$Ru_2(O_2CC_3H_7)_4Cl$. For the latter compound, as we noted earlier, the conclusion drawn from the magnetic data was that "in spite of its polymeric structure, [it] is a complex in which the $Ru_2(but)_4^+$ units can be treated as isolated $S = {}^3/_2$ systems." A slight temperature dependence of the magnetic moments, as can be seen in Figure 4, is expected for this type of system, as explained in ref 1a,c, because of zero-field splitting. The contrast between the two temperature dependencies in Figure 4 is obvious and of such a nature as to imply that there is in $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ an antiferromagnetic interaction between the $[Ru_2(O_2CC_2H_5)_4]^+$ units. From the structure, which has been described above, we would find it difficult to attribute this to *inter*chain interactions since the chains are well separated by intervening BF_4^- ions. We therefore find it reasonable to conclude that what is occurring is *intra*chain coupling; that is, we have here an ODAFM system.

It should be recalled that in the previous paper in this series we compared the $[Ru_2(chp)_4(pyrazine)Ru_2(chp)_4]^{2+}$ ion with $[Ru_2(chp)_4(pyridine)]^+$, and from the close similarity of the magnetic behavior of the two species, it was concluded that no significant magnetic coupling across the pyrazine bridge occurs in the first cation. To account for the different result in the present case, we must ask what structural and/or chemical differences exist. The bridging ligands are different but similar. Phenazine (phz) is simply pyrazine with benzene rings fused to both sides. However, this could conceivably alter the shapes and energies of the π and π^* orbitals enough to change significantly the strength of interaction with the Ru_2 units. Another difference concerning the bridging is that the Ru–N distances are appreciably different, being 2.275 (5) Å for pyrazine and 2.44 Å for phenazine. The sense of this difference is such that, by itself, it would tend to lessen the coupling in the phenazine compound, contrary to observation.

Finally, however, we must recognize that the $Ru_2(chp)_4^+$ and $Ru_2(O_2CC_2H_5)_4^+$ units may also have significant differences, despite their grossly similar nature. It is possible that molecular orbital calculations could show that the differences are more enabling in one case than in the other with respect to interaction through the bridges. However, it might be more direct and convincing to carry out an experimental study in which we reverse the pairings of Ru_2 units and bridging ligand; that is, we prepare and study $[Ru_2(chp)_4(phz)Ru_2(chp)_4](BF_4)_2$ and $[Ru_2(O_2CC_2H_5)(pyz)]BF_4$. We have, in fact, already initiated such a study.

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Supplementary Material Available: Full tables of crystal data, anisotropic thermal parameters, bond length and angle data, and variable-temperature magnetic susceptibility data (8 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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A Pentavalent W_4S_4 Cuboidal Cluster

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The W(V) complex $[W(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)(\mu_3\text{-}S)]_4$ was prepared and characterized. The compound, in solution, is engaged in an associative equilibrium from two dimers, with $K_{eq} = 1600\ M^{-1}$. When this compound is in solution with $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)(\mu_3\text{-}S)]_4$, the mixed-metal cluster $[W_2Mo_2(NC_6H_4CH_3)_4(S_2P(OC_2H_5)_2)_4(\mu_3\text{-}S)_4]$ is formed. The crystal structure of $[W(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)(\mu_3\text{-}S)]_4$ was determined: a = 14.650 (3) Å, b = 19.133 (4) Å, c = 13.073 (3) Å, α = 101.82 (2)°, β = 104.61 (2)°, γ = 75.92 (2)°; triclinic; $P\bar{1}$; Z = 2. The crystallography showed a distorted W_4S_4 cubic arrangement.

Introduction

Sulfidomolybdenum(V) dimers of the general form $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^n$ (for abbreviations, see footnote 1) have been shown to display a versatile sulfur-centered reactivity at the bridge sulfur positions. Both an anionic (n = −1) and a radical (n = 0) form have been demonstrated, and observed reactions therewith include nucleophilic and radical chemistry, with strong parallels to that of organic thiols, thiolates, and thiyls.[2-5]

Much of the interest in this system and in many other metallosulfur complexes which display sulfur-centered reactivity derives from the roles of metal sulfides in catalytic processes, both biological and industrial. This is especially true for molybdenum, since molybdenum–sulfur compounds comprise active sites in several key enzymes[6,7] and in hydrotreating catalysts.[8] Of particular interest in the area of catalysis is the possible involvement of the sulfur sites in the catalytic mechanism, in addition to catalytic activity of the metal sites therein. Various notions for catalytic mechanisms have considered a covalent role for sulfur,[7-10] although for the most part exact mechanistic details remain unknown.

