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Preparation and Characterization of $NaW_2Cl_7(THF)_5$. A Synthetically Useful Precursor for $X_3W{\equiv}WX_3$ Compounds Where X = CH_2-*t*-Bu, NMe_2, and O-*t*-Bu

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From the addition of Na/Hg (1 equiv) to a WCl_4 slurry in THF (THF = tetrahydrofuran) was obtained the green crystalline compound $NaW_2Cl_7(THF)_5$ in 60–70% recrystallized yields. The compound has been shown to involve a confacial bioctahedral $W_2Cl_7(THF)_2^-$ anion coordinated to a $(THF)_3Na^+$ cation via two chloride ligands that are terminally bonded to W atoms. The W–W distance 2.4028 (15) Å is essentially identical with that seen in other $W_2X_9^{3-}$ anions (X = Cl or Br) and is indicative of strong t_{2g}^3–t_{2g}^3 M–M bonding. The compound provides a useful synthetic starting material for metathetic reactions involving Li–X leading to the known $X_3W{\equiv}WX_3$ compounds where X = CH_2-*t*-Bu, NMe_2, and O-*t*-Bu. The latter are obtained in 60–80% yield based on W by either sublimation or crystallization. The compound $NaW_2Cl_7(THF)_5$ bears a striking similarity in terms of both its preparation and its reactivity to the compound formulated as $W_2Cl_6(THF)_4$ by Schrock, Sturgeoff, and Sharp,[4b] though it is not presently known how the two are related. Crystal data for $NaW_2Cl_7(THF)_5$ at –151 °C: a = 18.817 (7) Å, b = 8.397 (3) Å, c = 20.964 (10) Å, β = 107.09 (3)°, Z = 4, V = 3166.2 (1) Å^3, d_{calcd} = 2.097 g cm^{-3}, space group $P2_1/c$.

Introduction

Central to the development of the chemistry of the $(M{\equiv}M)^{6+}$ unit where M = Mo and W[1] have been the syntheses of the compounds $M_2(NMe_2)_6$ and $M_2(OR)_6$. For molybdenum the metathetic reaction shown in eq 1 works well, and subsequent

$$2MoCl_3 + 6LiNMe_2 \xrightarrow[\text{hexane/Et}_2\text{O}]{0\ ^\circ\text{C}} Mo_2(NMe_2)_6 + 6LiCl \quad (1)$$

alcoholyses of the dinuclear molybdenum amide complex proceed readily to give $Mo_2(OR)_6$ compounds.

For tungsten the lack of a simple halide of empirical formula WX_3 has caused problems since reactions involving WCl_4 and $LiNMe_2$ invariably lead to mixtures of $W_2(NMe_2)_6$ and $W(NMe_2)_6$. Though these mixtures contain more W(III) d^3–d^3 dinuclear compound than would be anticipated from a simple disproportionation reaction [3W(IV) → 2W(III) + W(VI)], the synthetic utility of preparing $W_2(NMe_2)_6$ in this manner is compromised by the cocrystallization of 1:1 mixtures of $W_2(NMe_2)_6$ and $W(NMe_2)_6$ from hydrocarbon solutions.[2] Although the purification of $W_2(NMe_2)_6$ is inefficient and time-consuming, the chemistry derived by this compound is unusually rich. For example, certain alcoholysis reactions employing $W_2(NMe_2)_6$ lead to a wide variety of products depending upon the details of the reaction conditions; e.g.,[3] with *i*-PrOH one may obtain any one or more of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$, $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$, and $W_4(O\text{-}i\text{-}Pr)_{12}$.

When Schrock, Sturgeoff, and Sharp[4] described the stepwise reduction of WCl_4 by Na/Hg amalgam in THF according to eq 2, we were attracted to the utility of the green crystalline compound $W_2Cl_6(THF)_4$ as a precursor for $X_3W{\equiv}WX_3$ compounds.

$$2WCl_4 + 2Na/Hg \xrightarrow[\text{THF}]{} W_2Cl_6(THF)_4 + 2NaCl \quad (2i)$$

$$W_2Cl_6(THF)_4 + 2Na/Hg + 2NaCl \xrightarrow[\text{THF}]{} Na_4W_2Cl_8(THF)_x \quad (2ii)$$

Indeed it was noted[5] that $W_2Cl_6(THF)_4$ reacts with LiO-*t*-Bu to give $W_2(O\text{-}t\text{-}Bu)_6$, a compound previously well characterized in this laboratory but formerly prepared by the addition of *t*-BuOH to $W_2(NMe_2)_6$.[6]

In principle it is possible to prepare $W_2Cl_6(THF)_4$ according to eq 2i and then add LiO-*t*-Bu (6 equiv) to obtain a one-pot synthesis of $W_2(O\text{-}t\text{-}Bu)_6$. This one-pot reaction has been carried out many times in this laboratory, but the resulting $W_2(O\text{-}t\text{-}Bu)_6$ is invariably contaminated with LiCl and THF. Thus it became desirable to develop a high-yield synthesis of sublimable $W_2(NMe_2)_6$ that could be quantitatively converted into $W_2(O\text{-}t\text{-}Bu)_6$, free of LiCl or THF impurities. During the course of our studies, we have discovered a high-yield synthesis of the relatively air-stable compound $NaW_2Cl_7(THF)_5$ and show here that this is indeed a useful precursor for $X_3W{\equiv}WX_3$ compounds. It is not entirely clear how this compound relates to $W_2Cl_6(THF)_4$ reported by Schrock, except in the obvious way that it contains an added equivalent of NaCl together with an additional molecule of THF of solvation. We describe here our synthesis and characterization of the new compound, compare our procedure with that outlined by Schrock et al.,[4] and note its utility in the preparation of the known compounds $X_3W{\equiv}WX_3$ where X = CH_2-*t*-Bu, NMe_2, and O-*t*-Bu.[1]

