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The Tungsten–Tungsten Triple Bond. 9.[1] Bis(1,3-diphenyltriazenido)tetrakis(dimethylamido)ditungsten

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$W_2(NMe_2)_6$ reacts in hydrocarbon solvents with 1,3-diphenyltriazine, PhNNNHPh, to give the title compound $W_2(NMe_2)_4(PhN_3Ph)_2$ as a brick red, crystalline solid. An X-ray study shows that in the solid state each tungsten atom is coordinated to four nitrogen atoms which lie in a plane; there is an unbridged tungsten-to-tungsten triple bond with a W–W distance of 2.314 (1) Å. The two $W(NMe_2)_2(PhN_3Ph)$ units are joined together so that the molecule has C_2 symmetry. The molecule may be viewed as one of the class of *gauche*-$M_2X_2(NMe_2)_4$ compounds (M≡M). The low-temperature limiting ^1H NMR spectrum at 220 MHz is attained at −40 °C and is consistent with the structure found in the solid state: apparently the rotamers (the two enantiomers) with C_2 symmetry are favored relative to other isomeric forms of the molecule. On increase of temperature, rotations about the W–N bonds interconvert proximal and distal methyl groups of the two types of NMe_2 ligands at different rates. However, these processes do not cause enantiomerization (gauche to gauche isomerization) on the NMR time scale. These observations are compared with earlier findings in dimolybdenum and ditungsten chemistry.

Introduction

Early transition metal dimethylamides exhibit high reactivity toward substrates with active (protic) hydrogen atoms.[2] The general equation for this type of reaction may be represented by eq 1.

$$M(NMe_2)_x + yLH \rightarrow M(NMe_2)_{x-y}(L)_y + yHNMe_2 \quad (1)$$

Ligand substitution reactions of this type have been extended to dinuclear dimethylamides in our laboratory and have proved important in the synthesis of dinuclear metal alkoxides $M_2(OR)_6$ (M≡M, M = Mo,[3] W[1]). The insertion of CO_2 into the M–NMe_2 bond in the formation of the dinuclear *N,N*-dimethylcarbamato compounds, e.g.,[4] $W_2Me_2(O_2CNMe_2)_4$ and $W_2(O_2CNMe_2)_6$, has been found[5] to proceed by an amine-catalyzed mechanism shown in eq 2. This is also a form of reaction 1.

$$HNMe_2 + CO_2 \rightleftharpoons Me_2NCOOH$$

$$MNMe_2 + Me_2NCOOH \rightarrow M(O_2CNMe_2) + HNMe_2 \quad (2)$$

The insertion of carbon dioxide into M–OR bonds in reaction 3 has been shown[6] to proceed by both direct and catalyzed mechanisms.

$$Mo_2(OR)_6 + CO_2 \rightleftharpoons Mo_2(OR)_4(O_2COR)_2 \quad (3)$$

In this paper we report the preparation and characterization of a triazenidoditungsten compound, formed according to reaction 4. This, to our knowledge, is the first preparation

$$M_2(NMe_2)_6 + 2PhNNNHPh \rightarrow M_2(NMe_2)_4(PhN_3Ph)_2 + 2HNMe_2 \quad (4)$$

of a triazenido compound from a triazene and a transition metal dimethylamide. The structural aspects of this work are compared with those reported for alkylcarbonato and dimethylcarbamato complexes of dimolybdenum and ditungsten (M≡M).

Results and Discussion

Synthesis. In hydrocarbon solvents, $W_2(NMe_2)_6$ and 1,3-diphenyltriazene, PhNNNHPh, react upon mixing at room temperature. This rapid reaction is accompanied by color changes of the solutions from pale yellow, $W_2(NMe_2)_6$, and pale orange, PhNNNHPh, to deep red, $W_2(NMe_2)_4(PhN_3Ph)_2$. The triazenidoditungsten compound was obtained as deep red crystals by crystallization from toluene–hexane solvent mixtures.

Crystals of $W_2(NMe_2)_4(PhN_3Ph)_2$ are stable in the atmosphere for several hours. We attribute this unusual insensitivity toward hydrolysis to (i) steric congestion in the molecule and (ii) the hydrophobic nature of the *N*-phenyl and *N*-methyl groups.

In the mass spectrometer the compound shows a molecular ion $Mo_2(NMe_2)_4(PhN_3Ph)_2^+$ followed by loss of one and two NMe_2 groups, $[M - 44]^+$ and $[M - 88]^+$. In addition there is an intense mononuclear ion $W(NMe_2)_2(NPh)_2^+$ which is possibly formed by a process in which molecular nitrogen is eliminated: $W_2(NMe_2)_4(PhN_3Ph)_2 \rightarrow 2W(NMe_2)_2(NPh)_2 + N_2$. This reaction has not been realized on the bench top, however.

Analytical data, infrared data, and other spectroscopic data are recorded in the Experimental Section.