While sulfur-centered reactivity of several molybdenum–sulfur complexes has been very well documented,[2-5,9-11] considerably less is known for tungsten–sulfur complexes.[12] The interest here is decidedly more than that of a simple parallel, since tungsten compounds are also used in some hydrodesulfurization[8] systems, and tungsten analogues of molybdenum enzymes are known,[13] although in many cases these are inactive. Because of this, studies of sulfur-centered reactivity in sulfidotungsten complexes are of interest per se. There is also the inherent interest in the comparison of sulfur reactivity between Mo–S and W–S complexes, especially in cases where isostructural complexes of both metals are available. For these reasons, synthesis of tungsten analogues, $[W_2(NAr)_2$-

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(1) Abbreviations used in this paper: Me, methyl; Et, ethyl; Bu, *n*-butyl; To, *p*-tolyl; Ar, aryl.
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(12) For example: Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419. Shaver, A.; Hartgerink, J. *Can. J. Chem.* **1987**, *65*, 1190. Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Polyhedron* **1988**, *7*, 471.
(13) Hales, B. J.; Case, E. E. *J. Biol. Chem.* **1987**, *262*, 16205 and references therein. Tungsten enzymes per se are also known (Cramer, S. P.; Liu, C.-L.; Mortenson, L. E.; Liu, S.-M.; Yamamoto, I.; Ljungdahl, L. G. *J. Inorg. Biochem.* **1985**, *23*, 119. White, H.; Strobl, G.; Feicht, R.; Simon, H. *Eur. J. Biochem.* **1989**, *184*, 89. Mukund, S.; Adams, M. W. W. *J. Biol. Chem.* **1990**, *265*, 11508), but it is not clear as to whether these are sulfidotungsten systems.

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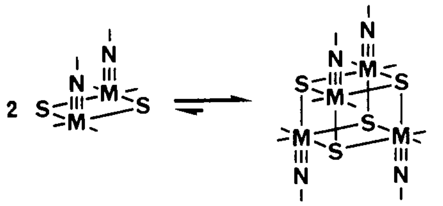
$(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^n$, of the aforementioned dimers became of interest.

The starting material for the molybdenum dimers is the cuboidal tetramer $[Mo(NAr)(S_2P(OEt)_2)(\mu_3\text{-}S)]_4$, which bisects to form dimers in solution. The very favorable solution equilibrium for this compound, eq 1, had been previously demonstrated.[14]



(1)

(Dithiophosphate and arylimido groups are absent in eq 1 for clarity.) Addition of carboxylate ions to solutions of the tetramer stabilizes the dimer by bridging the two metals, and thus provides the dimer anion $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^-$.[15] In order to investigate the chemistry of tungsten analogues, synthesis of the tungsten cuboidal tetramer, $[W(NAr)(S_2P(OEt)_2)(\mu_3\text{-}S)]_4$, was necessary. This compound is an example of a W_4S_4 cuboidal system containing pentavalent W. The W_4S_4 cuboidal class itself is not well-known: A $W_4S_4^{6+}$ complex has been reported which contains mixed, lower valent W(III)/W(IV).[16,17] The shortage of W_4S_4 examples is curious in light of the existence of several Mo_4S_4 types[18-24] and in light of the preponderance of heterometal $Mo_xM_{4-x}S_4$ and even $W_xM_{4-x}S_4$ types ($x = 1$–3).[24-34] The present paper describes the synthesis and characterization of $[W(NTo)(S_2P(OEt)_2)(\mu_3\text{-}S)]_4$, including crystallographic results.

Experimental Section

Reactions which were performed under N_2 were conducted on a vacuum line using solvents which had been dried, vacuum-transferred, and subsequently stored under N_2. $(EtO)_2PS_2H$ was vacuum-distilled. ToN_3 was prepared by the standard reaction of ToN_2^+ (from diazotization of $ToNH_2$) with N_3^- and was stored as a solution in c-C_6H_{12}. $[Mo(NTo)(S_2P(OEt)_2)S]_4$ was prepared as previously described,[15] but with the modification that the reaction was conducted in air, using freshly dried THF. Other reagents were used as commercially available.

Table I. Crystallographic Data for $[W(NTo)(S_2P(OEt)_2)S]_4$

$W_4C_{44}H_{68}N_4O_8P_4S_{12}$	fw = 2025.1
$a = 14.650$ (3) Å	space group $P\bar{1}$ (No. 2)
$b = 19.133$ (4) Å	$T = 23$ °C
$c = 13.073$ (3) Å	$\lambda = 0.709\,30$ Å
$\alpha = 101.82$ (2)°	$\rho_{calcd} = 1.98$ g cm^{-3}
$\beta = 104.61$ (2)°	$\mu = 73.9$ cm^{-1}
$\gamma = 75.92$ (2)°	transm coeff = 0.635–0.999
$V = 3398.8$ Å^3	$R^a = 0.043$
$Z = 2$	$R_w{}^b = 0.048$

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

$^{31}P\{^1H\}$, $^{15}N\{^1H\}$, and ^1H NMR spectra were obtained in $CDCl_3$ on a Varian XL-300 spectrometer at 121, 30, and 300 MHz and are reported as downfield shifts from external H_3PO_4, external $MeNO_2$, and internal Me_4Si. The infrared spectrum was obtained as a KBr pellet on a Perkin-Elmer 283 spectrophotometer.