Results and Discussion

Synthesis. The original description of the preparation of $W_2Cl_6(THF)_4$ involved the addition of WCl_4 to Na/Hg in THF.[4b,7] In an attempt to obviate problems associated with overreduction followed by subsequent redox reactions, we have chosen to change the order of addition so that Na/Hg liquid amalgam (1 equiv) is added to a slurry of WCl_4 in THF. It is also worth noting that our preparation of WCl_4 employs the phosphorus reduction of WCl_6 carried out in an evacuated tube.[8] This has the advantage that any $WOCl_4$, WO_2Cl_2, and WCl_5 are removed along with PCl_3 upon vacuum distillation/sublimation, leading to the residual nonvolatile WCl_4.

Following the slow addition of the Na/Hg solution, a deep green solution resulted above the mercury and other solids (some NaCl). The solution was collected by use of a cannula and filtered through Celite. The solids were washed with additional THF, and the filtrate was collected and reduced in volume by vacuum distillation of the THF solvent to yield a dark green oil. Crystallization of the oil, followed by recrystallization from THF, yielded $NaW_2Cl_7(THF)_5$ as dark green needles or cubes in greater than 60% yield. The compound is air-stable in the crystalline state, at least

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(1) Chisholm, M. H.; *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 21. Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356 and references therein.

(2) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

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(4) (a) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430. (b) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801.

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(7) There is a contradiction in ref 4b between the Results and the Experimental Section concerning the number of equivalents of Na/Hg used in the reduction of WCl_4 to give $W_2Cl_6(THF)_4$. In the Experimental Section $W_2Cl_6(THF)_4$ was prepared from a reaction employing WCl_4 (13 g, 40 mmol) and sodium amalgam (80 mmol). We believe the latter statement is in error since 2 equiv of Na/Hg leads to the blue, thermally unstable compound formulated as $Na_4W_2Cl_8(THF)_4$.

(8) Novikou, G. I.; Andreeva, W. V.; Polyachenok, O. G. *Zh. Neorg. Khim.* **1961**, *6*, 1990.

Table I. Summary of Crystal Data for the $NaW_2Cl_7(THF)_5$ Molecule

empirical formula	$W_2Cl_7NaO_5C_{20}H_{40}$
color of cryst	greenish yellow
cryst dimens, mm	0.10 × 0.12 × 0.18
space group	$P2_1/c$
cell dimens	
temp, °C	−151
a, Å	18.817 (7)
b, Å	8.397 (3)
c, Å	20.964 (10)
β, deg	107.09 (3)
Z, molecules/cell	4
vol, Å^3	3166.23
calcd density, g/cm^3	2.097
wavelength, Å	0.71069
mol wt	999.39
linear abs coeff, cm^{-1}	80.562
detector-to-sample dist, cm	22.5
sample-to-source dist, cm	23.5
av ω-scan width at half-height	0.25
scan speed, deg/min	6.0
scan width, deg + dispersion	1.2
individual bkgd, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
total no. of reflcns collected	5166
no. of unique intensities	4149
no. of reflcns with $F > 3.00\sigma(F)$	3125
$R(F)$	0.0581
$R_w(F)$	0.0572
goodness of fit for last cycle	1.060
max Δ/σ for last cycle	0.05

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $NaW_2Cl_7(THF)_5$ Molecule

atom	10^4x	10^4y	10^4z	B_{iso}, Å^2
W(1)	3078.2 (4)	6041 (1)	4685.4 (4)	13
W(2)	1742.2 (4)	6066 (1)	4335.3 (4)	15
Cl(3)	2401 (3)	4129 (6)	5200 (2)	21
Cl(4)	2411 (2)	5067 (6)	3555 (2)	18
Cl(5)	2423 (2)	8558 (6)	4717 (2)	19
Cl(6)	3771 (2)	6682 (6)	5809 (2)	18
Cl(7)	3822 (3)	7557 (6)	4161 (2)	18
Cl(8)	1085 (3)	6725 (7)	5114 (3)	24
Cl(9)	1018 (3)	7596 (7)	3420 (3)	27
O(10)	3798 (6)	4016 (16)	4728 (6)	17
C(11)	4139 (12)	3036 (27)	5316 (10)	27
C(12)	4216 (11)	1451 (21)	5022 (11)	24
C(13)	4437 (10)	1918 (25)	4424 (10)	20
C(14)	4039 (16)	3419 (31)	4189 (13)	46
O(15)	1013 (6)	4058 (17)	3986 (6)	20
C(16)	216 (13)	4188 (33)	3899 (13)	40
C(17)	−102 (13)	2729 (36)	3509 (13)	44
C(18)	466 (15)	1652 (32)	3600 (22)	86
C(19)	1195 (15)	2506 (31)	3773 (14)	46
Na(20)	2413 (4)	7838 (9)	6123 (4)	22
O(21)	2511 (8)	5971 (19)	6930 (7)	30
C(22)	2245 (13)	6070 (29)	7498 (11)	34
C(23)	2539 (14)	4636 (29)	7944 (12)	38
C(24)	3207 (14)	4194 (25)	7710 (11)	31
C(25)	2951 (13)	4566 (29)	6980 (12)	35
O(26)	1605 (8)	9854 (19)	6205 (7)	33
C(27)	1191 (16)	10770 (30)	5666 (13)	46
C(28)	938 (15)	12261 (33)	5924 (15)	49
C(29)	1018 (12)	11837 (35)	6644 (13)	44
C(30)	1603 (14)	10566 (29)	6823 (12)	36
O(31)	3340 (8)	9507 (17)	6857 (7)	27
C(32)	3905 (13)	8936 (31)	7463 (10)	36
C(33)	4573 (15)	9915 (34)	7546 (14)	51
C(34)	4519 (14)	10404 (36)	6879 (13)	47
C(35)	3713 (13)	10540 (24)	6538 (11)	31