Solid-State Structure. In the crystalline state the compound is composed of discrete molecules of $W_2(NMe_2)_4(PhN_3Ph)_2$. ORTEP views indicating the coordination geometry and the atom numbering scheme are shown in Figures 1 and 2. Final atomic coordinates and thermal parameters are given in Table I. Complete listings of bond distances and angles are given in Tables II and III, respectively. A table listing a number of least-squares planes calculated for this molecule and the deviations of atoms from these planes is available as supplementary material.

From the view of the molecule shown in Figure 1, it can be seen that the molecule consists of two $W(NMe_2)_2(PhN_3Ph)$ units fused together by an unbridged tungsten–tungsten bond. Furthermore, it is seen that the molecule has C_2 symmetry and

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Table I. Fractional Coordinates for $W_2(NMe_2)_4(PhN_3Ph)_2$[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	2315.3 (8)	498.9 (4)	2817.6 (4)	18
W(2)	3091.6 (8)	−591.2 (4)	3340.6 (4)	20
N(1)	2762 (15)	−1400 (8)	2510 (8)	24 (3)
N(2)	1650 (15)	−1717 (8)	2731 (8)	21 (3)
N(3)	1395 (14)	8591 (8)	3337 (7)	20 (3)
N(4)	3502 (16)	610 (7)	1852 (8)	19 (3)
N(5)	2644 (15)	270 (9)	1410 (8)	25 (3)
N(6)	1672 (14)	53 (8)	1815 (7)	19 (3)
N(7)	2893 (16)	−372 (9)	4327 (8)	25 (3)
N(8)	5029 (17)	−602 (8)	3179 (9)	25 (3)
N(9)	486 (18)	590 (8)	3148 (9)	27 (3)
N(10)	3336 (14)	1291 (8)	3303 (7)	19 (3)
C(1)	3154 (19)	−1625 (10)	1814 (10)	25 (4)
C(2)	2323 (20)	−2070 (11)	1396 (10)	29 (4)
C(3)	2814 (23)	−2257 (12)	745 (12)	38 (4)
C(4)	4048 (19)	−1982 (11)	506 (10)	27 (4)
C(5)	4787 (20)	8476 (11)	941 (10)	29 (4)
C(6)	4387 (21)	−1361 (12)	1586 (11)	33 (4)
C(7)	329 (19)	−1739 (10)	3708 (10)	26 (4)
C(8)	249 (22)	−1605 (12)	4432 (11)	35 (4)
C(9)	−855 (24)	−1941 (12)	4790 (12)	38 (4)
C(10)	−1694 (22)	−2378 (12)	4481 (11)	35 (4)
C(11)	−1604 (19)	−2493 (10)	3786 (10)	25 (4)
C(12)	9326 (20)	7832 (11)	3387 (10)	28 (4)
C(13)	4701 (18)	863 (10)	1547 (9)	22 (3)
C(14)	5357 (21)	1435 (11)	1857 (11)	33 (4)
C(15)	6608 (23)	1674 (12)	1627 (11)	37 (4)
C(16)	7253 (25)	1271 (14)	1088 (13)	45 (5)
C(17)	6496 (26)	711 (14)	767 (14)	47 (5)
C(18)	5318 (21)	495 (10)	986 (11)	30 (4)
C(19)	674 (19)	−354 (10)	1464 (10)	22 (3)
C(20)	−343 (18)	−645 (9)	1899 (9)	17 (3)
C(21)	−1334 (21)	−1063 (12)	1563 (11)	33 (4)
C(22)	8665 (21)	8787 (11)	877 (10)	30 (4)
C(23)	−294 (22)	−937 (13)	473 (12)	39 (5)
C(24)	645 (22)	−480 (10)	770 (11)	28 (4)
C(25)	3558 (23)	−913 (12)	4813 (11)	37
C(26)	2384 (22)	264 (13)	4721 (9)	34
C(27)	6030 (18)	−49 (11)	2916 (12)	33
C(28)	5633 (21)	−1284 (12)	3357 (13)	41
C(29)	−327 (21)	1090 (11)	2757 (11)	32
C(30)	−326 (20)	200 (13)	3676 (11)	36
C(31)	4392 (21)	1325 (11)	3783 (11)	33
C(32)	2719 (25)	2085 (10)	3171 (13)	41

[a] The isotropic thermal parameter listed for those atoms refined anisotropically are the isotropic equivalent. Numbers in parentheses in this and all following tables refer to the error in the least significant digits. Estimated standard deviations greater than 29 are not statistically significant but are left "unrounded" since the tables are all produced automatically by the X-TEL interactive programs.

in this respect may be viewed as a member of a large class of $M_2X_2(NMe_2)_4$ molecules (M≡M, M = Mo, W).[7] There are two types of dimethylamido ligands, each having proximal and distal methyl groups. As with all other structurally characterized members of the $M_2X_2(NMe_2)_4$ class of compounds, the MNC_2 units are planar.