Equilibrium constants for the associative reaction, eq 1, were determined by visible spectroscopy in spectral grade $CHCl_3$ using a Perkin-Elmer 330 spectrophotometer. Samples were thermally equilibrated at 28 °C in a constant-temperature bath prior to scanning a narrow range in the vicinity of λ_{max}. Equilibrium constants (K_{eq}) and extinction coefficients (ϵ) of the tetramer at λ_{max} were calculated using eq 2, wherein

$$F/A = 0.5(K_{eq}\epsilon)^{-1/2}A^{-1/2} + 1/\epsilon \qquad (2)$$

F = formal concentration of the tetramer and A = total absorbance. Equation 2 was derived by assuming that dimer absorbance was insignificant compared to total absorbance at the concentrations utilized. Data from each series of eight different concentrations were plotted as F/A vs $A^{-1/2}$. Least-squares methods provided the intercept and slope, from which ϵ and then K_{eq} were calculated. Three separate series were conducted for each tetramer to provide a measure of precision; standard deviations cited herein are those from the three different series.

$[W(NTo)(S_2P(OEt)_2)S]_4$. Under N_2, a slurry of $W(CO)_6$ (9.50 g, 0.0270 mol) in THF (~75 mL) was cooled in a dry ice/alcohol bath and then treated with Br_2 (2.09 mL, 0.0406 mol). Following addition, the ice bath was removed and the mixture was stirred for 1 h while warming to room temperature. As the mixture warmed, vigorous gas evolution occurred, and the color changed from red-brown to black. After ambient temperature was attained, volatiles were removed under vacuum. THF (~75 mL) was added, followed after several minutes by ToN_3 (11.4 mL of 2.02 M in c-C_6H_{12}, 0.023 mol). The slurry was stirred for 18 h, becoming dark brown in color. A premixed salt solution of $(EtO)_2PS_2H$ (4.10 mL, 0.026 mol) and Et_2NH (2.79 mL, 0.027 mol) in THF (~20 mL) was added to the pot. After being stirred for 24 h, the blue-green mixture was treated with $(Bu_3Sn)_2S$ (13.2 mL, 0.026 mol), followed again by 24 h of stirring, to give a red-brown slurry. The volatiles were then removed under vacuum, the system was opened to the air, and benzene (50 mL) was added. The mixture was stirred briefly and then filtered. The filtrate was rotavapped to an oil and then treated with acetonitrile (20 mL). The crude product was filtered off and washed (MeCN). Recrystallization was performed by dissolving in minimal dichloromethane and treating the resulting solution dropwise with methanol. Filtration, washing (MeOH), and vacuum-drying gave ruby red crystals (1.77 g, 13%). ^{31}P NMR (ppm): 124.3. ^{15}N NMR (ppm): 9.92. ^1H NMR (ppm): 6.34 d, To meta H; 6.08 d, To ortho H; 4.69 m, 3.71 m, $POCH_2$; 1.99 s, To CH_3; 1.60 t, 0.81 t, $POCCH_3$. IR (cm^{-1}): 1492 m, 1353 s, 1161 m, 1029 s, 1009 vs, 956 vs, 943 vs, 813 m, 765 s, 647 m, 537 m.

Crystallography. A ruby red block crystal from $C_6H_5Cl/C_{12}H_{26}$ measuring 0.19 × 0.37 × 0.48 mm was used for data collection. Crystal data and experimental details are given in Table I. Cell constants and an orientation matrix were obtained from least-squares refinement, using setting angles of 24 reflections in the range $12° < \theta < 14°$. There were no systematic absences. Data were collected on an Enraf-Nonius CAD4 automated diffractometer with Mo Kα radiation (graphite monochromator), using the ω–2θ scan technique over the range $\pm h,+k,\pm l$. Three representative reflections were measured every 60 min; their intensities remained constant within experimental error. An absorption correction was applied using a series of ψ scans; a secondary extinction correction (final coefficient 1.6 (4) × 10^{-7}) was employed. Computations utilized the Enraf-Nonius VAX/SDP package.[36] A total of 8633 reflections were

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Table II. Selected Positional Parameters