for short periods, though we have routinely handled it using standard procedures for air-sensitive materials. It is virtually insoluble in hydrocarbon solvents such as toluene and benzene, sparingly soluble in CH_2Cl_2 and $CHCl_3$, but appreciably soluble in THF.

Table III. Selected Bond Distances (Å) for the $NaW_2Cl_7(THF)_5$ Molecule

W(1)–W(2)	2.4028 (15)	W(2)–Cl(5)	2.461 (5)
W(1)–Cl(3)	2.485 (5)	W(2)–Cl(8)	2.384 (5)
W(1)–Cl(4)	2.473 (5)	W(2)–Cl(9)	2.378 (5)
W(1)–Cl(5)	2.458 (5)	W(2)–O(15)	2.162 (13)
W(1)–Cl(6)	2.394 (5)	Cl(6)–Na(20)	2.982 (9)
W(1)–Cl(7)	2.386 (5)	Cl(8)–Na(20)	2.913 (9)
W(1)–O(10)	2.159 (12)	Na(20)–O(21)	2.274 (16)
W(2)–Cl(3)	2.480 (5)	Na(20)–O(26)	2.315 (16)
W(2)–Cl(4)	2.485 (5)	Na(20)–O(31)	2.407 (16)

Table IV. Selected Bond Angles (deg) for the $NaW_2Cl_7(THF)_5$ Molecule

W(2)–W(1)–Cl(3)	60.94 (12)	W(1)–W(2)–Cl(9)	123.46 (14)
W(2)–W(1)–Cl(4)	61.26 (11)	W(1)–W(2)–O(15)	126.9 (3)
W(2)–W(1)–Cl(5)	60.83 (11)	Cl(3)–W(2)–Cl(4)	91.10 (16)
W(2)–W(1)–Cl(6)	121.11 (12)	Cl(3)–W(2)–Cl(5)	102.68 (16)
W(2)–W(1)–Cl(7)	123.88 (12)	Cl(3)–W(2)–Cl(8)	84.26 (18)
W(2)–W(1)–O(10)	127.3 (3)	Cl(3)–W(2)–Cl(9)	171.65 (18)
Cl(3)–W(1)–Cl(4)	91.27 (16)	Cl(3)–W(2)–O(15)	82.4 (4)
Cl(3)–W(1)–Cl(5)	102.62 (16)	Cl(4)–W(2)–Cl(5)	100.68 (16)
Cl(3)–W(1)–Cl(6)	85.32 (17)	Cl(4)–W(2)–Cl(8)	173.69 (18)
Cl(3)–W(1)–Cl(7)	171.91 (17)	Cl(4)–W(2)–Cl(9)	86.10 (17)
Cl(3)–W(1)–O(10)	82.5 (3)	Cl(4)–W(2)–O(15)	84.7 (3)
Cl(4)–W(1)–Cl(5)	101.11 (16)	Cl(5)–W(2)–Cl(8)	84.56 (17)
Cl(4)–W(1)–Cl(6)	173.57 (17)	Cl(5)–W(2)–Cl(9)	85.59 (18)
Cl(4)–W(1)–Cl(7)	86.34 (16)	Cl(5)–W(2)–O(15)	172.4 (3)
Cl(4)–W(1)–O(10)	85.1 (3)	Cl(8)–W(2)–Cl(9)	97.90 (19)
Cl(5)–W(1)–Cl(6)	84.98 (16)	Cl(8)–W(2)–O(15)	90.4 (3)
Cl(5)–W(1)–Cl(7)	85.43 (17)	Cl(9)–W(2)–O(15)	89.5 (4)
Cl(5)–W(1)–O(10)	171.8 (4)	W(1)–Cl(3)–W(2)	57.90 (11)
Cl(6)–W(1)–Cl(7)	96.30 (17)	W(1)–Cl(4)–W(2)	57.98 (11)
Cl(6)–W(1)–O(10)	89.0 (3)	W(1)–Cl(5)–W(2)	58.48 (11)
Cl(7)–W(1)–O(10)	89.6 (3)	W(1)–Cl(6)–Na(20)	92.09 (20)
W(1)–W(2)–Cl(3)	61.16 (11)	W(2)–Cl(8)–Na(20)	93.72 (21)
W(1)–W(2)–Cl(4)	60.75 (11)	Cl(6)–Na(20)–Cl(8)	110.05 (28)
W(1)–W(2)–Cl(5)	60.70 (11)	Cl(6)–Na(20)–O(21)	93.0 (4)
W(1)–W(2)–Cl(8)	119.97 (13)	Cl(6)–Na(20)–O(26)	151.4 (6)

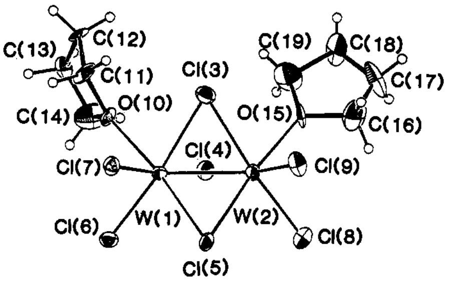


Figure 1. ORTEP view of the $W_2Cl_7(THF)_2^-$ ion.

