atom in **3** may possess stronger Lewis acidity due to the formal substitution of the electronegative metalla moiety into the backbone of the β-diketonate ligands.

The postulated Cu–axial carbonyl interaction is structurally different from the normal semibridging carbonyl structures so the Re–C(6)–O(6) angle of 177.9 (6)° need not differ significantly from linearity.[18] The average value of the C(6)–Re–C(1) and C(6)–Re–C(2) angles is 88.5 (2)° while the average value of the C(5)–Re–C(1) and C(5)–Re–C(2) angles is 89.2 (2)°. These values may suggest a barely significant (0.7°) increased tilting of the C(6)–axial carbonyl ligand toward the Cu atom. Presumably, the two axial carbonyl ligands would be weakly donating electrons from their π molecular orbitals to the Cu atom, thus acting as formal four-electron ligands. This type of bonding for carbon monoxide has been observed recently for the dimeric molecule $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$.[19] As observed in **3**, the Mo–C–O angles of 175.9 (1.2)° found in this complex are within the normal range expected for linear, terminally coordinated carbonyl ligands and show no excessive bending from linearity even though the carbonyl to metal π bonding within this dimeric complex must surely be greater than that postulated for complex **3**. As expected, the C(5)–O(5) and C(6)–O(6) distances of **3** are not significantly different due to this weak carbonyl–copper interaction.

Another explanation for the nonplanarity of the atoms comprising the backbone of the metallachelate ring is the presence of considerable angle strain within the chelate ring. The sum of the internal angles of a six-membered ring must be 720° if the ring is planar. In complex **1**, the sum of the internal angles of the metallachelate ring is 720°, because the internal angles are able to open up and compensate for the relatively short Mn–acyl carbon distances while maintaining the required geometry and O–O "bite" distance at the Al atom. However, in complex **3**, the sum of the internal angles of the metallachelate ring is only 679°. For this complex these internal angles can not open up sufficiently to compensate for the much longer Re–acyl carbon distances while maintaining the required geometry and O–O "bite" distance at the Cu atom. Additional structural studies should substantiate this effect of internal angle strain.

Recent data may indicate that the "chaise longue chair" structure of **3** persists in the solution phase. The relative intensity pattern for the terminal carbonyl stretching bands of metallaacetylacetonate complexes like **1** and **2** are essentially identical.[20] The assignment of these bands to the particular stretching vibrations of the axial and equatorial sets of carbonyl ligands has been determined.[21] For complex **3**, the relative intensities of the four IR-active carbonyl stretching bands have the expected pattern; however, the axial B_1 band is shifted 17 cm^{-1} to lower energy relative to the equatorial A_1 band. This shift in complex **2** is only 7 cm^{-1}, and the equatorial A_1 bands for **2** and **3** appear at the same frequency. The additional shift in the axial B_1 band of **3** may be caused by the weak coordination of one of the axial carbonyl ligands to the Cu atom. When pyridine is added to a solution of **3**, the axial B_1 band shifts back to its expected position relative to the equatorial A_1 band, apparently, due to the formation of a pyridine adduct which permits a planar conformation of the metallaacetylacetonate ligand. The preparation and characterization of these adducts are currently under investigation.[22]

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Registry No. 3, 67634-87-1.

Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of Heptakis(*tert*-butyl isocyanide)tungsten(II) Hexatungstate, $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$[1]

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The reaction of tripotassium enneachloroditungstate, $K_3W_2Cl_9$, with excess *tert*-butyl isocyanide is promoted by the presence of a small quantity of water and produces the complex heptakis(*tert*-butyl isocyanide)tungsten(II) hexatungstate, $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$. Similar treatment of $Mo_2Cl_9^{3-}$ and $Mo_2Cl_8H^{3-}$ yields the corresponding molybdenum complex ion $(t\text{-}C_4H_9NC)_7Mo^{2+}$. The structure of $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$ has been determined by single-crystal X-ray diffraction. The compound crystallizes in a monoclinic system. Refinement was performed in group $P2_1/n$ with $a = 11.225$ (1) Å, $b = 33.309$ (4) Å, $c = 16.852$ (3) Å, $\beta = 92.86$ (1)°, and $Z = 4$. The seven-coordinate cation has a coordination geometry which can be described as a distorted monocapped trigonal prism. The structure reveals several similarities and contrasts to that of the corresponding molybdenum cation.

Seven-coordination is becoming a generally recognized occurrence in second- and third-row elements of the early transition metals.[2,3] The electronic and stereochemical principles that govern the selection of such coordination polyhedra as well as the chemical reactivity of these higher

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(1) This work was supported by the National Institutes of Health, Grant AM-18713-03.

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coordinate molecules are not well-defined. Investigations aimed at elucidating an understanding of these factors are most informative when they permit comparison between structures in a homologous series involving equivalent monodentate ligands.

The isocyanide complexes ML_6X^+ and ML_7^{2+} of molybdenum(II) are well-characterized ions.[2,4] Thus, the synthesis and structural characterization of the related tungsten(II) ion, WL_7^{2+}, provide the unique opportunity to compare the influence of such coordination within two consecutive members of a triad. Moreover, mononuclear complexes of tungsten(II) are relatively rare and ionic heptaleptic complexes appear to be unknown; consequently, such an investigation would also lend insight into the nature of this unusual oxidation state of tungsten. We report here the synthesis and single-crystal X-ray crystal structure determination of the first such complex, $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$.

Experimental Procedure

Preparation and Data Collection and Reduction. In a typical preparation, tripotassium enneachloroditungstate[5] ($K_3W_2Cl_9$; 2.0 g, 2.5 mmol) was placed in a 25-mL flask equipped with a reflux condenser and a Teflon-coated stirring bar. The system was flushed with nitrogen before adding *tert*-butyl isocyanide[6] (5 mL) and benzene (1 mL). This mixture was refluxed under nitrogen until it darkened to a near black color. The resulting viscous reaction mixture was dissolved in acetone (10 mL) and filtered, and the filtrate was stored at −20 °C for 48 h. The crystals that formed were collected by suction filtration (yield 1.5 g) and rinsed with 20 mL of a 1:1 solution of ether–ethanol. Purification was accomplished by dissolution in a minimal amount of acetone and the resulting solution eluted through a short (4 in. × 0.5 in.) column of neutral alumina. The eluent was concentrated under reduced pressure. The residual brown oil was warmed on a steam bath and treated dropwise with ether–ethanol (1:1) until it became cloudy at which point sufficient acetone was added to produce a clear solution. Upon gradual cooling to ambient temperature, bright yellow needles were obtained. The infrared spectrum of this material (mulled in CCl_4) exhibited absorptions at 2128 cm^{-1} (br, m) assigned to terminal isocyanide stretching modes. The ^1H NMR ($CDCl_3$) examined at ambient temperature revealed only a single absorption at δ 1.58, assigned as CH_3. The exact nature of this substance was established by a single-crystal X-ray crystallographic determination.[7]

Suitable crystals were obtained by slow recrystallization of the purified product from acetone. A single prism was mounted in a quick-drying epoxy in a glass capillary. Employing an Enraf-Nonius CAD 4 diffractometer using graphite monochromatized Mo Kα radiation (λ 0.710 73 Å), we collected 8380 independent (8587 observed) reflections. The observed systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) require the space group to be $P2_1/n$. The cell constants are a = 11.225 (1) Å, b = 33.309 (4) Å, c = 16.852 (3) Å, β = 92.86 (1)°, and Z = 4. The calculated density of 2.344 g/cm^3 agreed with the observed value of 2.40 g/cm^3 obtained by neutral buoyancy in methyl iodide–diethyl ether solution.