atom	x	y	z	B_{eq} (Å^2)^a
W(1)	0.85664 (5)	0.13615 (3)	0.72113 (5)	4.05 (2)
W(2)	0.67306 (5)	0.19677 (3)	0.59688 (5)	4.40 (2)
W(3)	0.81599 (5)	0.33714 (3)	0.73445 (5)	4.19 (2)
W(4)	0.72395 (5)	0.29440 (3)	0.87467 (5)	4.24 (2)
S(1)	0.8276 (3)	0.2114 (2)	0.5894 (3)	4.5 (1)
S(2)	0.7043 (3)	0.1606 (2)	0.7672 (3)	4.4 (1)
S(3)	0.6510 (3)	0.3338 (2)	0.7069 (3)	4.7 (1)
S(4)	0.8882 (3)	0.2581 (2)	0.8637 (3)	4.12 (9)
S(5)	1.0362 (3)	0.1265 (3)	0.7427 (4)	5.7 (1)
S(6)	0.9252 (3)	0.0824 (2)	0.8934 (4)	5.4 (1)
S(7)	0.6045 (4)	0.2724 (3)	0.4466 (4)	6.5 (1)
S(8)	0.4934 (3)	0.2281 (3)	0.5981 (4)	6.2 (1)
S(9)	0.9826 (3)	0.3224 (2)	0.6945 (4)	5.5 (1)
S(10)	0.7737 (3)	0.3882 (2)	0.5596 (4)	6.0 (1)
S(11)	0.7674 (3)	0.2233 (3)	1.0287 (3)	5.7 (1)
S(12)	0.5585 (3)	0.2859 (3)	0.8967 (4)	6.6 (1)
P(1)	1.0551 (4)	0.0777 (3)	0.8688 (4)	6.3 (1)
P(2)	0.4758 (4)	0.2642 (3)	0.4612 (4)	6.7 (1)
P(3)	0.9144 (3	0.3860 (3)	0.5839 (4)	5.9 (1)
P(4)	0.6275 (4)	0.2351 (3)	1.0217 (4)	6.4 (1)
O(1)	1.1223 (9)	0.1185 (7)	0.969 (1)	8.2 (4)
O(2)	1.117 (1)	−0.0003 (7)	0.860 (1)	9.2 (5)
O(3)	0.399 (1)	0.3358 (8)	0.449 (1)	9.4 (5)
O(4)	0.4264 (9)	0.2112 (7)	0.369 (1)	9.0 (4)
O(5)	0.9515 (9)	0.3644 (7)	0.4775 (9)	8.1 (4)
O(6)	0.9408 (9)	0.4631 (6)	0.626 (1)	7.8 (4)
O(7)	0.594 (1)	0.1616 (7)	1.015 (1)	9.0 (4)
O(8)	0.5951 (9)	0.2748 (8)	1.129 (1)	10.2 (4)
N(1)	0.8520 (9)	0.0515 (7)	0.648 (1)	5.3 (3)
N(2)	0.6609 (8)	0.1198 (6)	0.5128 (9)	5.5 (3)
N(3)	0.8187 (8)	0.4214 (6)	0.807 (1)	5.0 (3)
N(4)	0.7240 (9)	0.3749 (7)	0.960 (1)	5.4 (3)
C(1)	0.840 (1)	−0.0198 (7)	0.608 (1)	4.6 (4)
C(8)	0.647 (1)	0.0573 (7)	0.433 (1)	4.5 (4)
C(15)	0.815(1)	0.4950 (8)	0.855 (1)	5.3 (4)
C(22)	0.726 (1)	0.4366 (7)	1.038 (1)	4.4 (4)

^{a} $B_{eq} = (4/3)[\alpha^2\beta_{11} + b^2\beta_{22} + ... + ab(\cos\gamma)\beta_{12} + ...]$.

Table III. Selected Distances and Bond Lengths (Å)

W(1)–W(2)	2.8751 (8)	W(4)–S(2)	2.701 (4)
W(3)–W(4)	2.871 (1)	W(1)–S(5)	2.539 (5)
W(1)–S(1)	2.359 (4)	W(1)–S(6)	2.540 (5)
W(1)–S(2)	2.370 (4)	W(2)–S(7)	2.534 (6)
W(2)–S(1)	2.375 (5)	W(2)–S(8)	2.557 (5)
W(2)–S(2)	2.369 (4)	W(3)–S(9)	2.561 (5)
W(3)–S(3)	2.366 (4)	W(3)–S(10)	2.543 (5)
W(3)–S(4)	2.372 (4)	W(4)–S(11)	2.523 (5)
W(4)–S(3)	2.372 (4)	W(4)–S(12)	2.558 (5)
W(4)–S(4)	2.370 (5)	W(1)–N(1)	1.72 (1)
W(1)–S(4)	2.727 (4)	W(2)–N(2)	1.66 (1)
W(2)–S(3)	2.707 (4)	W(3)–N(3)	1.70 (1)
W(3)–S(1)	2.741 (4)	W(4)–N(4)	1.71 (1)
W(1)···W(3)	3.7196 (9)	W(2)···W(3)	3.6999 (9)
W(1)···W(4)	3.6866 (8)	W(3)···W(4)	3.7102 (9)

collected, of which 7689 were unique; 5797 reflections having intensities greater than 3.0 times their standard deviations were used in the final cycles of refinement. $R_{int}(F)$ for equivalent reflections was 0.016.

The structure was solved using the MULTAN 80 package.[36] Hydrogen atom locations were calculated, and their thermal parameters were assigned as $1.3B_{eq}$ of the bonded atoms; hydrogen atom parameters were not refined. The structure was refined in full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F) + (0.005F)^2 + 1.0]^{-1}$. Scattering factors and anomalous dispersion effects were taken from ref 37.

Selected crystallographic results are given in Tables II–IV. The structure is shown in Figures 1 and 2.