Solid-State and Molecular Structure. $NaW_2Cl_7(THF)_5$ crystallizes from THF solutions in two different morphologies. Long green needles are formed when crystallization is fairly fast whereas upon very slow crystallization large cubes are formed. Both types of crystals have been examined by X-ray crystallography and have the same space group and unit cell dimensions. A summary of crystal data is given in Table I, and atomic positional parameters are given in Table II. Listings of pertinent bond distances and angles are given in Tables III and IV, respectively.

Three stereoviews of the molecule are given in the supplementary material. The local geometry about each tungsten atom is slightly distorted from octahedral, and the two tungsten atoms share a common face formed by three bridging chloride ligands. The compound may be viewed as the sum of a $Na(THF)_3^+$ cation bonded to a $W_2Cl_7(THF)_2^-$ anion through the agency of two chloride ligands, Cl(6) and Cl(8), which are terminally bonded to the tungsten atoms W(1) and W(2), respectively. The local geometry of the formal $W_2Cl_7(THF)_2^-$ anion is shown in Figure 1, while the geometry about the Na^+ ion is shown in Figure 2. The angles about the Na^+ ion are indicative of a distorted square-based pyramidal geometry in which the two chloride ligands and two oxygen atoms from two molecules of THF occupy the basal positions.

There are some interesting comparisons to be made with related compounds. First, the W–W distance is 2.4028 (15) Å, essentially

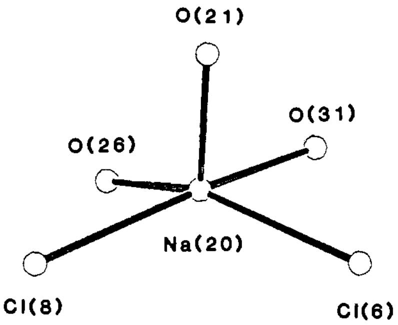


Figure 2. Ball-and-stick drawing of the coordination geometry about Na^+.

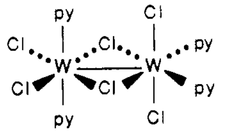
Table V. ^{23}Na NMR Data for a Series of Compounds in THF Solutions at 95.5 MHz

compd	δ	line width at half-height, Hz
$NaW_2Cl_7(THF)_5$	-2.01	90
$W_2H(O\text{-}i\text{-}Pr)_8Na(THF)_3$	0.377[a]	187[a]
$W_2H(OCH_2\text{-}t\text{-}Bu)_8Na(diglyme)$	-3.72[a]	249[a]
$Na(O\text{-}t\text{-}Bu)$	14.9	167
$NaBPh_4$	-5.30	43
NaCl[b]	0	11

[a] Smith, C. Ph.D. Thesis, Indiana University. [b] 0.1 M D_2O.

identical with that in the $W_2Cl_9^{3-}$ ion,[9] 2.409 (3) Å, indicative of a strong d^3–d^3 interaction between the t_{2g} sets of W atomic orbitals. This is formally a W–W triple bond but is somewhat longer than those distances found for $X_3W{\equiv}WX_3$ compounds, and is less easily described in terms of a pure M–M bonding picture. The second, and to us quite striking, comparison involves the recently characterized $NaW_2(H)(O\text{-}i\text{-}Pr)_8(diglyme)$ molecule.[3] Though the latter is a d^2–d^2 W(IV)–W(IV) dinuclear compound, the coordination of the $Na(diglyme)^+$ ion to the $W_2(H)(O\text{-}i\text{-}Pr)_8^-$ center is analogous in form to that seen in the present compound. Particularly noteworthy is that the W–X distances (X = Cl, O) fall in the order bridging > terminal and that ligation to the Na^+ ion causes an insignificant (within 3σ) lengthening of W–X bonds.

Last, we mention the comparison with the compound $W_2Cl_6(py)_4$, where py = pyridine, which was characterized at Indiana University many years ago.[10] The latter compound adopts the structure depicted by I and can be described as an edge-shared bioctahedral geometry, in contrast to the confacial bioctahedral geometry found for the $W_2Cl_7(THF)_2^-$ anion. In both there are t_{2g}^3–t_{2g}^3 interactions, but in the edge-shared bioctahedral geometry the overlap is poorer and is of a different symmetry type such that a limiting M–M description of $\sigma^2\pi^2\delta^2$ can be realized.[11] For example, the W–W distance in $W_2Cl_6(py)_4$, 2.737 (3) Å, is much longer than that seen in $NaW_2Cl_7(THF)_5$.



