. *Inorg. Chem.* **1978**, *17*, 1945.

(3) (a) Tiethof, J. A.; Stalick, J. K.; Meek, D. W. *Inorg. Chem.* **1973**, *12*, 1170. (b) Davis, P. H.; Belford, R. L.; Paul, I. C. *Ibid.* **1973**, *12*, 213. (c) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Ibid.* **1980**, *19*, 2993. (d) Weininger, M. S.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1140. (e) Eller, P. G.; Corfield, P. W. R. *Ibid.* **1971**, 105. (f) Bret, J.-M.; Castan, P.; Dubourg, A.; Roques, R. *J. Chem. Soc., Dalton Trans.* **1983**, 301. (g) Healy, P. C.; Pakawatchai, C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Ibid.* **1983**, 1905.

(4) Lewin, A. H.; Michl, R. J.; Ganis, P.; Lepore, V. *J. Chem. Soc., Chem. Commun.* **1972**, 661.

(5) (a) Karlin, K. D.; Gultneh, Y.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1982**, *104*, 5240. (b) Nelson, S. M.; Esho, F.; Lavery, A.; Drew, M. G. B. *Ibid.* **1983**, *105*, 5693. (c) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250. (d) Blackburn, N. J.; Karlin, K. D.; Concanon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 939.

(6) Gagnê, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917. Barrow, M.; Burgi, H. B.; Johnson, D. K.; Venanzi, L. M. *Ibid.* **1976**, *98*, 2356. Sorrell, T. M.; Malachowki, M. R. *Inorg. Chem.* **1983**, *22*, 1883. Dagdigian, J. V.; McKee, V. Reed; C. A. *Inorg. Chem.* **1982**, *21*, 1332.

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