Results

The one-pot, one-step synthesis of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ employs $Mo(CO)_6$, ToN_3, $(EtO)_2PS_2H$, and sulfur in nonstoichiometric ratios;[15] yields are routinely 35–40%, which is considered respectable in light of the complexity of the reaction which carries the metal through five oxidation states. Attempts to

Table IV. Selected Bond Angles (deg)

S(1)–W(1)–S(2)	102.0 (1)	S(1)–W(1)–N(1)	103.3 (5)
S(1)–W(2)–S(2)	101.6 (1)	S(2)–W(1)–N(1)	97.7 (5)
S(3)–W(3)–S(4)	101.9 (2)	S(1)–W(2)–N(2)	102.8 (5)
S(3)–W(4)–S(4)	101.8 (1)	S(2)–W(2)–N(2)	103.2 (5)
S(1)–W(1)–S(4)	85.1 (1)	S(3)–W(3)–N(3)	101.1 (4)
S(2)–W(1)–S(4)	85.8 (1)	S(4)–W(3)–N(3)	103.3 (4)
S(1)–W(2)–S(3)	86.2 (1)	S(3)–W(4)–N(4)	102.3 (4)
S(2)–W(2)–S(3)	84.5 (1)	S(4)–W(4)–N(4)	101.4 (5)
S(1)–W(3)–S(3)	85.6 (1)	S(5)–W(1)–N(1)	96.4 (4)
S(1)–W(3)–S(4)	84.6 (1)	S(6)–W(1)–N(1)	91.5 (4)
S(2)–W(4)–S(3)	84.6 (1)	S(7)–W(2)–N(2)	91.7 (4)
S(2)–W(4)–S(4)	86.4 (1)	S(8)–W(2)–N(2)	91.4 (4)
W(1)–S(1)–W(2)	74.8 (1)	S(9)–W(3)–N(3)	93.3 (5)
W(1)–S(2)–W(2)	74.7 (1)	S(10)–W(3)–N(3)	91.5 (5)
W(3)–S(3)–W(4)	74.6 (2)	S(11)–W(4)–N(4)	91.6 (5)
W(3)–S(4)–W(4)	74.5 (2)	S(12)–W(4)–N(4)	92.8 (5)
S(5)–W(1)–S(6)	78.0 (2)	W(1)–N(1)–C(1)	167 (1)
S(7)–W(2)–S(8)	78.0 (2)	W(2)–N(2)–C(8)	175 (1)
S(9)–W(3)–S(10)	78.2 (2)	W(3)–N(3)–C(15)	173 (1)
S(11)–W(4)–S(12)	77.8 (2)	W(4)–N(4)–C(22)	174 (1)

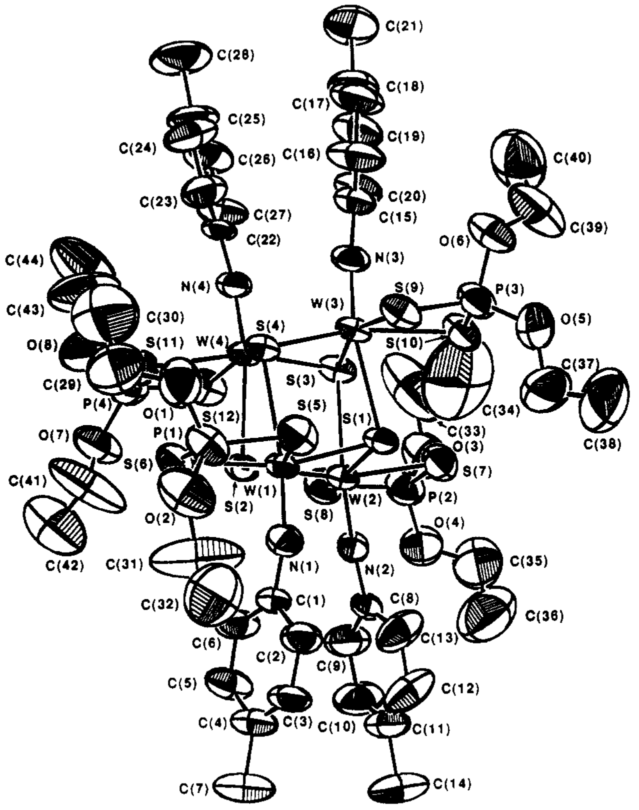

Figure 1. Full ORTEP view of $[W(NTo)(S_2P(OEt)_2)S]_4$. Thermal ellipsoids are at the 50% probability level.

