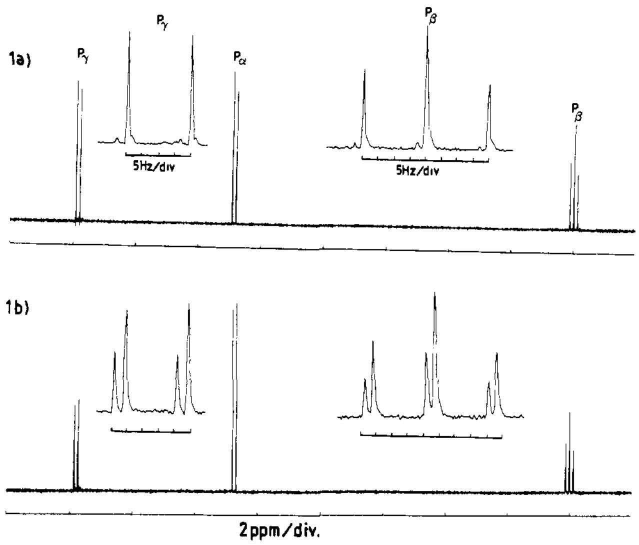

Figure 1. ^{31}P NMR spectrum (162 MHz) of (a) adenosine 5′-[β,γ-^{18}O]triphosphate with expansions of P_β and P_γ resonances and (b) adenosine 5′-[β,γ-^{18}O]triphosphate mixed with authentic ATP (ca. 2:1), in 0.1 M Tris buffer, pH 9.5, containing D_2O (50%) and ethylenediaminetetraacetic acid (10 mM). ^{31}P NMR parameters: offset 45 332 Hz; sweep width 3650 Hz; pulse width 14 μs; acquisition time 2.245 s; Guassian multiplication (no line broadening, Gaussian broadening 0.20 Hz).

The dithiopyrophosphate (**7**) when treated with excess bromine in water[1] gave bridge-^{18}O-labeled inorganic pyrophosphate (**8**) in almost quantitative yield. The location of ^{18}O in the bridging positions of **5**, **7**, and **8** was established by ^{31}P NMR, these intermediates all showed a small upfield shift, relative to the unlabeled materials, consistent with the isotope being singly bonded to phosphorus.[11] The mass spectrum of **5** demonstrated that only one ^{18}O had been incorporated and that the level of enrichment was 97 ± 2%, which was comparable to the enrichment of the $H_2{}^{18}O$ used. [β,γ-^{18}O]ATP (**1**) was synthesized in good yield (72%) from the bridge-labeled pyrophosphate (**8**) and adenosine 5′-phosphomorpholidate.[12] Although the procedure of Wehrli et al. requires the pyrophosphate to be used in approximately 5-fold excess, the unreacted pyrophosphate was readily recovered during the isolation of [β,γ-^{18}O]ATP (**1**) by ion exchange chromatography on DEAE sephadex.

The ^{31}P NMR of [β,γ-^{18}O]ATP is shown in Figure 1a. The spectrum is identical with that of authentic ATP; however, the expansions of P_β and P_γ reveal small duplicate resonances shifted to lower field[13] that correspond to 4% [β,γ-^{16}O]ATP that arises due to the residual ^{16}O in the $H_2{}^{18}O$ together with any dilutions that occurred during the synthesis. This assignment was confirmed by adding authentic ATP to the sample and rerecording the ^{31}P NMR spectrum (Figure 1b). The P_β and P_γ resonances are clearly split, the magnitudes of these shifts (2.63 and 3.37 Hz, respectively) being proof that the ^{18}O is in the $\beta\gamma$-bridge, while P_α remains a sharp doublet.

Although we report only the synthesis of [β,γ-^{18}O]ATP, since the nucleotide is introduced into the sequence in the last step and is coupled by a standard condensation reaction, this means that other nucleotides, deoxyribonucleotides, and nucleotide analogues can readily be incorporated. This synthesis is likely to be the preferred route to substrates for positional isotope exchange analysis. We are currently using such species to measure heavy-atom kinetic isotope effects for some the kinases.

Registry No. **1**, 87191-03-5; **2**, 68973-41-1; **3**, 87883-26-9; **4**, 2524-04-1; **5**, 87883-27-0; **6**, 87883-28-1; **7**, 87883-29-2; **8**, 87883-30-5; adenosine 5′-phosphomorpholidate, 7331-13-7; pyruvate kinase, 9001-59-6.