I

NMR and Conductivity Studies. The ^1H NMR spectrum of $NaW_2Cl_7(THF)_5$ shows only one type of THF molecule in $CDCl_3$ and CD_2Cl_2 even at -60 °C with chemical shifts very nearly the same as those observed for THF in CD_2Cl_2. When THF was added to the sample, the intensities of the signals were enhanced without affecting a change in the chemical shifts; i.e., exchange of free and coordinated THF molecules is rapid on the NMR time scale.

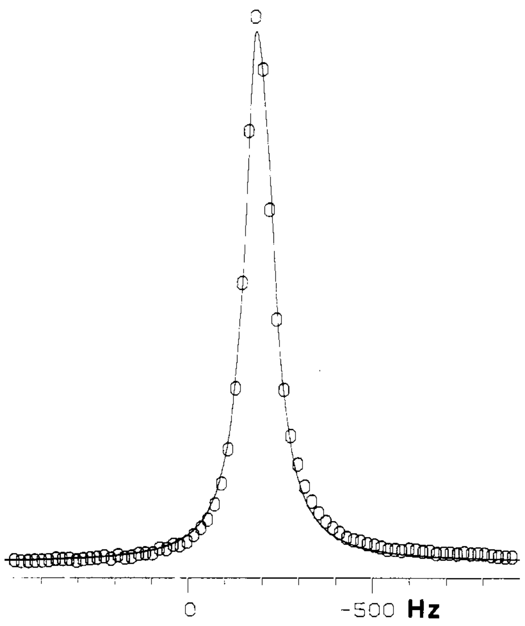


Figure 3. Simulated (—) and experimental (○) ^{23}Na spectra of $NaW_2Cl_7(THF)_5$ in THF at 95.5 MHz.

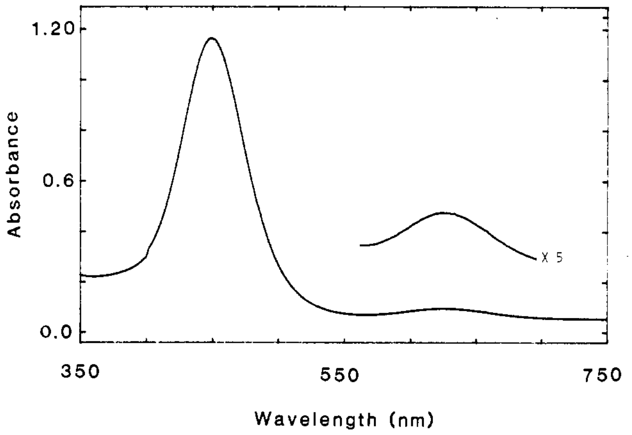


Figure 4. Electronic absorption spectrum of $NaW_2Cl_7(THF)_5$ in THF solution (3.1×10^{-4} M).

No magnetic moment could be detected by the Evans NMR method[12] in THF-d_8 at 22 °C.

The ^{23}Na NMR spectrum has been obtained in THF solutions and is shown in Figure 3. A line shape analysis has been used to simulate the spectrum and the width at half-height determined to be 90 Hz. Lazlo[13] has used the width of ^{23}Na signals in sodium salts as a measure of ion pairing. Table V reports some pertinent line width data for ^{23}Na signals from which we conclude that, in THF, $NaW_2Cl_7(THF)_5$ shows an ion-pairing intermediate between $NaBPh_4$ and $NaW_2(H)(O\text{-}i\text{-}Pr)_8(THF)_3$.[3] Furthermore, the conductivity of $NaW_2Cl_7(THF)_5$ in THF, 0.3 Ω^{-1} (3.6×10^{-2} M) and 0.6 Ω^{-1} (7.3×10^{-2} M), is significantly less than that of $NaBPh_4$ in THF at the same concentrations (20 and 40 Ω^{-1}, respectively). These data are consistent with expectations that the alkoxide complex, which is readily soluble in hexane, is essentially a covalent or mixed-metal alkoxide, while the present complex $NaW_2Cl_7(THF)_5$ shows behavior between a tight or contact ion pair and a separated ion pair in THF.

Electronic Absorption Spectra. The electronic absorption spectrum of $NaW_2Cl_7(THF)_5$ recorded in THF is shown in Figure 4. Spectra obtained in CH_2Cl_2 are virtually identical with those obtained in THF, aside from very slight shifts in λ_{max} values. These

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(9) Watson, W. H.; Waser, J. *Acta Crystallogr.* **1958**, *11*, 689.
(10) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.
(11) Other M–M configurations are also possible depending on the bridging ligand and the M–X–M angle. See: Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555. Chakravarty, A. R.; Cotton, F. A.; Diebold, M. P.; Lewis, D. B.; Weislaw, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 971.
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(13) Lazlo, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 254.