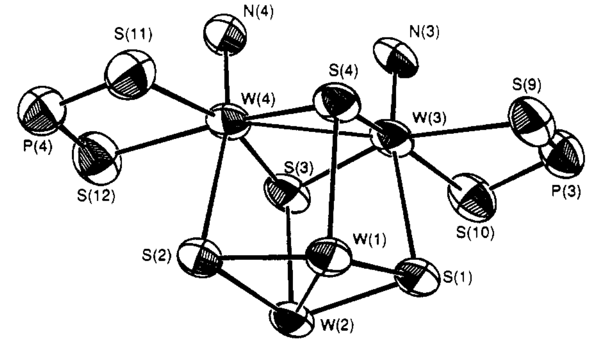

Figure 2. Partial structure of $[W(NTo)(S_2P(OEt)_2)S]_4$. The distorted W_4S_4 core is shown, as also is the coordination geometry of two of the four tungsten atoms.

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(37) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B, 2.3.1.

synthesize $[W(NTo)(S_2P(OEt)_2)S]_4$ via this method using $W(CO)_6$ failed, generally giving little reaction of the tungsten reagent. An alternative method was developed with multiple steps but without isolation of intermediates. In this method, $W(CO)_6$ is first oxidized by 1.5 equiv of Br_2. Two further oxidation equivalents are provied by ToN_3, which also serves as the source of the imido function. Ligand exchange with the $(EtO)_2PS_2^-$ salt follows. Finally, sulfide is provided by $(Bu_3Sn)_2S$. Use of $(Me_3Si)_2S$ as the sulfide reagent[38,39] gave a similar yield, but $(Bu_3Sn)_2S$ was preferred for handling and economic reasons. The overall synthetic approach was somewhat simplistic and no attempt was made to identify the presumed bromotungsten intermediates, but the desired compound $[W(NTo)(S_2P(OEt)_2)S]_4$ was thereby obtained in small yields (<20%).

The IR spectrum of the $[W(NTo)(S_2P(OEt)_2)S]_4$ product is nearly identical to that of the Mo_4S_4 derivative, with most of the significant bands within ± 5 cm^{-1} for the two compounds. An obvious exception is the peak at 1327 cm^{-1} in the latter, which is shifted to 1353 cm^{-1} in the former. This is an imido-related band,[40] and the shift probably reflects a difference in π contributions within the MNC linkage.

NMR spectra are consistent with the $[W(NTo)(S_2P(OEt)_2)S]_4$ formulation in solution. The ^1H NMR spectrum is similar to that of $[Mo(NTo)(S_2P(OEt)_2)S]_4$, except that the tolylimido ortho proton resonance is further upfield by 0.18 ppm. The ^{31}P and ^{15}N NMR spectra each show a single peak, at 124.3 and 9.92 ppm, respectively; these values compare to 111.9 and 40.8 ppm[41] for $[Mo(NTo)(S_2P(OEt)_2)S]_4$.

While the solid-phase and dominant solution-phase forms of $[W(NTo)(S_2P(OEt)_2)S]_4$ were clearly tetrameric by analogy to the known compound $[Mo(NTo)(S_2P(OEt)_2)S]_4$, visible spectra were consistent with the associative equilibrium of eq 1, and a measurement of the equilibrium was obtained in $CHCl_3$. The equilibrium was measured for both W_4S_4 and Mo_4S_4 derivatives at 28 °C for direct comparison. For $[W(NTo)(S_2P(OEt)_2)S]_4$, the results of measurements at $\lambda_{max} = 579$ nm gave an extinction coefficient of 4400 (400) M^{-1} cm^{-1} and a K_{eq} of 1600 (100) M^{-1}. For $[Mo(NTo)(S_2P(OEt)_2)S]_4$, $\lambda_{max} = 586$ nm, $\epsilon = 5020$ (40) M^{-1} cm^{-1}, and $K_{eq} = 8500$ (200) M^{-1}.[42] The spectroscopic parameters are reasonably similar, but the equilibrium constants derived therefrom differ significantly.

The existence of the separate equilibria for each of the M_4S_4 complexes suggested that a heterometal cluster should be obtained in mixtures of the two. Such was indeed realized. The ^{31}P NMR spectrum of a $CDCl_3$ solution of equal amounts of $[W(NTo)(S_2P(OEt)_2)S]_4$ and $[Mo(NTo)(S_2P(OEt)_2)S]_4$ clearly showed the presence of $[W_2Mo_2(NTo)_4(S_2P(OEt)_2)_4S_4]$ in equilibrium with the homometal reagents: ^{31}P NMR resonances of the $W_2Mo_2S_4$ cuboidal cluster (125.2, 111.0 ppm) were clearly removed from the resonances for the homometal complexes. The distribution of the three clusters showed a slight preference for the heterometal cluster, as indicated by a $[W_2Mo_2S_4]/([W_4S_4] + [Mo_4S_4])$ ratio of ~ 1.2. The ^1H NMR spectrum supported the presence of a mixture of clusters but was poorly resolved due to overlap.