The four nitrogen atoms directly bonded to each tungsten atom lie in a plane in a similar manner to the WO_3N moiety found in $W_2(O\text{-}i\text{-}Pr)_6(py)_2$[1] and to the MoO_3N moiety in $Mo_2(OSiMe_3)_6(HNMe_2)_2$.[8] A similar situation is seen in $Mo_2(O_2CO\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)_4$[6] though here the presence of bridging O_2COR ligands imposes an eclipsed geometry with respect to each half of the molecule.

The geometry of the triazenido ligand atoms is typical of that found in other triazenido–transition metal complexes.[9,10] The central C–N–N–N–C unit is planar and the bite of the ligand, the N–Mo–N angle, is ca. 56°, which is comparable to that of the terminally bonded bidentate O_2CNMe_2 ligands in $W_2(O_2CNMe_2)_6$.[4]

Bonding in $W_2(NMe_2)_4(PhN_3Ph)_2$. The observed diamagnetism and short unbridged tungsten–tungsten distance, 2.314 (1) Å, are comparable to that in a number of structurally characterized $W_2X_2(NR_2)_4$ compounds[7] which have been proposed to contain W-to-W triple bonds. The triple bond can be viewed as being formed by the interaction of tungsten atomic d_{z^2}–d_{z^2} orbitals to give a σ bond and d_{xz}–d_{xz}, d_{yz}–d_{yz}

Table II. Bonded Distances, in Angstroms, for $W_2(NMe_2)_4(PhN_3Ph)_2$

A	B	dist	A	B	dist
W(1)	W(2)	2.314 (1)	C(1)	C(2)	1.40 (3)
W(1)	N(4)	2.215 (15)	C(1)	C(6)	1.39 (3)
W(1)	N(6)	2.194 (14)	C(2)	C(3)	1.39 (3)
W(1)	N(9)	1.940 (17)	C(3)	C(4)	1.40 (3)
W(1)	N(10)	1.974 (14)	C(4)	C(5)	1.38 (3)
W(2)	N(1)	2.178 (15)	C(5)	C(6)	1.34 (3)
W(2)	N(3)	2.229 (14)	C(7)	C(8)	1.42 (3)
W(2)	N(7)	1.957 (16)	C(7)	C(12)	1.40 (3)
W(2)	N(8)	1.959 (17)	C(8)	C(9)	1.43 (3)
N(1)	N(2)	1.31 (2)	C(9)	C(10)	1.29 (3)
N(1)	C(1)	1.45 (2)	C(10)	C(11)	1.36 (3)
N(2)	N(3)	1.32 (2)	C(11)	C(12)	1.34 (3)
N(3)	C(7)	1.41 (2)	C(13)	C(14)	1.35 (3)
N(4)	N(5)	1.36 (2)	C(13)	C(18)	1.40 (3)
N(4)	C(13)	1.41 (2)	C(14)	C(15)	1.39 (3)
N(5)	N(6)	1.30 (2)	C(15)	C(16)	1.42 (3)
N(6)	C(19)	1.41 (2)	C(16)	C(17)	1.39 (4)
N(7)	C(25)	1.50 (3)	C(17)	C(18)	1.31 (3)
N(7)	C(26)	1.45 (3)	C(19)	C(20)	1.41 (3)
N(8)	C(27)	1.49 (3)	C(19)	C(24)	1.36 (3)
N(8)	C(28)	1.39 (3)	C(20)	C(21)	1.40 (3)
N(9)	C(29)	1.42 (3)	C(21)	C(22)	1.35 (3)
N(9)	C(30)	1.47 (3)	C(22)	C(23)	1.39 (3)
N(10)	C(31)	1.41 (2)	C(23)	C(24)	1.37 (3)
N(10)	C(32)	1.56 (2)			