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(13) The partially resolved peaks appearing upfield of the main resonance for P_γ and probably P_β in Figure 1a are tentatively assigned to [γ-^{18}O]ATP and [β-^{18}O]ATP, respectively, since an isotope in the nonbridge position, having a higher bond order, will shift the ^{31}P resonance further upfield than ^{18}O in the bridge position. The implication of this is that there has been ~5% scrambling out of the bridge at some stage during the synthesis; we are currently clarifying this.

Soluble Metal Sulfides. Synthesis and Structures of $[M_6S_{17}]^{4-}$ (M = Nb, Ta): Icosahedral-Fragment Cages Containing Four Types of Coordinated Sulfide

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An emerging class of transition-element compounds consists of soluble salts of metal–sulfur anions $[M_xS_y]^{z-}$. Examples include $[MS_4]^{3-,2-,1-}$ [2] (M = V, Mo, W, Re), $[MoS_9]^{2-}$,[3,4] $[Mo_2S_{10}]^{2-}$,[4,5] $[Mo_2S_{12}]^{2-}$,[4,6] $[M_3S_9]^{2-}$ [7,8] (M = Mo, W), $[Mo_3S_{13}]^{2-}$,[9] and $[W_4S_{12}]^{2-}$.[10] The chemistry of $[MS_4]^{2-}$ (M = Mo, W) has been substantially elaborated, especially as ligands in heterometallic complexes.[2,11,12] Among group 5A thiometalates the derivative chemistry of tractable $(NH_4)_3[VS_4]$ has been initiated.[13] $[NbS_4]^{3-}$, $[NbOS_3]^{3-}$, and $[TaS_4]^{3-}$ are known only as insoluble salts synthesized at high temperatures,[14] and the preparation of $(Me_4N)_3[NbO_2S_2]$[15] has not been repeatable in our hands. Consequently, a search for soluble Nb and Ta sulfides was undertaken.

An anaerobic reaction mixture containing the mol ratio $M(OEt)_5$ (11 mmol):$(Me_3Si)_2S$:Et_4NCl = 1:6:3 in 350 mL of dry acetonitrile was stirred for 4–12 h at ~25 °C. Anaerobic recrystallization (acetonitrile) of the solids obtained by slow addition of ether to the reaction mixture filtrates afforded 1.75 g of black (M = Nb) or 1.25 g of dark brown (M = Ta) crystalline salts, which are sensitive to dioxygen and water. On the basis of data for $Tl_3[MS_4]$,[16] absorption spectra of these materials do not conform to those of anticipated compounds of $[MS_4]^{3-}$.[17] Values

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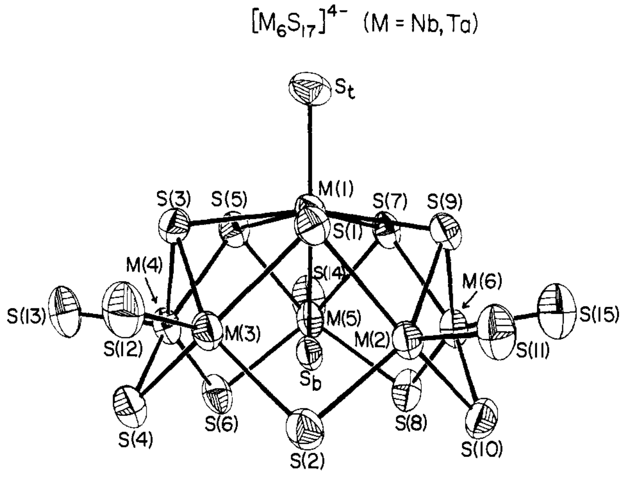

Figure 1. Structures of $[M_6S_{17}]^{4-}$ (M = Nb, Ta) showing the atom labeling scheme and 50% probability ellipsoids. The relatively long M(2–6)–S_b interactions (2.89–3.01 Å) are not depicted for sake of clarity.

of λ_{max} (Ta < Nb[18a]) are consistent with LMCT transitions and IR spectra demonstrated both M=S (483 (Nb), 471 (Ta) cm^{-1}, vs) and M—S groups.[18b] The compositions and crystal structures of the compounds were established by single-crystal X-ray analysis, which revealed a remarkable structure of the M-S anions.