Data on the randomly mounted crystal were collected from a takeoff angle of 2.8° employing a 2θ scan with a scan rate ranging from 4 to 40°/min. (The variable scan rate allows rapid data collection for intense reflection where a fast scan rate is used and assures accurate counting statistics for weak reflections where a slow scan rate is used.) Moving-crystal/moving-counter background counts were recorded at the ends of the scan range. The ratio of the scan time to background counting time was 2.0. No standard deviated by more than ±2% of its average value for the entire run.

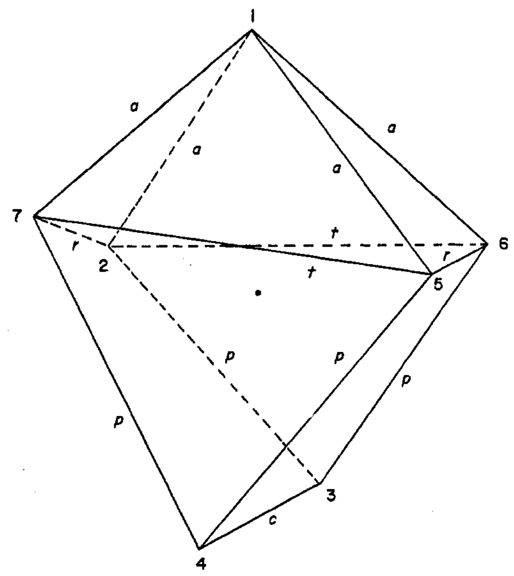

Figure 1. Structure and labeling scheme for the $(t\text{-}C_4H_9NC)_7W^{2+}$ cation.

Intensities and standard deviations on intensities were computed by using the formulas

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + RB)^2 + (pI)^2]^{1/2}$$

where S is the scan rate, C is the total integrated peak count, R = 2 is the ratio of scan time to background counting time, B is the total background count, and the parameter p is a factor introduced to downweight the intense reflections. In this instance a value of p = 0.05 was used. Lorentz and polarization corrections were applied to the data. An absorption correction based on a series of ψ scans was also applied to the data. Transmission coefficients ranged from 0.66 to 1.00 with an average value of 0.87.

Determination and Refinement of the Structure. The structure was solved by direct methods. By use of 407 reflections ($E_{\min}$ = 2.00) and 200 phase relationships, a total of 16 phase sets were produced. The seven tungsten atoms were located by using an E map prepared from the phase set showing the best probability statistics (an absolute figure of merit = 1.00, residual = 0.20). These atoms were included in a least-squares refinement, resulting in agreement factors (defined below) of R_1 = 0.15 and 0.17. The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses.

In full-matrix least-squares refinement, the function minimized was $w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from Cromer and Waber.[8] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta d'$ were those of Cromer and Liberman.[9] Only the 5181 reflections having $F_o^2 \geq 3\sigma(F_o^2)$ were used in the refinement. The following values pertain to the final cycle of least-squares refinement:

$$R_1 = ||F_o| - |F_c||/\sum|F_o| = 0.047$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.057$$

No attempt was made to locate or refine the hydrogen atoms. Thermal parameters and observed and calculated structure factors are listed in the supplementary material. The molecular geometry is summarized in Tables I–III.

Discussion

The coordination geometry of the tungsten atom in the $(t\text{-}C_4H_9NC)_7W^{2+}$ cation may be described as that of a distorted, monocapped trigonal prism, as defined by C(7), C(2),

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Table I. Molecular Dimensions of the [$(t\text{-}C_4H_9NC)_7W]^{2+}$ Ion

Distance (Å)			
W(7)–C(1)	2.11 (2)	C(8)–C(9)	1.48 (3)
W(7)–C(2)	2.07 (2)	C(8)–C(10)	1.46 (3)
W(7)–C(3)	2.09 (2)	C(3)–C(11)	1.62 (3)
W(7)–C(4)	2.08 (2)	C(12)–C(13)	1.55 (3)
W(7)–C(5)	2.12 (2)	C(12)–C(14)	1.55 (3)
W(7)–C(6)	2.10 (2)	C(12)–C(15)	1.50 (3)
W(7)–C(7)	2.06 (2)	C(16)–C(17)	1.52 (3)
C(1)–N(1)	1.14 (2)	C(16)–C(18)	1.59 (3)
C(2)–N(2)	1.17 (2)	C(16)–C(19)	1.53 (3)
C(3)–N(3)	1.13 (2)	C(20)–C(21)	1.57 (3)
C(4)–N(4)	1.14 (2)	C(20)–C(22)	1.48 (3)
C(5)–N(5)	1.13 (2)	C(20)–C(23)	1.58 (3)
C(6)–N(6)	1.14 (2)	C(24)–C(25)	1.53 (3)
C(7)–N(7)	1.16 (2)	C(24)–C(26)	1.55 (3)
N(1)–C(8)	1.52 (2)	C(24)–C(27)	1.50 (3)
N(2)–C(12)	1.46 (2)	C(28)–C(29)	1.55 (2)
N(3)–C(16)	1.43 (2)	C(28)–C(30)	1.53 (2)
N(4)–C(20)	1.48 (2)	C(28)–C(31)	1.48 (2)
N(5)–C(24)	1.49 (2)	C(32)–C(33)	1.49 (5)
N(6)–C(28)	1.48 (2)	C(32)–C(34)	1.43 (5)
N(7)–C(32)	1.59 (4)	C(32)–C(35)	1.27 (7)