Table VI. Electronic Absorption Data for Selected d^3–d^3 Tungsten–Halide Dinuclear Compounds

compd		λ, nm	$\bar{\nu}$, cm^{-1}	ε, L mol^{-1} cm^{-1}	assignt[c]
$K_3W_2Cl_9$[a,b]		758	13 200	50	$e' \rightarrow e'$
		628	15 900	160	$a'_1 \rightarrow e'$
		457	21 900	4730	$a'_1 \rightarrow a'_2$
	sh	380	26 300	1200	
$K_3W_2Br_9$[b]		806	12 400	43	$e' \rightarrow e'$
		654	15 300	120	$a'_1 \rightarrow e'$
		493	20 300	28000	$a'_1 \rightarrow a'_2$
	sh	400	25 000	100	
$NaW_2Cl_7(THF)_5$		754	13 300	150	$e' \rightarrow e'$
		634	15 800	290	$a'_1 \rightarrow e'$
		450	22 200	3800	$a'_1 \rightarrow a'_2$
$W_2Cl_6(py)_4$	sh	847	11 800	130	
	sh	800	12 500	178	
		729	13 700	340	
		599	16 700	880	
		481	20 800	6300	
		379	26 400	11000	
		328	30 500	12500	
		294	34 000	16600	

[a] Reference 15a. [b] Hayden, J. L.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1968**, *90*, 5291. [c] Reference 14; $e' \rightarrow e' = \pi \rightarrow \pi^*$, $a'_1 \rightarrow e' = \sigma \rightarrow \pi^*$, $a'_1 \rightarrow a'_2 = \sigma \rightarrow \sigma^*$, under D_{3h} point symmetry.

spectra are remarkably similar to that reported for $W_2Cl_9^{3-}$, for which assignments have been suggested by Trogler.[14] The data are summarized in Table VI together with suggested assignments.

We believe the electronic absorption data indicate that $NaW_2Cl_7(THF)_5$ maintains the confacial bioctahedral W(III)–W(III) unit in solution. An edge-shared bioctahedral geometry with a longer W–W distance would undoubtedly result in a different spectrum, as is seen for $W_2Cl_6(py)_4$.[15]

Reactivity of $NaW_2Cl_7(THF)_5$. Metathetic reactions involving $LiNMe_2$, LiO-*t*-Bu, and $LiCH_2$-*t*-Bu have been carried out according to eq 3.

$$NaW_2Cl_7(THF)_5 + 6LiX \xrightarrow[THF]{0\ °C} X_3W{\equiv}WX_3 + 6LiCl + NaCl \quad (3)$$

The d^3–d^3 ethane-like dinuclear compounds W_2X_6 have been obtained in ca. 60–80% yield by either sublimation (X = NMe_2 and CH_2-*t*-Bu) or crystallization from hexane (X = O-*t*-Bu). These reactions represent significant improvements over alternate[2] syntheses. Particularly noteworthy in this regard is the high-yield synthesis of $W_2(NMe_2)_6$ that can be produced without $W(NMe_2)_6$ impurities. Nevertheless, a one-pot synthesis of $W_2(NMe_2)_6$ from the reduction of WCl_4 with Na/Hg amalgam followed by addition of $LiNMe_2$ is the most convenient and efficient method to obtain the highest overall yields (ca. 70% based on WCl_4) of pure $W_2(NMe_2)_6$. In addition, $W_2(CH_2\text{-}t\text{-}Bu)_6$, which previously had been prepared in *very* low yield from the reaction between WCl_6 and *t*-$BuCH_2MgX$ (and accordingly not well characterized),[16] can now be prepared in *high* yield. The direct synthesis of $W_2(O\text{-}t\text{-}Bu)_6$, according to eq 3, however, leads to a product contaminated with LiCl. Thus, the most efficient way of producing pure $W_2(O\text{-}t\text{-}Bu)_6$ in good yields is by alcoholysis of sublimed $W_2(NMe_2)_6$.

Addition of PMe_3 to $NaW_2Cl_7(THF)_5$ in CH_2Cl_2 or THF leads to the formation of the structurally characterized[19] compound $W_2Cl_6(PMe_3)_4$[4b] in nearly quantitative yield. The latter has the edge-shared bioctahedral geometry of the type shown in I where PMe_3 substitutes for pyridine. Thus, starting with the title compound, it is possible to prepare unbridged $X_3M{\equiv}MX_3$ compounds and d^3–d^3 $L_2X_2M(\mu\text{-}X)_2MX_2L_2$ compounds.

Concluding Remarks

A straightforward, high-yield synthesis of the green, air-stable, crystalline compound $NaW_2Cl_7(THF)_5$ has been achieved, and this in turn provides a good synthetic entry into the chemistry of $X_3W{\equiv}WX_3$ compounds (X = CH_2-*t*-Bu, NMe_2, O-*t*-Bu). Further studies of metathetic reactions employing this compound are under investigation. It is not clear how the green crystalline compound formulated as $W_2Cl_6(THF)_4$[4] by Schrock, Sturgeoff, and Sharp is related to the present compound, though the reactivity of $NaW_2Cl_7(THF)_5$ has been shown to mimic the former. The reactions appear identical with those described in detail by Sturgeoff.[17] A reviewer has suggested we try to make $W_2Cl_6(THF)_4$ from our compound. We have been unable to do so, though we can isolate[18] the anion free from the Na^+ cation, e.g. as $(PPh_4)^+W_2Cl_7(THF)_2^-$. This work will be reported subsequently, and we believe the challenge now lies in establishing the authenticity of $W_2Cl_6(THF)_4$.

Experimental Section

General Procedures. All procedures were carried out under a dry nitrogen atmosphere by using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated by refluxing over Na/benzophenone. Tungsten tetrachloride was prepared according to previously published procedures.[8] Lithium dimethylamide was prepared from $NHMe_2$ and *n*-butyllithium in hexane while LiO-*t*-Bu was prepared from *t*-BuOH and lithium metal in hexane. Neopentyllithium was prepared from the reaction of neopentyl chloride with lithium metal in refluxing hexane under argon.