Table III. Bonded Angles, in Degrees, for $W_2(NMe_2)_4(PhN_3Ph)_2$

A	B	C	angle	A	B	C	angle
W(2)	W(1)	N(4)	105.3 (4)	C(27)	N(8)	C(28)	111 (1)
W(2)	W(1)	N(6)	100.8 (4)	W(1)	N(9)	C(29)	115 (1)
W(2)	W(1)	N(9)	104.1 (5)	W(1)	N(9)	C(30)	135 (1)
W(2)	W(1)	N(10)	102.0 (4)	C(29)	N(9)	C(30)	110 (2)
N(4)	W(1)	N(6)	56.3 (5)	W(1)	N(10)	C(31)	137 (1)
N(4)	W(1)	N(9)	140.3 (7)	W(1)	N(10)	C(32)	111 (1)
N(4)	W(1)	N(10)	93.6 (5)	C(31)	N(10)	C(32)	112 (2)
N(6)	W(1)	N(9)	92.3 (6)	N(1)	C(1)	C(2)	122 (2)
N(6)	W(1)	N(10)	146.2 (5)	N(1)	C(1)	C(6)	116 (2)
N(9)	W(1)	N(10)	105.8 (6)	C(2)	C(1)	C(6)	122 (2)
W(1)	W(2)	N(1)	99.9 (4)	C(1)	C(2)	C(3)	117 (2)
W(1)	W(2)	N(3)	106.4 (4)	C(2)	C(3)	C(4)	121 (2)
W(1)	W(2)	N(7)	103.2 (5)	C(3)	C(4)	C(5)	118 (2)
W(1)	W(2)	N(8)	105.8 (4)	C(4)	C(5)	C(6)	122 (2)
N(1)	W(2)	N(3)	56.9 (5)	C(1)	C(6)	C(5)	119 (2)
N(1)	W(2)	N(7)	146.7 (6)	N(3)	C(7)	C(8)	118 (2)
N(1)	W(2)	N(8)	91.7 (6)	N(3)	C(7)	C(12)	123 (2)
N(3)	W(2)	N(7)	93.4 (6)	C(8)	C(7)	C(12)	119 (2)
N(3)	W(2)	N(8)	138.1 (6)	C(7)	C(8)	C(9)	117 (2)
N(7)	W(2)	N(8)	104.6 (7)	C(8)	C(9)	C(10)	122 (2)
W(2)	N(1)	N(2)	100 (1)	C(9)	C(10)	C(11)	121 (2)
W(2)	N(1)	C(1)	145 (1)	C(10)	C(11)	C(12)	123 (2)
N(2)	N(1)	C(1)	114 (1)	C(7)	C(12)	C(11)	118 (2)
N(1)	N(2)	N(3)	106 (1)	N(4)	C(13)	C(14)	118 (2)
W(2)	N(3)	N(2)	97 (1)	N(4)	C(13)	C(18)	123 (2)
W(2)	N(3)	C(7)	147 (1)	C(14)	C(13)	C(18)	119 (2)
N(2)	N(3)	C(7)	115 (1)	C(13)	C(14)	C(15)	122 (2)
W(1)	N(4)	N(5)	99 (1)	C(14)	C(15)	C(16)	119 (2)
W(1)	N(4)	C(13)	147 (1)	C(15)	C(16)	C(17)	116 (2)
N(5)	N(4)	C(13)	115 (1)	C(16)	C(17)	C(18)	124 (2)
N(4)	N(5)	N(6)	103 (1)	C(13)	C(18)	C(17)	120 (2)
W(1)	N(6)	N(5)	102 (1)	N(6)	C(19)	C(20)	114 (2)
W(1)	N(6)	C(19)	145 (1)	N(6)	C(19)	C(24)	125 (2)
N(5)	N(6)	C(19)	113 (1)	C(20)	C(19)	C(24)	121 (2)
W(2)	N(7)	C(25)	116 (1)	C(19)	C(20)	C(21)	115 (2)
W(2)	N(7)	C(26)	134 (1)	C(20)	C(21)	C(22)	124 (2)
C(25)	N(7)	C(26)	109 (1)	C(21)	C(22)	C(23)	119 (2)
W(2)	N(8)	C(27)	135 (1)	C(22)	C(23)	C(24)	119 (2)
W(2)	N(8)	C(28)	113 (1)	C(19)	C(24)	C(23)	122 (2)

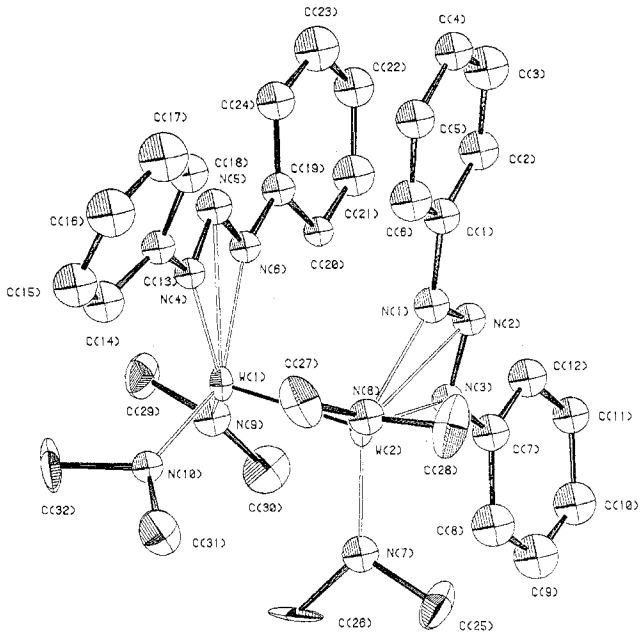

Figure 1. An ORTEP view of the $Mo_2(NMe_2)_4(PhN_3Ph)_2$ molecule showing the atomic numbering schemes used in Tables II and III. Thermal ellipsoids are drawn at the 50% probability level.