Interbond Angles (Deg)			
C(1)–W(7)–C(2)	78.6 (6)	C(9)–C(8)–C(11)	105 (2)
C(1)–W(7)–C(3)	134.5 (5)	C(10)–C(8)–C(11)	115 (2)
C(1)–W(7)–C(4)	152.6 (6)	N(2)–C(12)–C(13)	105 (2)
C(1)–W(7)–C(5)	89.4 (6)	N(2)–C(12)–C(14)	107 (1)
C(1)–W(7)–C(6)	77.3 (6)	N(2)–C(12)–C(15)	107 (2)
C(1)–W(7)–C(7)	79.3 (7)	C(13)–C(12)–C(14)	110 (2)
C(2)–W(7)–C(3)	77.7 (6)	C(13)–C(12)–C(15)	112 (2)
C(2)–W(7)–C(4)	109.8 (6)	C(14)–C(12)–C(15)	116 (2)
C(2)–W(7)–C(5)	166.0 (6)	N(3)–C(16)–C(17)	109 (2)
C(2)–W(7)–C(6)	105.7 (6)	N(3)–C(16)–C(18)	108 (2)
C(2)–W(7)–C(7)	81.0 (7)	N(3)–C(16)–C(19)	110 (2)
C(3)–W(7)–C(4)	72.7 (6)	C(17)–C(16)–C(18)	108 (2)
C(3)–W(7)–C(5)	116.1 (6)	C(17)–C(16)–C(19)	113 (2)
C(3)–W(7)–C(6)	72.5 (6)	C(18)–C(16)–C(19)	109 (2)
C(3)–W(7)–C(7)	133.4 (7)	N(4)–C(20)–C(21)	105 (2)
C(4)–W(7)–C(5)	77.8 (6)	N(4)–C(20)–C(22)	110 (2)
C(4)–W(7)–C(6)	122.5 (6)	N(4)–C(20)–C(23)	104 (2)
C(4)–W(7)–C(7)	76.5 (7)	C(21)–C(20)–C(22)	109 (2)
C(5)–W(7)–C(6)	78.3 (6)	C(21)–C(20)–C(23)	109 (2)
	89.8 (7)	C(22)–C(20)–C(23)	119 (2)
C(5)–W(7)–C(7)	153.8 (7)	N(5)–C(24)–C(25)	104 (2)
C(6)–W(7)–C(7)	177 (2)	N(5)–C(24)–C(26)	109 (2)
W(7)–C(1)–N(1)	175 (2)	N(5)–C(24)–C(27)	106 (2)
W(7)–C(2)–N(2)	175 (2)	C(25)–C(24)–C(26)	110 (2)
W(7)–C(3)–N(3)	178 (2)	C(25)–C(24)–C(27)	116 (2)
W(7)–C(4)–N(4)	175 (2)	C(26)–C(24)–C(27)	112 (2)
W(7)–C(5)–N(5)	174 (1)	N(6)–C(28)–C(29)	108 (1)
W(7)–C(6)–N(6)	175 (2)	N(6)–C(28)–C(30)	106 (1)
W(7)–C(7)–N(7)	175 (2)	N(6)–C(28)–C(31)	109 (1)
C(1)–N(1)–C(8)	172 (2)	C(29)–C(28)–C(30)	112 (2)
C(2)–N(2)–C(12)	172 (2)	C(29)–C(28)–C(31)	111 (1)
C(3)–N(3)–C(16)	174 (2)	C(30)–C(28)–C(31)	110 (1)
C(4)–N(4)–C(20)	174 (2)	N(7)–C(32)–C(33)	107 (3)
C(5)–N(5)–C(24)	178 (2)	N(7)–C(32)–C(34)	102 (3)
C(6)–N(6)–C(28)	174 (2)	N(7)–C(32)–C(35)	101 (5)
C(7)–N(7)–C(32)	177 (3)	C(33)–C(32)–C(34)	116 (4)
N(1)–C(8)–C(9)	108 (2)	C(33)–C(32)–C(35)	126 (5)
N(1)–C(8)–C(10)	107 (2)	C(34)–C(32)–C(35)	102 (5)
N(1)–C(8)–C(11)	104 (2)		
C(9)–C(8)–C(10)	116 (2)		

C(3), C(4), C(5), and C(6) with C(1) at the capped site.

The structure of the heptakis(*tert*-butyl isocyanide)tungsten(II) cation is similar to that of $(t\text{-}C_4H_9NC)_7Mo^{2+}$. The relationship between this latter complex and several other selected trigonal-prismatic structures has been summarized by Lippard and Lewis.[2] For comparison, the shape parameters of $(t\text{-}C_4H_9NC)_7Mo^{2+}$ are reproduced in Table II along with those of $(t\text{-}C_4H_9NC)_7W^{2+}$. One aspect of comparison merits brief discussion. The pattern of the M–C bond lengths in heptakis(*tert*-butyl isocyanide)molybdenum(II) cannot be discerned for $(t\text{-}C_4H_9NC)_7W^{2+}$ because of the relative inaccuracies of the corresponding W–C bond length values. Such inaccuracies are, of course, an inherent consequence of the considerable difference between the atomic number of tungsten and carbon.

An examination of Table II reveals that the monocapped trigonal prism which describes the geometry of the heptakis(*tert*-butyl isocyanide)tungsten(II) ion is in some ways more

Table II. A Comparison of the Shape Parameters for the Heptakis(*tert*-butyl isocyanide)molybdenum(II) and -tungsten(II) Cations

edge	length, Å	classification[a]	atoms	angle, deg
		$(MoL_7)^{2+}$ [b]		
C(1)–C(7)	2.82 (mean)	a	C(1)–Mo–C(7)	83.7 (3)
C(2)–C(7)		a	C(2)–Mo–C(7)	
C(4)–C(7)		a	C(4)–Mo–C(7)	80.3 (3)
C(5)–C(7)		a	C(5)–Mo–C(7)	
C(3)–C(6)	2.40	c	C(3)–Mo–C(6)	71.5 (4)
C(1)–C(2)	2.70 (mean)	r	C(1)–Mo–C(2)	78.7 (mean)
C(4)–C(5)		r	C(4)–Mo–C(5)	
C(1)–C(5)	3.24 (mean)	t	C(1)–Mo–C(5)	99.0 (2)
C(2)–C(4)		t	C(2)–Mo–C(4)	
C(5)–C(6)	2.55	p	C(5)–Mo–C(6)	75.2
C(2)–C(3)	2.55	p	C(2)–Mo–C(3)	75.0
		$(WL_7)^{2+}$ [c]		
C(1)–C(7)	2.65	a	C(1)–W–C(7)	79.3
C(1)–C(2)	2.64	a	C(1)–W–C(2)	78.7
C(1)–C(5)	2.96	a	C(1)–W–C(5)	89.4
C(1)–C(6)	2.62	a	C(1)–W–C(6)	77.3
	2.72 (mean)			81.2 (mean)
C(3)–C(4)	2.47	c	C(3)–W–C(4)	72.7
C(5)–C(6)	2.66	r	C(5)–W–C(6)	78.3
C(2)–C(7)	2.68	r	C(2)–W–C(7)	80.9
C(5)–C(7)	2.95	t	C(5)–W–C(7)	89.9
C(2)–C(6)	3.32	t	C(2)–W–C(6)	105.6
C(4)–C(5)	2.63	p	C(4)–W–C(5)	77.8
C(4)–C(7)	2.56	p	C(4)–W–C(7)	76.5
C(3)–C(6)	2.48	p	C(3)–W–C(6)	72.5
C(2)–C(3)	2.61	p	C(2)–W–C(3)	77.6
	2.57 (mean)			76.10 (mean)

[a] See Figure 2 for nomenclature. [b] Other angles: C(6)–Mo–C(7) = 144.2 (2)°; C(2)–Mo–C(5) = 164.0 (2)°; C(3)–Mo–C(5) = 119.0 (3)°; C(1)–Mo–C(3) = 118.8 (3)°. [c] Other angles: C(6)–W–C(7) = 153.8°; C(1)–W–C(4) = 152.5°; C(2)–W–C(5) = 166.1°; C(3)–W–C(5) = 116.2°; C(4)–W–C(6) = 122.5°; C(1)–W–C(3) = 134.5°.