The crystal structure of $[W(NTo)(S_2P(OEt)_2)S]_4$ is shown in Figures 1 and 2, and selected metrical results are given in Tables III and IV. The W_4S_4 core forms a distinctly distorted cube, elongated in one direction. Two opposite faces, W(1)–S(1)–W(2)–S(2) and W(3)–S(3)–W(4)–S(4), separated by the long dimension, are rhombic in geometry, with WSW angles averaging 74.6° (range 74.5 (2)–74.8 (1)°) and with SWS angles averaging 101.8° (range 101.6 (1)–120.0 (1)°). The other four sides are nearly rectangular, with WSW angles averaging 93.2° (range 92.4 (1)–93.9 (1)°) and with SWS angles averaging 85.4° (range 84.5 (1)–86.4 (1)°). Within the rhombic faces, the eight W–S bond lengths average 2.369 Å (range 2.359 (4)–2.375 (5) Å). Four long W–S bonds separate these faces and average 2.719 Å (range 2.701 (4)–2.741 (4) Å). W–W diagonals follow this trend: W–W distances in the four rectangular faces are quite long, averaging 3.704 Å (range 3.6866 (8)–3.7196 (9) Å), indicating no direct interaction. Within the two rhombic faces, however, W–W distances are substantially shorter, averaging 2.873 Å (2.8751 (8), 2.871 (1) Å). These latter distances are consistent with a single bond, although they are slightly longer than the range 2.795 (2)–2.862 (1) Å observed for dimeric, pentavalent *syn*-$W_2(\mu\text{-}S)_2$ complexes.[43-51] In the mixed-valent (III/IV) cluster $[W_4S_4(S_2P(OEt)_2)_6]$, W–W bond lengths average 2.746 and 2.882 Å (total range 2.742 (2)–2.896 (1) Å).[16]

Table V. Comparative Bond Lengths and Angles for $[M(NTo)(S_2P(OEt)_2)S]_4$[a]

	M = W	M = Mo[b]
Bond Lengths (Å)		
M–M	2.873 (1)	2.862 (1)
M–S(bridge), short	2.369 (4)	2.366 (4)
M–S(bridge), long	2.719 (4)	2.704 (4)
M–N	1.70 (1)	1.72 (1)
M–S(dithiophosphate)	2.544 (5)	2.552 (4)
Angles (deg)		
M–S–M (rhombic faces)	74.6 (2)	74.4 (1)
S–M–S (rhombic faces)	101.8 (1)	102.0 (1)
M–S–M (rectangular faces)	93.2 (1)	93.1 (1)
S–M–S (rectangular faces)	85.4 (1)	85.4 (1)
M–N–C	172 (1)	171 (1)
MS_2 dihedral angle	148.2 (2)	148

[a] Numbers in parentheses are averages of the standard deviations of the individual values. [b] From ref 18.

The rhombic faces are notably nonplanar. This is illustrated by WS_2 dihedral angles, which average 148.2° (148.4 (2), 148.1 (2)°).

Formally, the W_4S_4 core can be considered to be composed of two W_2S_2 dimers, W(1)–S(1)–W(2)–S(2) and W(3)–S(3)–W(4)–S(4), which constitute the rhombic faces. The dimers are held together by W–S bonds which are considerably longer and weaker than W–S bonds within the dimers. This visualization reflects the solution-phase equilibrium, eq 1.

Bonds external to the W_4S_4 core show no extraordinary features. W–N bond lengths and W–N–C angles are statistically within the ranges of values reported for mono- and dinuclear (arylimido)tungsten(V) complexes.[52-54] W–S(dithiophosphate) bond lengths are somewhat longer than those found in $[W_2S_4(S_2P(OEt)_2)_2]$; although this is a very restricted comparison for W(V), three separate crystallographic determinations have been reported for that one compound.[43,44] The W–S(dithiophosphate) bond lengths in $[W(NTo)(S_2P(OEt)_2)S]_4$ average 2.544 Å (range 2.523 (5)–2.561 (5) Å); this compares to averages of 2.456, 2.472, and

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2.482 Å (total range 2.430 (9)–2.498 (5) Å) for $[W_2S_4(S_2P(OEt)_2)_2]$. In lower valent $[W_4S_4(S_2P(OEt)_2)_6]$, W–S(dithiophosphate) bond lengths average 2.548 Å (range 2.542 (6)–2.560 (6) Å) for the bidentate ligand.[16]

Discussion

$[W(NTo)(S_2P(OEt)_2)S]_4$ has shown modest differences from $[Mo(NTo)(S_2P(OEt)_2)S]_4$, although the associative equilibrium of eq 1 is notably less favored for the former. Spectroscopic evidence (IR and NMR) suggests differences in σ and π interactions with the organic coligands, although a fuller evaluation of these would require examination of more derivatives. Structurally the two compounds are very similar, as demonstrated by the comparison in Table V. There are only two differences suggested by that comparison: W–W bonds are longer than Mo–Mo bonds, and the long M–S bonds are perhaps longer for W than for Mo. Interestingly, direct W vs Mo comparisons of structural results for analogous *syn*-$M_2(\mu\text{-}S)_2$ complexes of the pentavalent metals have previously revealed few differences, even in M–M bond lengths.[43,45-47,50]

Comparisons between pentavalent $[W(NTo)(S_2P(OEt)_2)S]_4$ and mixed-valent (III/IV) $[W_4S_4(S_2P(OEt)_2)_6]$ are somewhat limited, due in part to their different symmetries. The latter is distorted trigonally from a cube and can be idealized to C_{3v} symmetry, giving a $W_3W'S_3S'$ arrangement.[55] The elongation in $[W(NTo)(S_2P(OEt)_2)S]_4$ gives idealized D_{2d} symmetry and retains equivalence of all metal positions. The two compounds also differ substantially in cluster metal electron count,[24] giving different numbers of W–W bonds.