^1H and ^{23}Na NMR spectra are reported in δ and were obtained on a Nicolet NT-360 spectrometer at 360.1 and 95.5 MHz, respectively. $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer operating at 75.43 MHz. Carbon spectra were referenced against benzene-d_6 (128 ppm). Proton spectra were referenced against the residual proton impurity in chloroform-d_1 (7.24 ppm) or benzene-d_6 (7.15 ppm). An external standard was used for ^{23}Na NMR spectra (0.1 M NaCl in D_2O). In all cases, positive chemical shift values denote resonances downfield from the standard. Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between CsI plates. Electronic absorption spectra were acquired in CH_2Cl_2 and THF solvents by using matched 10 mm path length cells on a Hewlett-Packard 8450A spectrophotometer over a scan range from 200 to 800 nm. Elemental analyses were obtained from Alfred Bernhardt Microanalytisches Laboratorium, Elbach, West Germany.

Preparation of $NaW_2Cl_7(THF)_5$. A 1-L three-neck flask, charged with WCl_4 (53.7 g, 165 mmol), was cooled to 0 °C, and ca. 350 mL of THF was added. Sodium amalgam (0.4 wt.% Na, 165 mmol) was slowly added (90 min) via a pressure-equalized dropping funnel. The slurry was then warmed to room temperature and magnetically stirred for 12 h, producing a deep green solution. The solution was filtered through Celite to remove sodium chloride formed during the reaction. The Celite pad and all glassware were thoroughly washed (2 × 100 mL of THF) in order to ensure complete extraction of the soluble green product. The volume of the filtered solution was reduced to a viscous green oil. As the solution stood at room temperature for several hours, green crystals formed. The solution was subsequently cooled to −20 °C in order to induce further crystallization. Green cubes were isolated by decanting the mother liquor and dried under vacuum. A second crop of crystals (green needles) was obtained by further reduction of the volume of the mother liquor followed by cooling to −20 °C for 1 day. The total crystalline yield of $NaW_2Cl_7(THF)_5$ was 52.5 g (63% based on WCl_4 used). ^1H NMR (23 °C, $CDCl_3$): δ 3.72 (m, 4 H), 1.83 (m, 4 H). IR (cm^{-1}): 1342 (m), 1300 (w), 1250 (m), 1176 (m), 1054 (vs), 1005 (s), 919 (s), 896 (s), 850 (vs), 274 (s), 258 (s). Anal. Calcd for $W_2Cl_7NaO_5C_{20}H_{40}$: C, 24.03; H, 4.03; Cl, 24.83; Na, 2.30. Found: C, 23.80; H, 3.90; Cl, 24.56; Na, 2.72. The elemental analysis reported above was obtained on a large cubic crystal. In general, if the removal of THF from the green viscous oil is carried out as crystallization of $NaW_2Cl_7(THF)_5$ is occurring, a higher yield of *crude* $NaW_2Cl_7(THF)_5$ is obtained. Recrystallization from THF solution is then required to yield pure $NaW_2Cl_7(THF)_5$.

Preparation of $W_2(NMe_2)_6$. $NaW_2Cl_7(THF)_5$ (0.50 g, 0.50 mmol) was added via a solids-addition tube to a 0 °C solution of $LiNMe_2$ (0.153 g, 3.0 mmol) in 10 mL of THF. Addition of $NaW_2Cl_7(THF)_5$ to the

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$LiNMe_2$/THF slurry resulted in an initially green solution that ultimately turned yellow. The yellow solution was stirred for 12 h at room temperature to ensure reaction completion. The solvent was then removed in vacuo to give a pale yellow solid, which was purified by sublimation (120 °C, 10^{-4} Torr), yielding 0.23 g (73% based on tungsten) of $W_2(NMe_2)_6$. Anal. Calcd for $W_2C_{12}H_{36}N_6$: C, 22.78; H, 5.74; N, 13.34. Found: C, 22.53; H, 5.51; N, 13.02.

One-Pot Synthesis of $W_2(NMe_2)_6$. A 1-L three-neck flask was charged with WCl_4 (36.6 g, 112 mmol) and cooled to 0 °C, and THF (ca. 350 mL) was added via cannula. Sodium amalgam (1.0 wt.% Na, 112 mmol) was slowly added over a 90-min period by using a pressure-equalized dropping funnel. The solution was then warmed to room temperature and magnetically stirred for 3 h, resulting in a deep green color. The reaction flask was then cooled to 0 °C, and 3 equiv (based on WCl_4) of $LiNMe_2$ (17.1 g, 336 mmol) was added slowly (2 h) by using a solids-addition tube. The solution slowly turned from green to yellow-brown upon addition of $LiNMe_2$. After all the $LiNMe_2$ was added, the solution was warmed to room temperature, magnetically stirred for 12 h, and filtered through Celite, by cannula transfer, into a one-neck 1-L flask. The original reaction flask and the Celite pad were washed with THF (2 × 75 mL) to ensure complete product extraction. The solvent was removed in vacuo, leaving a brown solid which, upon sublimation (120 °C, 10^{-4} Torr), yielded bright yellow $W_2(NMe_2)_6$ (26.4 g, 75% based on WCl_4). The first isolated fraction (i.e., the first 10%) is occasionally contaminated with small quantities of $W(NMe_2)_6$.