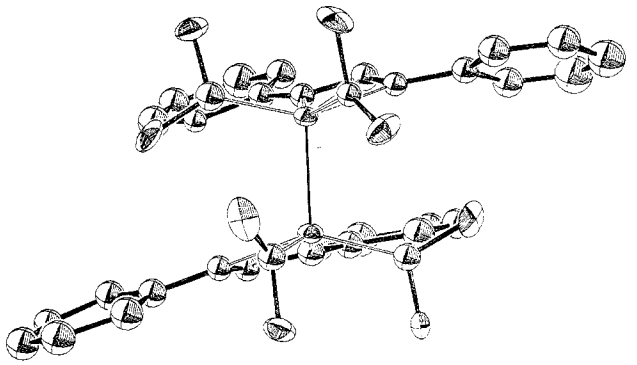

Figure 2. An ORTEP view of the $W_2(NMe_2)_4(PhN_3Ph)_2$ molecule viewed perpendicularly to the W–W triple bond and approximately down the twofold rotational axis of symmetry. Thermal ellipsoids are drawn at the 50% probability level.

atomic orbitals to yield a symmetrical π bond. The formation of the four tungsten-to-nitrogen σ bonds which lie in-plane may involve tungsten 6 s, 6 p_x, 6 p_y, and 5 $d_{x^2-y^2}$ atomic orbitals. In addition the dimethylamido ligand may act as a π-donor ligand. Evidence for π donation is seen here in (i) the planarity of the W–NC_2 units and (ii) the shortness of the W–NC_2 bonds, 1.96 Å (averaged), and has been noted previously in other $M_2X_2(NMe_2)_4$ compounds.[7] If all the lone pairs on the four NMe_2 ligands were used in ligand-to-metal π bonding, each tungsten atom would attain an 18-valence-shell electron configuration. However, this is not possible in the ground-state structure since only one tungsten atomic orbital, which has not been used in either M–M bonding or M–N σ bonding, has the appropriate symmetry, namely, the tungsten 5 d_{xy} atomic orbital. Thus in $W_2(NMe_2)_4(PhN_3Ph)_2$, and not unlike the parent compound $W_2(NMe_2)_6$, a 16-valence-shell electronic configuration is attained as a result of formation of the M–M triple, M–N σ bonds, and delocalized N-to-M π bonds.

It is also pertinent to question why this isomer of the molecule appears to be favored over all others and specifically those having bridging triazenido groups[11] or those[12] having trans or anti conformations of the present form of the molecule (we say appears because we have no direct evidence for the existence of another isomer, not even in solution, and thus it

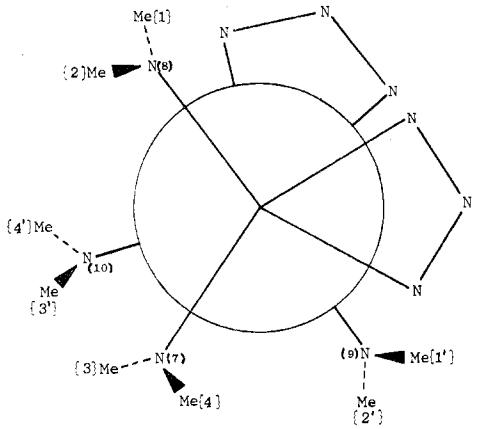

Figure 3. Schematic view down the W–W bond in $W_2(NMe_2)_4(PhN_3Ph)_2$ showing the four types of *N*-methyl groups which are related by the C_2 symmetry operation.

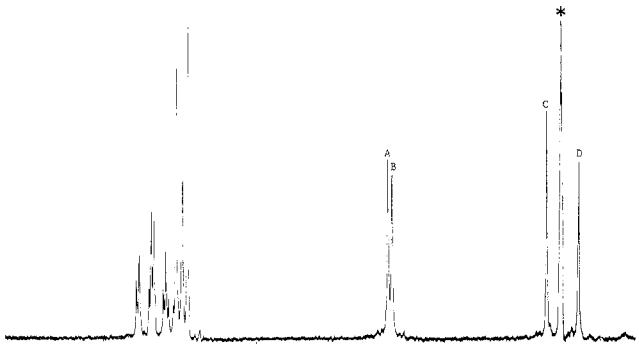

Figure 4. Low-temperature limiting ^1H NMR spectrum of $W_2(NMe_2)_4(PhNNNPh)_2$ (−45 °C) 220 MHz in toluene-d_8. Asterisk represents proton impurities in solvent.

is possible, but seems unlikely to us, that the isomer which we have characterized is formed under kinetic rather than thermodynamic control).