The mixed-metal cluster $[W_2Mo_2(NTo)_4(S_2P(OEt)_2)_4S_4]$, observed in solution, represents an example of a W/Mo cuboidal complex constructed from dimer fragments. Two forms of a mixed-metal, Mo_3WS_4, compound, $[Mo_3WS_4(S_2PEt_2)_6]$, have been reported; these were obtained from the reaction of a Mo_3 trimer and a W monomer.[30] The use of two different metal dimers and the use of the trimer/monomer combination have proven useful for other mixed-metal cuboidal complexes.[25,30,31,56] One form of $[Mo_3WS_4(S_2PEt_2)_6]$ was also crystallographically characterized, and the structure is, in fact, analogous (except for the phosphinate/phosphate difference) to the above-cited W_4S_4 derivative, $[W_4S_4(S_2P(OEt)_2)_6]$.

Use of $[W(NTo)(S_2P(OEt)_2)S]_4$ for generating sulfur-reactive dimers of the type $[W_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^-$ has been undertaken. Interestingly, despite the similarities in the cuboidal W_4S_4 and Mo_4S_4 precursors, notable differences have been realized between the sulfur-based chemistries of the W_2S_2 and Mo_2S_2 dimers, particularly in the chemistries of $M_2(\mu\text{-}SH)$ types.[15] This work is in progress.

Acknowledgment. This work was supported by a research award from the National Science Foundation.

Supplementary Material Available: Tables of full crystallographic parameters, positional parameters of all atoms, general displacement parameters, bond lengths, bond angles, and least-squares WS_2 planes (19 pages); a table of structure factors (28 pages). Ordering information is given on any current masthead page.

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Reactivity of Complexes with Weak Metal–Metal Bonds. Reactions of Lewis Acids with $[AuIr(CO)Cl(\mu\text{-}Ph_2PCH_2PPh_2)_2](PF_6)$

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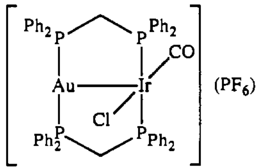
The dinuclear complex $[AuIr(CO)Cl(\mu\text{-}dpm)_2](PF_6)$ (**1**; dpm is bis(diphenylphosphino)methane) is unreactive in dichloromethane solution toward substances (trifluoroacetic acid, hydrogen chloride, sulfur dioxide, dihydrogen, tetracyanoethylene) that are known to bind to $Ir(CO)Cl(PPh_3)_2$. A weak adduct is formed with boron trifluoride. Both **1** and $[AuIr(CNMe)_2(\mu\text{-}dpm)_2](PF_6)_2$ react with mercury(II) chloride in a two-step process. At low temperature an unstable intermediate with the $Au(\mu\text{-}dpm)_2Ir$ core intact is formed. This is formulated as an A-frame with a $HgCl_2$ moiety bonded to the AuIr unit. On warming, one of the bridging dpm units opens and $Cl_2Hg(\mu\text{-}Cl)_2HgIr(CO)Cl(dpm)(\mu\text{-}dpmAuCl)$ is formed. Ivory parallelepipeds of this form in the monoclinic space group $P2_1/c$ with a = 10.594 (7) Å, b = 25.12 (2) Å, c = 21.397 (13) Å, β = 91.04 (5)° at 130 K with Z = 4. Refinement of 3974 reflections and 365 parameters yielded R = 0.067 and R_w = 0.061. The structure contains four metal centers each with a different coordination number, 2 for gold, 3 and 4 for mercury, and 6 for iridium.

Introduction

The nature of the metal–metal bonding in dinuclear d^8–d^8 and d^{10}–d^{10} dimers has led to considerable understanding of their characteristic electronic absorption and emission spectra.[1-4] Some aspects of their chemical reactivity have been probed, particularly the photoinduced oxidative addition chemistry of $[Pt_2(P_2O_5H_2)_4]^{4-}$. We have recently explored the structural and spectroscopic features of heterodinuclear species involving one d^{10} metal center and one d^8 metal center.[5,6] One of these, $[AuIr(CO)Cl(\mu\text{-}dpm)_2](PF_6)$ (**1**; dpm is bis(diphenylphosphino)methane), contains a planar Vaska-type $Ir(CO)Cl(PR_3)_2$ unit that is capped by a linear P–Au–P portion. The Au–Ir distance is 2.986 (1) Å.[5] This is significantly longer than simple Ir–Au single bonds where the corresponding distances fall in the 2.59–2.81-Å range.[6-10]



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