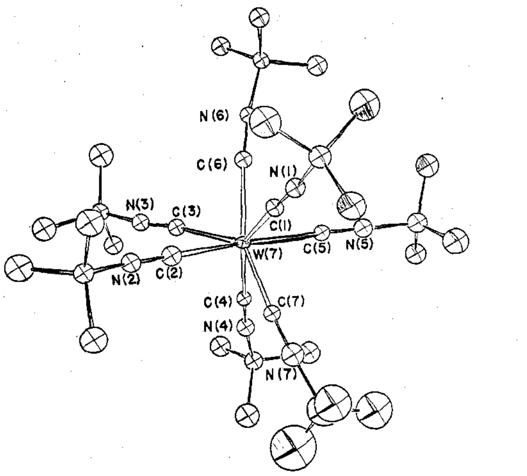

Figure 2. Geometry of the polyhedron described by tungsten-bound carbon atoms in $(t\text{-}C_4H_9NC)_7W^{2+}$. Drawn to scale, this figure illustrates the distortion from ideality. The position of the tungsten atom is also shown.

Table III. Dimensions of the Hexatungstate Ion, $[W_6O_{19}]^{2-}$

Distance (Å)

W(1)-W(3)	3.275 (1)	W(1)-O(1)	2.298 (9)	W(3)-O(1)	2.328 (9)	W(5)-O(1)	2.297 (9)
W(1)-W(4)	3.272 (1)	W(1)-O(2)	1.673 (14)	W(3)-O(4)	1.70 (2)	W(5)-O(6)	1.701 (14)
W(1)-W(5)	3.271 (1)	W(1)-O(8)	1.892 (12)	W(3)-O(8)	1.922 (12)	W(5)-O(10)	1.903 (10)
W(1)-W(6)	3.277 (1)	W(1)-O(9)	1.891 (11)	W(3)-O(12)	1.904 (13)	W(5)-O(14)	1.889 (11)
W(2)-W(3)	3.276 (1)	W(1)-O(10)	1.929 (11)	W(3)-O(16)	1.938 (12)	W(5)-O(17)	1.906 (12)
W(2)-W(4)	3.271 (1)	W(1)-O(11)	1.893 (11)	W(3)-O(19)	1.904 (13)	W(5)-O(18)	1.925 (12)
W(2)-W(5)	3.260 (1)	W(2)-O(1)	2.327 (9)	W(4)-O(1)	2.324 (9)	W(6)-O(1)	2.316 (9)
W(2)-W(6)	3.283 (1)	W(2)-O(3)	1.704 (15)	W(4)-O(5)	1.711 (15)	W(6)-O(7)	1.672 (15)
W(3)-W(4)	3.278 (1)	W(2)-O(12)	1.899 (13)	W(4)-O(9)	1.913 (11)	W(6)-O(11)	1.934 (11)
W(3)-W(6)	3.277 (1)	W(2)-O(13)	1.888 (12)	W(4)-O(13)	1.891 (12)	W(6)-O(15)	1.941 (13)
W(4)-W(5)	3.279 (1)	W(2)-O(14)	1.925 (11)	W(4)-O(16)	1.883 (12)	W(6)-O(18)	1.874 (12)
W(5)-W(6)	3.269 (1)	W(2)-O(15)	1.873 (13)	W(4)-O(17)	1.942 (12)	W(6)-O(19)	1.918 (13)

Interbond Angles (Deg)