We believe this isomer is the thermodynamically favored isomer for the following reasons. (1) The presence of bridging PhN_3Ph ligands would impose an eclipsed geometry on the molecule which for steric reasons alone is less favored. Furthermore, in order to minimize methyl–methyl repulsions the NC_2 units in this isomer would be forced to adopt a skew conformation of the NC_2 blades. As the dihedral angle formed between the NC_2 planes and the respective W–W–N plane increases from zero, nitrogen lone pair to tungsten π bonding involving the tungsten d_{xy} orbital will decrease. Of course a π interaction with tungsten atomic d_{xz} and d_{yz} orbitals becomes possible, but this is less favored because these atomic orbitals are used to form the M–M π bonds. (2) In the observed conformation two dimethylamido groups, those represented by N(7) and N(10) in Figure 3, are perfectly cogged: they lie between the two NC_2 units of the other end of the molecules. The other symmetry-related NMe_2 groups represented by N(8) and N(9) in Figure 3 are flanked by one NMe_2 group and one end of the PhN_3Ph ligand at the other end of the molecule. Rotating the molecule about the W–W bond from the observed conformation (i) destroys the maximum degree of cogging of NC_2 blades and (ii) increases the NC_2–Ph_2N_3 repulsions between each end of the molecule. This in turn would have the effect of promoting a twist about the W–NC_2 blade away from its favored position with regard to Me_2N-to-W π bonding as described above.

^1H NMR Studies. ^1H NMR spectra were obtained for $W_2(NMe_2)_4(PhN_3Ph)_2$ at 220 MHz over the temperature range −45 to +80 °C in toluene-d_8. The low-temperature limiting spectrum is shown in Figure 4. There are four signals

in the integral ratio 1:1:1:1 labeled A, B, C, and D assignable to *N*-methyl protons. As is shown in Figure 3, the C_2 axis of symmetry yields symmetry related pairs of *N*-methyl groups: Me(1), Me(1′), etc. Thus the ^{1}H NMR spectrum is entirely consistent with that found in the solid state. It may also be noted that neither the anti rotomer, which would yield only two signals at low temperature, nor any other isomer is present to any significant extent.

On increase of the temperature, A and D broaden, until at +16 °C they are lost in the base line of the spectrum. B and C on the other hand remain sharp at this temperature. On increase of the temperature to +50 °C, A and D coalesce to a single line while B and C broaden. At +80 °C, there is one sharp single resonance and one broad one. Thus it is evident that the two types of dimethylamido groups have different energies of activation for proximal ⇌ distal methyl group exchange and furthermore, at high temperature when proximal ⇌ distal methyl exchange becomes rapid, the two types of NMe_2 ligands are not equilibrated on the NMR scale. A similar situation was first noted for $W_2Me_2(NEt_2)_4$[7] which exists in an equilibrium mixture of anti and gauche rotamers. In the present instance it is particularly interesting to note that enantiomerization does not occur rapidly on the NMR time scale, since, in addition to processes involving rotations about the W-to-W triple bond (g ⇌ a ⇌ g; g ⇌ g), a terminal to bridge site exchange of the PhN_3Ph ligands would cause the two types of NMe_2 ligands to become equivalent; cf. in $W_2(O_2CNMe_2)_6$ and $W_2Me_2(O_2CNEt_2)_4$ where bridging and terminal O_2CNMe_2 exchange is rapid on the NMR time scale at +70 °C.[4] Thus it appears that the presence of the NMe_2 ligands in $W_2(NMe_2)_4(PhN_3Ph)_2$ have both dynamic and static stereochemical consequences on the molecule's behavior.

Finally if we assume[14] that proximal and distal methyl site exchange is brought about by rotations about tungsten–nitrogen bonds, then one is led to wonder whether or not an assignment of *N*-methyl signals A, B, C, and D is possible.

Since in isolation each $W(NMe_2)_2(PhN_3Ph)$ moiety contains a plane of symmetry and has equivalent NMe_2 groups, the differences in energies of activation for M–N bond rotations that exist in $W_2(NMe_2)_4(PhN_3Ph)_2$ must result from interactions of the two halves of the molecule. The greatest nonbonding interactions are between the NMe_2 ligands. Now one type of NMe_2 ligand, N(7) and N(10) in Figure 3, is directed between two opposite NMe_2 groups while the other type, N(8) and N(9) in Figure 3, lies between one NMe_2 ligand and a PhN_3Ph group. Consequently, we believe that A and D are proximal and distal methyl groups associated with N(8) and N(9) and correspondingly B and C are the proximal and distal methyl associated with N(7) and N(10) dimethylamido groups.[15]

Experimental Section

General procedures including the syntheses of $W_2(NMe_2)_6$ have been reported.[16] 1,3-Diphenyltriazene was purchased from Eastman Kodak Co. and dried prior to use. Elemental analyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques. Infrared spectra were obtained from Nujol mulls between CsI plates with a Beckman 257 spectrophotometer. ^{1}H NMR spectra were obtained from a Varian Associates 220-MHz instrument equipped with a variable-temperature probe. Temperatures were calibrated with methanol (low temperatures) and ethylene glycol (high temperatures). Mass spectra were obtained on an AEI MS9 by the method of direct insertion.