Preparation of $W_2(O\text{-}t\text{-}Bu)_6$. In a Schlenk flask, LiO-*t*-Bu (0.24 g, 3.0 mmol) was dissolved in 10 mL of THF, and the solution was cooled to 0 °C. By means of a solids-addition tube, $NaW_2Cl_7(THF)_5$ (0.50 g, 0.50 mmol) was added, and the solution was stirred at room temperature for 12 h. The solvent was removed in vacuo, producing a red solid. Hexane was added, and the solution was filtered through Celite in an attempt to remove LiCl. Removal of solvent in vacuo produced 0.27 g of a crude red solid. Recrystallization from hexane gave red needles of $W_2(O\text{-}t\text{-}Bu)_6$ (0.21 g, 52% based on tungsten), which were isolated by filtration. However, a satisfactory elemental analysis was not obtained. For a satisfactory elemental analysis of $W_2(O\text{-}t\text{-}Bu)_6$ prepared from $W_2(NMe_2)_6$ see ref 6.

Preparation of $W_2(CH_2\text{-}t\text{-}Bu)_6$. In a Schlenk flask, $LiCH_2$-*t*-Bu (0.23 g, 3.0 mmol) was dissolved in 10 mL of THF, and the pale yellow solution was cooled to 0 °C. $NaW_2Cl_7(THF)_5$ (0.50 g, 0.50 mmol) was slowly added (10 min) via a solids-addition tube, and the mixture was stirred for 12 h at room temperature, resulting in an orange-yellow solution. Removal of solvent in vacuo yielded an orange solid, which was purified by sublimation (120 °C, 10^{-4} Torr) to give 0.22 g of $W_2(CH_2\text{-}t\text{-}Bu)_6$ (55% yield based on tungsten). ^1H NMR (23 °C, C_6D_6): δ 1.24 ($CH_2C\mathit{Me}_3$, s, 9 H), 2.52 ($C\mathit{H}_2CMe_3$, s, 2 H, $^2J_{^{183}W-^1H} = 10$ Hz). $^{13}C\{^1H\}$ NMR (23 °C, C_6D_6): δ 105.2 ($\mathit{C}H_2CMe_3$, $^1J_{^{183}W-^{13}C} = 91.4$ Hz), 35.0 ($CH_2C\mathit{Me}_3$), 34.2 ($CH_2\mathit{C}Me_3$). Anal. Calcd for $W_2C_{30}H_{66}$: C, 45.36; H, 8.32. Found: C, 45.24; H, 8.19.

Crystallographic Studies. The sample was handled by using previously described procedures.[20] An irregularly shaped crystal, approximately 0.10 × 0.12 × 0.18 mm, was selected for study. There were no prominent faces to facilitate accurate crystal measurement for absorption correction, so none was made. The crystal was mounted by using silicone grease and was transferred to the goniostat, where it was cooled to −151 °C for characterization and data collection. After eliminating a few diffraction maxima as being erroneous, the space group was identified as $P2_1/c$. The quality of the data appeared good. Four standards, measured every 300 data, showed no systematic trends. The averaging for 504 redundant data had a residual of 0.037.

The structure was solved by a combination of direct method (MULTAN78) and Fourier techniques. No attempt was made to find hydrogens from the difference map. After anisotropic refinement of all non-hydrogen atoms using a full-matrix least-squares method, the hydrogen atoms were placed in idealized positions and were held fixed during final anisotropic refinement of the non-hydrogen atoms. The final residuals were $R(F) = 0.058$ and $R_w(F) = 0.057$.

There were numerous peaks on the order of 1–2 e/Å^3 in the final difference map, probably due to the fact that the crystal was large and no absorption correction was made. Most of these were in the immediate vicinity of the heavy-atom (W_2Cl_7) group. The largest peak was 2.17 e/Å^3.

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Registry No. $NaW_2Cl_7(THF)_5$, 109764-48-9; $W_2(NMe_2)_6$, 54935-70-5; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $W_2(CH_2\text{-}t\text{-}Bu)_6$, 54453-68-8; W, 7440-33-7.

Supplementary Material Available: Stereoviews of the $NaW_2Cl_7(THF)_5$ molecule and tables of anisotropic thermal parameters and complete bond distances and angles (5 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Ferromagnetic Exchange Interaction in a Binuclear Chromium(III) Complex: Magnetic and Spectroscopic Properties of $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4][(CH_3)_3C_6H_2SO_3]_4\cdot 4H_2O$

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The exchange interactions in $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4][(CH_3)_3C_6H_2SO_3]_4\cdot 4H_2O$ have been investigated by polarized single-crystal absorption spectroscopy and powder magnetic susceptibility measurements. Within the binuclear complex unit the exchange is ferromagnetic with $J = 5.0$ cm^{-1}. A dehydrated sample showed much weaker ferromagnetic behavior ($J = 0.8$ cm^{-1}), indicating a strong dependence of the exchange interaction on small changes in molecular geometry. At temperatures below 5 K two-dimensional antiferromagnetic ordering sets in. The lowest energy absorption transitions gain intensity through a single-ion mechanism. Their energetic positions can be rationalized with a set of orbital exchange parameters confirming the overall ferromagnetic intradimer interaction.

1. Introduction

The study of exchange interactions in binuclear chromium(III) complexes has been an active field of research in recent years. Bis(μ-hydroxo)-bridged dimeric complexes represent an especially well investigated set of compounds.[2] Usually the exchange coupling within these binuclear molecular units turns out to be antiferromagnetic. For the ground state the well-known Heisenberg Hamiltonian (eq 1) gives an accurate description of the

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