The isomorphous and isostructural compounds $(Et_4N)_4[M_6S_{17}]\cdot 3MeCN$ crystallize in monoclinic space group $P2_1/c$ ($Z = 4$)[21] with discrete ions and solvate molecules, thus distinguishing them from the infinite lattice compounds $M_4Nb_6O_{17}\cdot 0.3H_2O$.[22] Crystals from three independent preparations of the M = Nb compound were shown to have identical cell constants. The structure of $[M_6S_{17}]^{4-}$ (Figure 1) contains 10 nonplanar M_2S_2 rhombs in convex fusion forming a crown-shaped M_6S_{10} cage. The three parallel planes (5 μ_2-S, 5 M, 5 μ_3-S; dihedral angles 0.1–0.5°) are normal to the five vertical planes (e.g., $S_tS_bM(1,2)$–S(5,6,11); dihedral angles 88–91°). Atom displacements from these least-squares planes do not exceed 0.075 Å and are usually <0.040 Å. Each M(V) atom is additionally bonded to a terminal atom S_t or S(11–15) and to the atom S_b *inside* the cage, completing pentagonal seven-coordination of M(1) and tetragonal six-coordination of M(2–6). The entire anion, $[(MS)_6(\mu_2\text{-}S)_5(\mu_3\text{-}S)_5(\mu_6\text{-}S)]^{4-}$, contains *four* structural types of sulfur atoms and closely approaches infrequently realized C_{5v} symmetry. Sets of independent distances (7) and angles (20) involving bonded atoms (d(M–S) $\lesssim$ 3.0 Å), averaged under this symmetry, are provided in Table I. Corresponding values for $[Ta_6S_{17}]^{4-}$ differ by $\leq$0.02 Å and $\leq$1.5°. The distances Nb(1)–Nb(2–6) and Nb–Nb in the 2–6 set average to 3.63 (1) and 3.41 (2) Å, respectively. The bond-length order is $M\text{–}S_{terminal} < M\text{–}\mu_2\text{-}S < M\text{–}\mu_3\text{-}S < M\text{–}S_b$.

Table I. Mean Values of Distances (Å) and Angles (deg) in $[Nb_6S_{17}]^{4-}$ under C_{5v} Symmetry

type	value	type	value
Nb(1)–S_t	2.196 (4)[a]	S(11)–Nb(2)–S_b	177.8 (6)[c]
Nb(1)–S(1)	2.590 (7)[b,c]	S(1)–Nb(2)–S(9)	73.6 (9)[c]
Nb(1)–S_b	2.636 (4)[a]	S(1)–Nb(2)–S(2)	85.2 (12)[d]
Nb(2)–S(11)	2.177 (18)[c]	S(1)–Nb(2)–S(10)	151.4 (6)[d]
Nb(2)–S(1)	2.516 (9)[d]	S(1)–Nb(2)–S_b	77.7 (8)[d]
Nb(2)–S(2)	2.414 (4)[d]	S(2)–Nb(2)–S(10)	106.7 (21)[c]
Nb(2)–S_b	2.94 (5)[c]	S(2)–Nb(2)–S_b	79.2 (15)[d]
S_t–Nb(1)–S(1)	97.8 (16)	Nb(1)–S(1)–Nb(2)	90.7 (5)[d]
S_t–Nb(1)–S_b	178.2 (1)[a,e]	Nb(2)–S(1)–Nb(3)	85.4 (5)[c]
S(1)–Nb(1)–S(3)	71.3 (8)[c]	Nb(2)–S(2)–Nb(3)	89.9 (7)[c]
S(1)–Nb(1)–S(5)	140.9 (5)[c]	Nb(1)–S_b–Nb(2)	81.2 (9)[c]
S(1)–Nb(1)–S_b	80.2 (6)[c]	Nb(2)–S_b–Nb(3)	71.0 (5)[c]
S(11)–Nb(2)–S(1)	103.0 (11)[d]	Nb(2)–S_b–Nb(4)	140.0 (6)[c]
S(11)–Nb(2)–S(2)	100.3 (15)[d]		

[a] Unique value. [b] Esd of the mean in parentheses. [c] Mean of 5 values. [d] Mean of 10 values. [e] Required to be 180° under actual C_{5v} symmetry.