W(3)-W(1)-W(4)	60.09 (2)	W(6)-W(2)-O(15)	31.2 (4)	O(9)-W(4)-O(17)	86.1 (5)	W(2)-O(1)-W(6)	90.0 (3)
W(3)-W(1)-W(5)	89.90 (2)	O(1)-W(2)-O(3)	178.5 (5)	O(13)-W(4)-O(16)	86.1 (5)	W(3)-O(1)-W(4)	89.6 (3)
W(3)-W(1)-W(6)	60.01 (2)	O(1)-W(2)-O(12)	75.9 (5)	O(13)-W(4)-O(17)	87.2 (5)	W(3)-O(1)-W(5)	179.1 (5)
W(3)-W(1)-O(1)	45.3 (2)	O(1)-W(2)-O(13)	75.4 (4)	O(16)-W(4)-O(17)	152.4 (5)	W(3)-O(1)-W(6)	89.8 (3)
W(3)-W(1)-O(2)	135.4 (5)	O(1)-W(2)-O(14)	75.8 (4)	W(1)-W(5)-W(2)	90.17 (3)	W(4)-O(1)-W(5)	90.4 (3)
W(3)-W(1)-O(8)	31.1 (3)	O(1)-W(2)-O(15)	76.1 (4)	W(1)-W(5)-W(4)	59.93 (2)	W(4)-O(1)-W(6)	179.1 (5)
W(3)-W(1)-O(9)	80.0 (3)	O(3)-W(2)-O(12)	105.5 (7)	W(1)-W(5)-W(6)	60.14 (2)	W(5)-O(1)-W(6)	90.3 (3)
W(3)-W(1)-O(10)	121.0 (3)	O(3)-W(2)-O(13)	104.2 (6)	W(1)-W(5)-O(1)	44.6 (2)	W(1)-O(8)-W(3)	118.3 (6)
W(3)-W(1)-O(11)	80.7 (4)	O(3)-W(2)-O(14)	102.9 (6)	W(1)-W(5)-O(6)	135.3 (5)	W(1)-O(9)-W(4)	118.6 (6)
W(4)-W(1)-W(5)	60.15 (2)	O(3)-W(2)-O(15)	104.4 (6)	W(1)-W(5)-O(10)	31.6 (3)	W(1)-O(10)-W(5)	117.3 (6)
W(4)-W(1)-W(6)	90.23 (2)	O(12)-W(2)-O(13)	85.7 (5)	W(1)-W(5)-O(14)	121.8 (3)	W(1)-O(11)-W(6)	117.8 (6)
W(4)-W(1)-O(1)	45.3 (2)	O(12)-W(2)-O(14)	151.6 (5)	W(1)-W(5)-O(17)	80.2 (3)	W(2)-O(12)-W(3)	118.9 (7)
W(4)-W(1)-O(2)	135.5 (5)	O(12)-W(2)-O(15)	86.4 (6)	W(1)-W(5)-O(18)	80.1 (3)	W(2)-O(13)-W(4)	119.9 (6)
W(4)-W(1)-O(8)	80.9 (4)	O(13)-W(2)-O(14)	86.6 (5)	W(2)-W(5)-W(4)	60.02 (2)	W(2)-O(14)-W(5)	117.4 (6)
W(4)-W(1)-O(9)	30.9 (3)	O(13)-W(2)-O(15)	151.4 (5)	W(2)-W(5)-W(6)	60.37 (3)	W(2)-O(15)-W(6)	118.8 (6)
W(4)-W(1)-O(10)	80.0 (3)	O(14)-W(2)-O(15)	87.4 (5)	W(2)-W(5)-O(1)	45.5 (2)	W(3)-O(16)-W(4)	118.1 (6)
W(4)-W(1)-O(11)	121.7 (3)	W(1)-W(3)-W(2)	89.83 (3)	W(2)-W(5)-O(6)	134.6 (5)	W(4)-O(17)-W(5)	116.9 (6)
W(5)-W(1)-W(6)	59.90 (2)	W(1)-W(3)-W(4)	59.91 (2)	W(2)-W(5)-O(10)	121.8 (3)	W(5)-O(18)-W(6)	118.8 (6)
W(5)-W(1)-O(1)	44.6 (2)	W(1)-W(3)-W(6)	60.03 (2)	W(2)-W(5)-O(14)	31.6 (3)	W(3)-O(19)-W(6)	118.0 (7)
W(5)-W(1)-O(2)	134.7 (5)	W(1)-W(3)-O(1)	44.6 (2)	W(2)-W(5)-O(17)	81.2 (4)	W(1)-W(3)-O(19)	80.6 (4)
W(5)-W(1)-O(8)	121.0 (3)	W(1)-W(3)-O(4)	137.3 (5)	W(2)-W(5)-O(18)	79.6 (4)	W(2)-W(3)-W(4)	59.88 (2)
W(5)-W(1)-O(9)	80.4 (3)	W(1)-W(3)-O(8)	30.6 (4)	W(4)-W(5)-W(6)	90.24 (3)	W(2)-W(3)-W(6)	60.14 (2)
W(5)-W(1)-O(10)	31.1 (3)	W(1)-W(3)-O(12)	120.3 (4)	W(4)-W(5)-O(1)	45.1 (2)	W(2)-W(3)-O(1)	45.3 (2)
W(5)-W(1)-O(11)	80.2 (3)	W(1)-W(3)-O(16)	79.8 (4)	W(4)-W(5)-O(6)	134.9 (5)	W(2)-W(3)-O(4)	132.9 (5)
W(6)-W(1)-O(1)	45.0 (2)	O(4)-W(3)-O(12)	102.4 (6)	W(4)-W(5)-O(10)	80.2 (3)	W(2)-W(3)-O(8)	120.4 (4)
W(6)-W(1)-O(2)	134.3 (5)	O(4)-W(3)-O(16)	104.5 (6)	W(4)-W(5)-O(14)	80.2 (4)	W(2)-W(3)-O(12)	30.5 (4)
W(6)-W(1)-O(8)	79.5 (3)	O(4)-W(3)-O(19)	103.8 (7)	W(4)-W(5)-O(17)	31.9 (4)	W(2)-W(3)-O(16)	79.6 (3)
W(6)-W(1)-O(9)	121.1 (3)	O(8)-W(3)-O(12)	150.9 (5)	W(4)-W(5)-O(18)	120.4 (4)	W(2)-W(3)-O(19)	80.2 (4)
W(6)-W(1)-O(10)	80.4 (3)	O(8)-W(3)-O(16)	87.3 (5)	W(6)-W(5)-O(1)	45.1 (2)	W(4)-W(3)-W(6)	90.14 (3)
W(6)-W(1)-O(11)	31.5 (3)	O(8)-W(3)-O(19)	86.1 (5)	W(6)-W(5)-O(6)	134.8 (5)	W(4)-W(3)-O(1)	45.2 (2)
O(1)-W(1)-O(2)	179.0 (6)	O(12)-W(3)-O(16)	85.8 (5)	W(6)-W(5)-O(10)	80.9 (3)	W(4)-W(3)-O(4)	134.9 (5)
O(1)-W(1)-O(8)	76.4 (4)	O(12)-W(3)-O(19)	86.7 (6)	W(6)-W(5)-O(14)	81.3 (3)	W(4)-W(3)-O(8)	80.4 (4)
O(1)-W(1)-O(9)	76.1 (4)	O(16)-W(3)-[illegible]	151.7 (5)	W(6)-W(5)-O(17)	122.1 (4)	W(4)-W(3)-O(12)	79.4 (4)
O(1)-W(1)-O(10)	75.7 (4)	W(1)-W(4)-W(2)	89.97 (3)	W(6)-W(5)-O(18)	30.2 (4)	W(4)-W(3)-O(16)	30.5 (4)
O(1)-W(1)-O(11)	76.4 (4)	W(1)-W(4)-W(3)	60.00 (2)	O(1)-W(5)-O(6)	179.9 (6)	W(4)-W(3)-O(19)	121.2 (4)
O(2)-W(1)-O(8)	104.3 (6)	W(1)-W(4)-W(5)	59.92 (2)	O(1)-W(5)-O(10)	76.2 (4)	W(6)-W(3)-O(1)	45.0 (2)
O(2)-W(1)-O(9)	104.6 (6)	W(1)-W(4)-O(1)	44.6 (2)	O(1)-W(5)-O(14)	77.2 (4)	W(6)-W(3)-O(4)	134.9 (5)
O(2)-W(1)-O(10)	103.6 (6)	W(1)-W(4)-O(5)	135.4 (5)	O(1)-W(5)-O(17)	77.0 (4)	W(6)-W(3)-O(8)	79.2 (4)
O(2)-W(1)-O(11)	102.8 (6)	W(1)-W(4)-O(9)	30.5 (3)	O(1)-W(5)-O(18)	75.3 (4)	W(6)-W(3)-O(12)	80.1 (4)
O(8)-W(1)-O(9)	87.4 (5)	W(1)-W(4)-O(13)	120.0 (4)	O(6)-W(5)-O(10)	103.7 (6)	W(6)-W(3)-O(16)	120.6 (4)
O(8)-W(1)-O(10)	152.1 (5)	W(1)-W(4)-O(16)	80.6 (4)	O(6)-W(5)-O(14)	103.0 (6)	W(6)-W(3)-O(19)	31.1 (4)
O(8)-W(1)-O(11)	86.1 (5)	W(1)-W(4)-O(17)	79.7 (3)	O(6)-W(5)-O(17)	103.1 (6)	O(1)-W(3)-O(4)	178.2 (5)
O(9)-W(1)-O(10)	86.6 (5)	W(2)-W(4)-W(3)	60.03 (2)	O(6)-W(5)-O(18)	104.7 (6)	O(1)-W(3)-O(8)	75.1 (4)
O(9)-W(1)-O(11)	152.6 (5)	W(2)-W(4)-W(5)	59.69 (2)	O(10)-W(5)-O(14)	153.4 (5)	O(1)-W(3)-O(12)	75.8 (5)
O(10)-W(1)-O(11)	86.8 (5)	W(2)-W(4)-O(1)	45.4 (2)	O(10)-W(5)-O(17)	85.7 (5)	O(1)-W(3)-O(16)	75.6 (4)
W(3)-W(2)-W(4)	60.09 (2)	W(2)-W(4)-O(5)	134.6 (5)	O(10)-W(5)-O(18)	87.6 (5)	O(1)-W(3)-O(19)	76.1 (5)
W(3)-W(2)-W(5)	90.10 (2)	W(2)-W(4)-O(9)	120.4 (3)	O(14)-W(5)-O(17)	87.1 (5)	O(4)-W(3)-O(8)	106.7 (6)
W(3)-W(2)-W(6)	59.95 (2)	W(2)-W(4)-O(13)	30.0 (4)	O(14)-W(5)-O(18)	86.9 (5)	O(17)-W(5)-O(18)	152.2 (5)
W(3)-W(2)-O(1)	45.3 (2)	W(2)-W(4)-O(16)	80.4 (4)	W(5)-W(6)--O(15)	79.4 (4)	W(1)-W(6)-W(2)	89.66 (3)
W(3)-W(2)-O(3)	136.1 (5)	W(2)-W(4)-O(17)	80.4 (3)	W(5)-W(6)-O(18)	31.1 (4)	W(1)-W(6)-W(3)	59.96 (2)
W(3)-W(2)-O(12)	30.6 (4)	W(3)-W(4)-W(5)	89.72 (3)	W(5)-W(6)-O(19)	120.8 (4)	W(1)-W(6)-W(5)	59.96 (2)
W(3)-W(2)-O(13)	79.3 (4)	W(3)-W(4)-O(1)	45.3 (2)	O(1)-W(6)-O(7)	178.6 (6)	W(1)-W(6)-O(1)	44.5 (2)
W(3)-W(2)-O(14)	121.0 (3)	W(3)-W(4)-O(5)	134.5 (5)	O(1)-W(6)-O(11)	75.2 (4)	W(1)-W(6)-O(7)	134.1 (5)
W(3)-W(2)-O(15)	79.9 (4)	W(3)-W(4)-O(9)	79.7 (3)	O(1)-W(6)-O(15)	75.1 (4)	W(1)-W(6)-O(11)	30.7 (3)
W(4)-W(2)-W(5)	60.28 (2)	W(3)-W(4)-O(13)	79.2 (4)	O(1)-W(6)-O(18)	75.7 (4)	W(1)-W(6)-O(15)	119.7 (4)
W(4)-W(2)-W(6)	90.15 (2)	W(3)-W(4)-O(16)	31.4 (4)	O(1)-W(6)-O(19)	76.1 (5)	W(1)-W(6)-O(18)	80.5 (4)
W(4)-W(2)-O(1)	45.3 (2)	W(3)-W(4)-O(17)	120.9 (3)	O(7)-W(6)-O(11)	103.4 (6)	W(1)-W(6)-O(19)	80.3 (4)
W(4)-W(2)-O(3)	134.2 (5)	W(5)-W(4)-O(1)	44.5 (2)	O(7)-W(6)-O(15)	106.3 (6)	W(2)-W(6)-W(3)	59.91 (2)
W(4)-W(2)-O(12)	79.7 (4)	W(5)-W(4)-O(5)	135.8 (5)	O(7)-W(6)-O(18)	104.6 (6)	W(2)-W(6)-W(5)	59.67 (2)
W(4)-W(2)-O(13)	30.1 (4)	W(5)-W(4)-O(9)	80.0 (3)	O(7)-W(6)-O(19)	103.6 (7)	W(2)-W(6)-O(1)	45.1 (2)
W(4)-W(2)-O(14)	80.0 (3)	W(5)-W(4)-O(13)	79.5 (4)	O(11)-W(6)-O(15)	150.4 (5)	W(2)-W(6)-O(7)	136.3 (5)
W(4)-W(2)-O(15)	121.3 (4)	W(5)-W(4)-O(16)	121.2 (4)	O(11)-W(6)-O(18)	86.8 (5)	W(2)-W(6)-O(11)	120.4 (3)
W(5)-W(2)-W(6)	59.96 (2)	W(5)-W(4)-O(17)	31.2 (3)	O(11)-W(6)-O(19)	87.3 (5)	W(2)-W(6)-O(15)	30.0 (4)