Preparation of $W_2(NMe_2)_4(PhN_3Ph)_2$. To $W_2(NMe_2)_6$ (0.196 g, 0.31 mmol) in toluene (20 mL) was added a solution of 1,3-diphenyltriazene (0.123 g, 0.62 mmol) in toluene (10 mL). Upon mixture of the pale yellow ($W_2NMe_2)_6$) and pale orange (PhNNNHPh) solutions, an instantaneous color change occurred to produce a deep red solution. After 2 h the solvent was stripped to leave a deep red solid. Crystallization from toluene/hexane gave deep red crystals (0.18 g, 77% based on reaction 4). Anal. Calcd for $W_2(NMe_2)_4(PhN_3Ph)_2$: C, 41.04; H, 4.74; N, 14.96. Found: C, 40.75; H, 4.67; N, 14.75. IR data obtained from a Nujol mull between CsI plates: 1594 (s), 1482 (vs), 1380 (vs), 1298 (s), 1280 (vs), 1293 (m), 1165 (w), 1150 (m), 1073 (vw), 1046 (vw), 954 (s), 935 (s), 760 (s), 723 (w), 690 (m), 670 (w), 540 (vw), 516 (vw), 496 (vw), 364 (vw) cm^{-1}. ^{1}H NMR data obtained at 220 MHz, −45 °C, in toluene-d_8: δ(N–Me) A = 4.36, B = 4.30, C = 2.27, D = 1.81 (ppm relative to Me_4Si).

X-ray Structural Determination. A crystal of dimensions 0.08 × 0.20 × 0.25 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer.[17] The diffractometer used for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator is interfaced to a TI 980 minicomputer, with Slo-Syn stepping motors to drive the angles. Centering is accomplished by using automated top/bottom–left/right slit assemblies. The minicomputer is interfaced by low-speed data lines to a CYBER 172-CDC 6600 multimain frame system where all computations are performed.

The cell dimensions obtained from 22 reflections at −138 °C with Mo Kα (λ 0.710 69 Å) were a = 9.993 (3) Å, b = 17.689 (7) Å, c = 19.346 (7) Å, β = 89.65 (3)°, V = 3419.66 Å^3, Z = 4, d_{calcd} = 1.819 g cm^{-3}, and space group $P2_1/c$.

A total of 5266 reflections were collected by using standard moving-crystal moving-detector techniques with the following values: scan speed = 3 deg min^{-1}, scan width = 2 + dispersion, single background time at extremes of scan = 10 s, aperture size = 2.5 × 3.5 mm. The number of reflections with $F > 2.33\sigma(F)$ was 3572.

A power failure during data collection caused the sample temperature to increase and noticeable decomposition of the sample occurred. This was evident from a plot of the standard reflections. To correct for the decomposition, we subjected the data subject to a "DRIFT"[18] correction in which the data are scaled anisotropically to the values of the standards.

The data were corrected for absorption (linear absorption coefficient = 69.04 cm^{-1}, minimum and maximum corrections were 0.328 and 0.597).

Anisotropic refinement invariably led to nonpositive definite values for several of the phenyl carbons and the N–N–N groups of the triazemido ligand. While such behavior could be attributed to a poor absorption correction, it may well be due to the partial decomposition which occurred during data collection.

For the final refinement the two metal atoms and the methyl carbons were allowed to vary anisotropically, and all other atoms were restricted to isotropic thermal parameters. Hydrogen atom contributions for the phenyl carbons were used as fixed atoms in calculated positions (d(C–H) = 0.95 Å and B_{iso} = 3.0 Å^2), and no attempt was made to locate the methyl hydrogens.

A final difference map revealed peaks of 1.9 and 2.1 e/Å near each of the metal positions but was otherwise featureless.

The structure was solved by direct methods and Patterson techniques with little difficulty to give final residuals: $R(F)$ = 0.0727 and $R_w(F)$ = 0.0957. The goodness of the fit for the last cycle was 2.91 and the maximum Δ/σ was 0.2.

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Registry No. $W_2(NMe_2)_4(PhN_3Ph)_2$, 71597-18-7; $W_2(NMe_2)_6$, 54935-70-5.

Supplementary Material Available: A table of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 7898, is available upon request in microfiche form only from the Indiana University Chemistry Library.

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Preparation of Tetraammonium Octakis(isothiocyanato)dimolybdenum(II) and Structural Characterization of Two Crystalline Hydrates