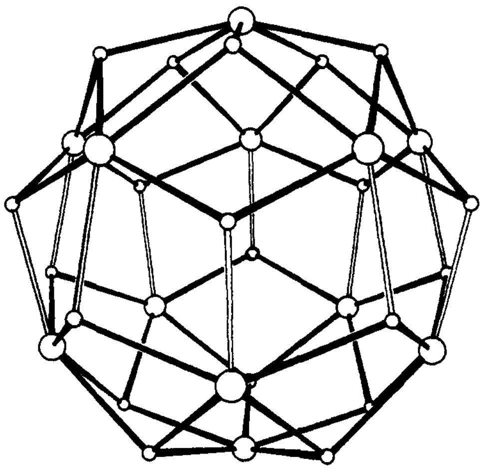

Figure 2. M_6S_{10} cage of $[M_6S_{17}]^{4-}$ represented as one-half of hypothetical stellated-icosahedral $M_{12}S_{20}$; the halves are separated by the unshaded bonds.

The short distances to terminal atoms (2.18–2.20 Å) and displacements of M atoms from the pentagonal S_5 plane (0.35 Å) and the five trapezoidal S_4 planes (mean 0.49 Å) toward terminal sulfur atoms are indicative of multiple bonds M=S, observed in IR spectra. These are among the few (Nb)[14c,23] and only the second (Ta)[24] structurally defined M=S interactions. Of aforementioned polynuclear ions $[M_xS_y]^{z-}$ only $[M_3S_9]^{2-}$ and $[W_4S_{12}]^{2-}$ resemble $[M_6S_{17}]^{4-}$ by containing sulfur as sulfide only.

Two additional features of $[M_6S_{17}]^{4-}$ merit special comment. First, the M_6S_{10} framework, which has not been previously encountered, can be conceptualized as one-half of closo-$M_{12}S_{20}$. The parent structure, a stellated icosahedron (triakis icosahedron[25]) of I_h symmetry (Figure 2), consists of a regular M_{12} icosahedron with a sulfur atom capping each of the 20 faces. Considered separately, the sulfur atoms define the vertices of a regular pentagonal dodecahedron. Second, the cage is internally occupied by an unprecedented μ_6-S (S_b) atom, which lies 0.45 (0.43) Å below the $Nb_5(Ta_5)$ mean plane. The M(1)–S_b distance is only ~0.05 Å and the M(2–6)–S_b distances ~0.3 Å longer than the M(1)–μ_3-S distance. To provide some clarification of the

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(18) (a) Absorption spectra (ϵ_M, based on $(Et_4N)_4[M_6S_{17}]\cdot 3MeCN$) in MeCN: λ_{max} 255 (sh, 70 600), 302 (42 700), 385 (16 100), 470 (sh, 8500) nm, M = Nb; λ_{max} 238 (sh, 82 700), 269 (66 000), 346 (22 800), 390 (sh, 13 000) nm, M = Ta. (b) IR spectra (CsI): ν_{NbS} = 377 (m), 358 (m), 335–329 (d, s) cm^{-1}; ν_{TaS} = 356 (m), 331 (s), 311 (s) cm^{-1}. The order $\nu_{Nb=S} > \nu_{Ta=S}$ has been observed in other homologous pairs of M = Nb(V), Ta(V) complexes.[19,20]

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structural role of S_b, extended Hückel MO calculations were performed on $[Nb_6S_{17}]^{4-}$,[26] with these findings: (i) the interaction of $Nb_6S_{16}^{2-}$ and S_b^{2-} affords a stabilization of $\sim$1.9 eV over the isolated fragments; (ii) the overlap populations of Nb(1)–S_t (0.58), Nb(1)–μ_3-S $\simeq$ Nb(1)–S_b (0.23), Nb(2)–$S_{terminal}$ (0.60), Nb(2)–μ_3-S (0.28), Nb(2)–μ_2-S (0.36), and Nb(2)–S_b (0.11) suggest that Nb(2–6)–S_b interactions are significant, with a bond order slightly less than one-half that of the Nb(1)–S_b bond. These results indicate that the S_b atom is an integral part of the $[M_6S_{17}]^{4-}$ structure, which is the first example of a 16-atom C_{5v} cage. Full details of the structural and electronic properties of $[M_6S_{17}]^{4-}$ will be provided subsequently. The reactivity properties of these species are under investigation.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017. X-ray and NMR equipment used in this research were obtained by NSF Grants CHE 80-00670 and CHE 80-08891. We thank S. Rubenstein and Dr. Jay Dorfman for assistance with MO calculations.