Table III (*Continued*)

Interbond Angles (Deg)

W(5)-W(2)-O(1)	44.8 (2)	O(1)-W(4)-O(5)	179.8 (5)	O(15)-W(6)-O(18)	86.0 (5)	W(2)-W(6)-O(18)	79.6 (4)
W(5)-W(2)-O(3)	133.8 (5)	O(1)-W(4)-O(9)	75.1 (4)	O(15)-W(6)-O(19)	85.6 (5)	W(2)-W(6)-O(19)	79.8 (4)
W(5)-W(2)-O(12)	120.7 (4)	O(1)-W(4)-O(13)	75.4 (4)	O(18)-W(6)-O(19)	151.8 (5)	W(3)-W(6)-W(5)	89.91 (3)
W(5)-W(2)-O(13)	80.1 (4)	O(1)-W(4)-O(16)	76.7 (4)	W(1)-O(1)-W(2)	179.3 (5)	W(3)-W(6)-O(1)	45.3 (2)
W(5)-W(2)-O(14)	31.0 (3)	O(1)-W(4)-O(17)	75.7 (4)	W(1)-O(1)-W(3)	90.1 (3)	W(3)-W(6)-O(7)	134.4 (5)
W(5)-W(2)-O(15)	80.5 (4)	O(5)-W(4)-O(9)	104.9 (6)	W(1)-O(1)-W(4)	90.1 (3)	W(3)-W(6)-O(11)	80.1 (3)
W(6)-W(2)-O(1)	44.9 (2)	O(5)-W(4)-O(13)	104.6 (6)	W(1)-O(1)-W(5)	90.8 (3)	W(3)-W(6)-O(15)	79.1 (4)
W(6)-W(2)-O(3)	135.6 (5)	O(5)-W(4)-O(16)	103.1 (6)	W(1)-O(1)-W(6)	90.5 (3)	W(3)-W(6)-O(18)	121.0 (4)
W(6)-W(2)-O(12)	80.0 (4)	O(5)-W(4)-O(17)	104.6 (6)	W(2)-O(1)-W(3)	89.4 (3)	W(3)-W(6)-O(19)	30.9 (4)
W(6)-W(2)-O(13)	120.2 (4)	O(9)-W(4)-O(13)	150.5 (5)	W(2)-O(1)-W(4)	89.4 (3)	W(5)-W(6)-O(1)	44.6 (2)
W(6)-W(2)-O(14)	80.4 (3)	O(9)-W(4)-O(16)	86.6 (5)	W(2)-O(1)-W(5)	89.6 (3)	W(5)-W(6)-O(7)	135.6 (5)
						W(5)-W(6)-O(11)	79.7 (3)