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By a ligand replacement reaction in aqueous solution the $[Mo_2(NCS)_8]^{4-}$ ion has been prepared and isolated in two compounds: $(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$ (**1**) and $(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$ (**2**). The structures of these deep blue-green substances have been determined by X-ray crystallography and the electronic absorption spectrum of the $[Mo_2(NCS)_8]^{4-}$ ion has been measured. Compound **1** crystallizes in space group *Pbca* with $a = 13.859$ (3) Å, $b = 13.012$ (4) Å, $c = 16.937$ (4) Å, $V = 3054$ Å^3, and $Z = 4$. Compound **2** crystallizes in space group $P\bar{1}$ with $a = 10.706$ (2) Å, $b = 11.708$ (3) Å, $c = 14.346$ (3) Å, $\alpha = 105.79$ (2)°, $\beta = 93.37$ (2)°, $\gamma = 105.71$ (2)°, $V = 1649$ (1) Å^3, and $Z = 2$. In **2** there are two crystallographically independent $[Mo_2(NCS)_8]^{4-}$ ions, each on an inversion center, and the $[Mo_2(NCS)_8]^{4-}$ in **1** also resides on an inversion center. All three crystallographically distinct anions have virtual D_{4h} symmetry with approximately linear MoNCS chains. The Mo–Mo distances are 2.162 (1) Å in **1** and 2.177 (1) and 2.174 (1) Å in **2**. These distances are slightly longer than Mo–Mo quadrupole bond distances previously observed in any compound except the allyl, $Mo_2(allyl)_4$. The small differences between the three Mo–Mo bond lengths appear to be due to differences in the intermolecular interactions. The NH_4^+ ions in each case are hydrogen bonded to water molecules. The visible spectrum contains a band at about 14 500 cm^{-1} which may be assigned to the $\delta \rightarrow \delta^*$ transition.

Introduction

The chemistry of quadruply bonded dinuclear complexes containing halide ions as ligands is quite extensive.[1] The ions $[Re_2Cl_8]^{2-}$, $[Mo_2Cl_8]^{4-}$, and $[Tc_2Cl_8]^{3-}$ were first recognized and characterized[2-4] more than a decade ago, and numerous derivatives are known in which halide ions are partly replaced to give complexes of the types $M_2L_4X_4$[5] or $M_2(LL)_2X_4$,[5,6] where L and LL represent mono- and bidentate phosphine, arsine, or alkyl sulfide type ligands. On the other hand, relatively little has yet been learned about the chemistry of comparable compounds with pseudohalogen ions as ligands. Even for the thiocyanate ion, which is perhaps the most obvious candidate to give comparable compounds, little has been done.

The $[Re_2(NCS)_8]^{2-}$ ion was reported[7] in 1967, and, more recently, the compound $Mo_2(dppm)_2(NCS)_4$ (where dppm = $Ph_2PCH_2PPh_2$) has been fully characterized.[8] We have also described the mixed (carboxylato)(thiocyanato)molybdenum species $Mo_2(O_2CR)_2(NCS)_4$, in which the carboxylate groups are the neutral, zwitterionic amino acids glycine and L-isoleucine.[9] In all of these compounds the NCS^- ligands are isothiocyanato groups; that is, they are bound to the metal atoms through the nitrogen atoms.

The objective of the present study was to prepare and characterize the simple $[Mo_2(NCS)_8]^{4-}$ ion, which has not previously been unambiguously shown to exist. Nimry and Walton,[10] while isolating a number of other NCS-containing dimolybdenum(II) complexes, were not successful in preparing any compound containing the $[Mo_2(NCS)_8]^{4-}$ ion. Hochberg and Abbott[11] described "highly air-sensitive...diamagnetic green needle-like crystals" to which they assigned the formula $(NH_4)_4Mo_2(NCS)_8(CH_3OCH_2CH_2OCH_3)_4$ on the basis of elemental analyses and spectroscopic data, but this substance has not been conclusively identified.[12] We report here that the $[Mo_2(NCS)_8]^{4-}$ ion can be isolated in the form of crystalline, hydrated ammonium salts, $(NH_4)_4[Mo_2(NCS)_8] \cdot xH_2O$, and we have carried out full structure determinations on those with $x = 4$ and 6.

Experimental Section

Preparation of $(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$ (1) and $(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$ (2). $K_4Mo_2Cl_8$ (0.02 g), prepared by a literature method,[4] was dissolved in 1 mL of 2 M NH_4NCS under argon. The deep turquoise solution was allowed to mix by diffusion through a glass frit with a saturated solution of NH_4NCS at 0 °C. Deep blue-green crystals were formed over a 24-h period. It was observed that a few crystals had an approximately cubic morphology while the majority were elongated plates with well-developed faces. The former were found to be orthorhombic and to contain compound **1** while the latter are triclinic and contain compound **2**. The structures of both have been determined.

X-ray Crystallography. Data were collected for both compounds on an Enraf-Nonius CAD-4F automatic diffractomator, using Mo $K\alpha$ radiation ($\lambda_{\bar{\alpha}}$ 0.71073 Å) with a graphite crystal monochromator in the incident beam. The takeoff angle of the X-ray tube was 2.80° and the temperature during data collection was 26 ± 1 °C. The standard CAD-4 centering, indexing, and data collection programs were used.

Twenty-five reflections between 12° and 15° in θ were located by a random search procedure and subsequently centered. These reflections were used as the basis for the indexing. The cell constants and the orientation matrix that were obtained were refined by a least-squares fit.

The scan width for each reflection was determined as 0.8 + 0.347 tan θ. Reflections were first measured with a scan rate of 20.12°/min. The rate for the final scan was calculated from the preliminary scan

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