Supplementary Material Available: X-ray structural data for $(Et_4N)_4[Nb_6S_{17}]\cdot3MeCN$—positional and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Photochemical Wolff Rearrangement of a Triplet Ground-State Carbene

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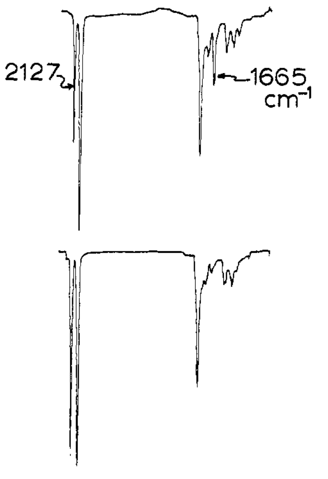
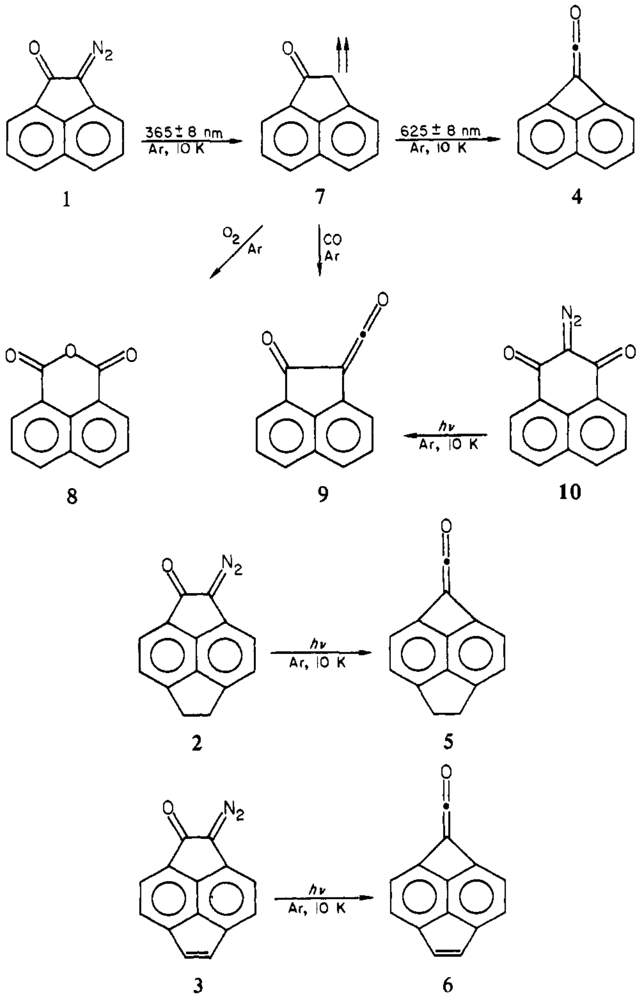


Figure 1. Top: Infrared spectrum (2200–1500 cm^{-1}) of diazo ketone **1** matrix isolated in argon after irradiation (365 ± 8 nm) for 45 min. Ketene **4** (2127 cm^{-1}) and α-ketocarbene **7** (1665 cm^{-1}) are visible. The bands at 2085 and 1702 cm^{-1} are due to diazo ketone **1**. Botton: The same sample after irradiation (625 ± 8 nm) for 182 min. The disappearance of the α-ketocarbene **7** and the concomittant increase in the ketene **4** are readily apparent.

Scheme I



The mechanism of the photochemical Wolff rearrangement is of special interest because of its importance in photolithography.[1] Stereochemical[2,3] and CIDNP[3] evidence is consistent, in most cases, with concerted loss of nitrogen and migration of the carbon–carbon bond.[4] Singlet α-ketocarbenes have been suggested as intermediates in Wolff rearrangements in which oxirene intermediates are believed to be involved and in reactions in which nitrogen loss is considered to occur before rearrangement.[4,5] Relatively few α-ketocarbenes have been studied spectroscopically, but those studied have triplet ground states.[6-9] In all cases, except perfluoro-2-oxo-3-butylidene, triplet α-ketocarbenes do not undergo the Wolff rearrangement. Triplet α-ketocarbenes produced

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