Table IV. Final Atomic Positional and Thermal Parameters[a-c]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.733 70 (7)	0.345 60 (3)	0.251 33 (5)	0.006 65 (7)	0.001 31 (1)	0.002 60 (3)	−0.000 47 (5)	−0.002 05 (8)	−0.000 82 (3)
W(2)	0.524 93 (9)	0.340 11 (3)	0.007 93 (5)	0.009 23 (9)	0.001 76 (1)	0.002 32 (3)	0.000 61 (6)	−0.002 29 (9)	0.000 48 (4)
W(3)	0.783 03 (8)	0.376 81 (3)	0.071 64 (6)	0.007 93 (8)	0.001 25 (1)	0.004 73 (4)	−0.001 15 (5)	0.004 88 (10)	0.000 45 (5)
W(4)	0.719 58 (8)	0.282 24 (3)	0.102 80 (5)	0.008 87 (8)	0.000 94 (1)	0.003 91 (4)	0.001 04 (5)	−0.000 69 (10)	−0.001 04 (3)
W(5)	0.475 37 (7)	0.309 62 (3)	0.187 11 (5)	0.006 51 (7)	0.001 15 (1)	0.003 13 (3)	−0.001 77 (5)	0.000 35 (8)	0.000 25 (3)
W(6)	0.539 35 (8)	0.403 95 (3)	0.156 54 (6)	0.008 93 (8)	0.000 84 (1)	0.005 38 (4)	0.001 21 (5)	0.003 28 (10)	0.000 10 (4)
W(7)	0.304 30 (7)	0.377 59 (2)	0.720 83 (4)	0.005 97 (6)	0.000 67 (1)	0.001 72 (2)	0.000 41 (4)	−0.000 19 (7)	−0.000 24 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.629 (1)	0.3430 (3)	0.1307 (6)	2.9 (2)	O(17)	0.577 (1)	0.2672 (4)	0.1563 (8)	5.2 (3)
O(2)	0.808 (1)	0.3478 (5)	0.3399 (10)	7.1 (4)	O(18)	0.435 (1)	0.3656 (4)	0.1957 (8)	5.2 (3)
O(3)	0.447 (2)	0.3370 (5)	−0.0811 (11)	8.2 (5)	O(19)	0.680 (1)	0.4187 (5)	0.1038 (9)	6.4 (4)
O(4)	0.893 (2)	0.4015 (5)	0.0257 (11)	8.3 (5)	O(20)	0.627 (3)	0.0794 (9)	0.8441 (19)	16.7 (10)
O(5)	0.787 (2)	0.2376 (5)	0.0820 (10)	7.5 (4)	N(1)	0.402 (1)	0.3646 (5)	0.5448 (10)	4.4 (4)
O(6)	0.362 (1)	0.2850 (5)	0.2291 (10)	7.3 (4)	C(28)	0.566 (2)	0.2685 (6)	0.756 (1)	3.8 (4)
O(7)	0.477 (2)	0.4481 (6)	0.1771 (11)	8.3 (5)	C(29)	0.581 (2)	0.2463 (6)	0.677 (1)	4.9 (5)
O(8)	0.834 (1)	0.3727 (4)	0.1819 (8)	5.2 (3)	C(30)	0.679 (2)	0.2913 (7)	0.783 (1)	6.5 (6)
O(9)	0.785 (1)	0.2971 (4)	0.2057 (8)	4.7 (3)	C(31)	0.532 (2)	0.2406 (7)	0.820 (1)	5.2 (5)
O(10)	0.589 (1)	0.3176 (4)	0.2735 (8)	4.5 (3)	C(32)	0.221 (4)	0.5056 (12)	0.599 (2)	13.9 (13)
O(11)	0.642 (1)	0.3933 (4)	0.2498 (8)	5.0 (3)	C(33)	0.222 (4)	0.4995 (14)	0.512 (3)	16.9 (16)
O(12)	0.669 (1)	0.3673 (5)	−0.0135 (9)	6.4 (4)	C(34)	0.320 (5)	0.5280 (16)	0.634 (3)	19.1 (18)
O(13)	0.619 (1)	0.2931 (4)	0.0121 (9)	5.4 (3)	C(35)	0.136 (6)	0.5190 (22)	0.637 (4)	28.3 (32)
O(14)	0.422 (1)	0.3132 (4)	0.0792 (8)	4.9 (3)	C(36)	0.628 (4)	0.0899 (13)	0.774 (3)	15.6 (15)
O(15)	0.475 (1)	0.3886 (5)	0.0518 (9)	6.1 (4)	C(37)	0.620 (4)	0.1352 (12)	0.761 (2)	13.5 (12)
O(16)	0.824 (1)	0.3205 (4)	0.0619 (9)	5.5 (3)	C(38)	0.629 (4)	0.0627 (13)	0.701 (3)	14.6 (13)

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant digit for each parameter. [c] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

distorted than that of the corresponding molybdenum complex which has very nearly C_{2v} symmetry. This distortion is illustrated in Figure 2. Other features of the structure of this cation are relatively normal. Thus, the dimensions of the *tert*-butyl isocyanide ligands are comparable to related parameters in both $(t\text{-}C_4H_9)_7Mo^{2+}$ and $(t\text{-}C_4H_9)_6MoI^+$.

An alternative description of the geometry of the $W[CNC(CH_3)_3]_7^{2+}$ ion deserves mention. Lippard and coworkers have recently argued that the structure of the complex $W[CNC(CH_3)_3]_3(CO)_2I_2$ is best described as a 4:3 "piano stool". The criterion for this assignment rests on a comparison of the ideal and observed dihedral angles (δ') for each structure as discussed by Muetterties and Guggenberger.[14] On the basis of such considerations it could be argued that the 4:3 piano stool is an alternative and perhaps more accurate description of the geometry of $W[CNC(CH_3)_3]_4^{2+}$. Such an assignment, however, is not without criticism.[3] Additional structural studies of heptaleptic complexes are needed to determine how meaningful such distinctions are between so closely related polyhedra.

The origin and the structure of the anion $W_6O_{19}^{2-}$ merit comment. A single-crystal X-ray structure determination of the $W_6O_{19}^{2-}$ anion was recently reported in two independent investigations.[10,11] Both determinations report a centrosymmetric structure in which the W atoms are octahedrally arranged about a central oxygen atom. In addition, each W atom is also bonded to four bridging oxygens and one terminal oxo ligand, ensuring octahedral coordination about each metal center. The dimensions observed in this work are listed in Table III. They describe a structure of nearly perfect octahedral symmetry.

The production of hexatungstate in the reaction of $K_3W_2Cl_9$ with *tert*-butyl isocyanide is surprising, since neither reagent contains any source of oxygen. However, the preparation of *tert*-butyl isocyanide[6] suggested possible contamination with water. Indeed, when extraordinary precautions were taken to remove traces of water from the *tert*-butyl isocyanide, no reaction with $K_3W_2Cl_9$ was observed.

In a previous study[12] we described the reaction of selected dinuclear molybdenum complexes with pyridine. Depending upon reaction conditions, dinuclear $Mo_2X_4(py)_4$ or mononuclear *mer*-$MoX_3(py)_3$ products resulted. However, treatment of $K_3W_2Cl_9$ with pyridine appears to produce only the dinuclear complex $W_2Cl_6(py)_4$.[5] Since the reaction of $K_3W_2Cl_9$ with *tert*-butyl isocyanide results in the rupture of the tungsten–tungsten bond, it seemed reasonable to expect that similar treatment of the dinuclear molybdenum complexes $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$ with *tert*-butyl isocyanide would produce the corresponding mononuclear complex heptakis(*tert*-butyl isocyanide)molybdenum(II). Indeed, we have observed that reaction of either $Mo_2X_9^{3-}$ or $Mo_2X_8H^{3-}$ with *tert*-butyl isocyanide under conditions comparable to those employed for

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$W_2Cl_9^{3-}$ produced high (~80%) yields of the heptakis(*tert*-butyl isocyanide)molybdenum(II) cation, isolated as its PF_6^- salt.[13]

$$\mathrm{Mo_2X_8H^{3-}} \xrightarrow[70\ ^\circ\mathrm{C},\ 8\ \mathrm{h}]{t\text{-}\mathrm{C_4H_9NC}} (t\text{-}\mathrm{C_4H_9NC})_7\mathrm{Mo}^{2+} \xleftarrow[70\ ^\circ\mathrm{C},\ 8\ \mathrm{h}]{t\text{-}\mathrm{C_4H_9NC}} \mathrm{Mo_2X_9^{3-}}$$

Conclusions

The reaction of tripotassium enneachloroditungstate with *tert*-butyl isocyanide, when carried out in the presence of a small amount of water, produces heptakis(*tert*-butyl isocyanide)tungsten(II) hexatungstate, $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$. The cation exhibits distorted capped trigonal-prismatic geometry, similar to that observed for several other heptaleptic complexes. The ready synthesis of this ion provides a unique opportunity to examine the chemical and dynamic properties of cationic tungsten(II) and, in particular, to explore its utility as a precursor to complexes of monuclear tungsten(III). Such studies are currently underway.

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Registry No. $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$, 72016-74-1; $K_3W_2Cl_9$, 23403-17-0.

Supplementary Material Available: Thermal parameters and observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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[13] Established by a comparison of the single-crystal X-ray crystallographic parameters of this material with those reported for $[(t\text{-}C_4H_9NC)_7Mo][PF_6]_2$.

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Structural Characterization of Two Tetrakis(μ-carbonato) Complexes of Dirhodium(II)

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The presence of the dinuclear $Rh_2(CO_3)_4^{4-}$ unit has been confirmed by using X-ray crystallography for the following two complexes of rhodium(II): $Cs_4[Rh_2(CO_3)_4(H_2O)_2]\cdot 6H_2O$ (**1**) and $Cs_4Na_2[Rh_2(CO_3)_4Cl_2]\cdot 8H_2O$ (**2**). Both compounds crystallize in the space group $P2_1/c$ with two formula weights in unit cells having the dimensions $a = 7.867$ (1) Å, $b = 7.963$ (1) Å, $c = 18.211$ (2) Å, $\beta = 91.83$ (1)°, and $V = 1140.2$ (3) Å^3 and $a = 9.798$ (2) Å, $b = 10.753$ (2) Å, $c = 12.906$ (3) Å, $\beta = 107.98$ (2)°, and $V = 1293.2$ (4) Å^3 for **1** and **2**, respectively. The structure of **1** was refined by using 1833 reflections with $I > 3\sigma(I)$ to final discrepancy indices of $R_1 = 0.051$ and $R_2 = 0.070$, while the structure of **2** converged with $R_1 = 0.037$ and $R_2 = 0.050$ for 1266 reflections with $I > 3\sigma(I)$. The $Rh_2(CO_3)_4^{4-}$ unit in **1** is located on a crystallographic center of inversion with a Rh–Rh distance of 2.378 (1) Å. Two water molecules occupy the axial positions with a Rh–O distance of 2.344 (5) Å. Compound **2** also has the $Rh_2(CO_3)_4^{4-}$ unit located on a crystallographic center of inversion with a Rh–Rh bond distance of 2.380 (2) Å. The axial positions are occupied by Cl^- ions with a Rh–Cl distance of 2.601 (3) Å. The Cl^- ions are associated in an ionic fashion with the Na^+ ions in the lattice.

Introduction

The dirhodium(II) tetracarboxylates have recently attracted much interest,[1-4] largely due to the variety of axial ligands which form stable adducts. The effect of axial ligation invariably has been an overall weakening of the Rh–Rh bond[1,2] which has been formulated[4] as primarily a single bond. Our recent work[5] on the Rh_2^{4+} system has shown that a small but significant shortening of the Rh–Rh bond occurs when noncarboxylate bridging ligands such as 2-oxo-6-methylpyridine (mhp) are employed which eliminate axial interactions.

Another factor which can influence the metal–metal bond length in tetracarboxylate systems is the nature of the R group substituent of the carboxylate bridge. An extensive investigation of $Cr_2(O_2CR)_4L_2$-type compounds[6] has shown that the Cr–Cr distance decreases as the parent carboxylic acid becomes weaker and, thus, a better donor ligand. In this series of dichromium(II) carboxylates, the Cr–Cr bond length in the $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ anion was found to be significantly shorter than that in any carboxylate complex. Accordingly, it was of interest to prepare the analogous rhodium(II) complex and observe the effect of the carbonate ligand on the Rh–Rh bond length.

Several years ago, Wilson and Taube reported[7] the preparation and characterization via elemental analysis, infrared and electronic spectra, magnetic susceptibility, and electrochemistry of several carbonate complexes of rhodium(II). They concluded that the complexes most probably resembled the $Rh_2(OAc)_4(H_2O)_2$ complex[8] with bridging bidentate carbonate ligands. The work reported here confirms their expectations with the presentation in detail of the structures of two compounds containing the $Rh_2(CO_3)_4^{4-}$ unit.

Experimental Section

Compound Preparation. Rhodium(II) acetate was prepared by using an established procedure.[9] A sample of $Cs_4[Rh_2(CO_3)_4(H_2O)_2]\cdot 6H_2O$ (**1**) was prepared by using a procedure given by Wilson and Taube.[7] A 0.1-g sample of $Rh_2(O_2CCH_3)_4$ was suspended in 2–3 mL of an aqueous 2 M Cs_2CO_3 solution. The solution was heated to 100 °C for about 15 min. A microcrystalline dark blue solid formed. Suitable crystals were obtained by slow evaporation of the reaction mixture.

$Cs_4Na_2[Rh_2(CO_3)_4Cl_2]\cdot 8H_2O$ (**2**) was isolated from a solution containing $Na_4[Rh_2(CO_3)_4]\cdot xH_2O$ (prepared as per the Cs analogue)

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