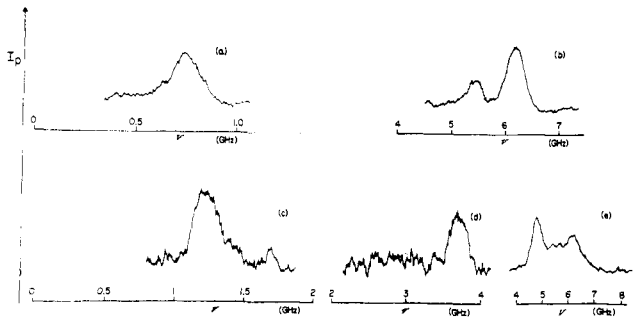

**Figure 1.** ODMR signals observed from Ag(I) complexes of (a) and (b) poly(dT); (c), (d), and (e) calf thymus DNA.

tensity showing that the steady state sublevel populations and radiative decay constants are inverted in order. It is apparent from Table I that binding of Ag(I) to the heterocyclic base causes little change in the zero-field splittings as determined by conventional EPR measurements of the triplet state of the uncomplexed molecule. Initial binding of Ag(I) to calf thymus DNA, $r = 0.1$, results in ODMR signals only from the triplet state of guanine indicating that the strongest binding (type I) results in Ag(I)-G complexes (Table II). Subsequent binding of additional Ag(I), $r = 0.5$, results in the appearance of ODMR signals due to the triplet state of thymine, showing that Ag(I)-T complexes form at higher $r_b$ than the Ag(I)-G complexes. The thymine ODMR signals probably result from type II complexes. It has been suggested[3,4] that type II complexes result from replacement of a proton between T(N3) and A(N1) or C(N3) and G(N1) by Ag(I), leading to linear N-Ag-N bonds. This is consistent with our results, since A and T when both bound to Ag(I) should result in phosphorescence from only T, which has the lower energy triplet state. When Ag(I) is increased to $r = 1.0$, an additional ODMR signal is observed at 2.53 GHz with little change in the frequencies of the signals assigned to G and T. We have assigned this new signal to the triplet state of A.[14] We think that the A ODMR signal in DNA might result from partial strand separation caused by Ag binding—possibly to A(N7) which is already engaged in type II complexing. Triplet energy trapping on Ag-adenine complexes then would be possible.

If type I complexes have the "$\pi$-sandwich" structure previously suggested,[3,4] the absence of T signals at $r_b \sim 0.1$ can be explained by a stronger perturbation of Ag(I) on G than on T in the case of G-Ag-T complexes. This could result in a lower triplet energy for G and prevent the normally expected G → T triplet energy transfer.[15]

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(15) The binding of Ag(I) to the bases is accompanied generally by a red shift of the optical absorption bands,[2] and we excite our samples to the red of the normal base absorption. We have found that Ag(I) binding to GMP results in a shift of the phosphorescence origin from $27.2 \times 10^3$ to $25.0 \times 10^3$ $cm^{-1}$, which is below the triplet energy of TMP ($26.3 \times 10^3$ $cm^{-1}$).

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## Hexakis(dimethylamido)ditungsten. The First Structurally Characterized Molecule with an Unbridged Triple Bond between Tungsten Atoms

*Sir:*

The great propensity of molybdenum to form M-M bonds of order 3 and 4 might naturally lead one to expect the same of tungsten.[1] This has not proved to be the case so far. Indeed, only $W_2(CH_2SiMe_3)_6$ has been prepared and reported to form crystals isomorphous to those of $Mo_2(CH_2SiMe_3)_6$.[2] The paucity of W-W multiple-bonded compounds raises interesting questions. If W-W multiple bonds are inherently weaker than those of molybdenum, what are the reasons? Or, have certain subtle factors in the coordination chemistry of tungsten thus far precluded their preparation?

We report here the preparation and characterization of $W_2(NMe_2)_6$. This work (i) provides the first X-ray structural characterization of a compound containing an unbridged W-W triple bond,[3] (ii) allows a direct comparison of the molybdenum and tungsten triple bonds in the compounds $M_2(NMe_2)_6$, and (iii) suggests answers to the above questions.

The preparation and characterization of $W(NMe_2)_6$ from the reaction of $WCl_6$ and $6LiNMe_2$ has previously been reported.[8] It was noted[8] that formation of $W(NMe_2)_6$ in the above reaction was always accompanied by some reduction of tungsten(VI) and, on the basis of analytical data, the reduced tungsten species was formulated as $W(NMe_2)_3$. Our recent characterization of $Mo_2(NMe_6)$[9,10] encouraged us to pursue synthetic routes to $[W(NMe_2)_3]_n$ since, clearly, this could answer important questions concerning W-W bonding. Since reactions involving $WCl_6$ and $6LiNMe_2$ led to some reduction of W(VI), reactions involving lower valent tungsten halides were expected to give only, or at least predominantly, $[W(NMe_2)_3]_2$. This was not the case. $WCl_4(THF)_2$[11] and $WCl_4(OEt_2)_2$[11] react with $4LiNMe_2$ (in THF-hexane) to yield $W(NMe_2)_6$ as the *only* isolable dimethylamide of tungsten; no $[W(NMe_2)_3]_n$ was obtained. The cluster compound $WCl_2$ reacts with $2LiNMe_2$ to give a mixture of $W(NMe_2)_6$ and $[W(NMe_2)_3]_n$, richer in $W(NMe_2)_6$ than many samples obtained from reactions involving $WCl_6$. However, we have found that if $WCl_4(OEt_2)_2$ is allowed to decompose in diethyl ether at room temperature for 1 hr under an atmosphere of nitrogen, and the resultant black sludge then treated with $3LiNMe_2$ (THF-hexane), a mixture of $[W(NMe_2)_3]_n$ and

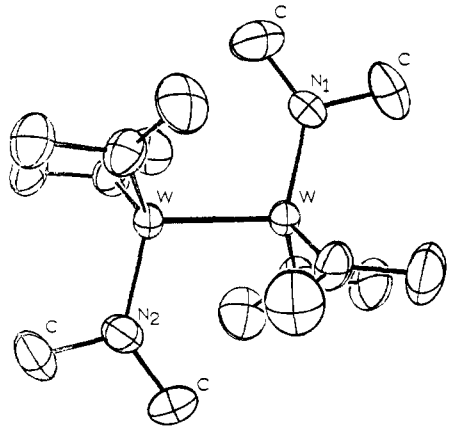


Figure 1.

$W(NMe_2)_6$ in 2:1 ratio based on tungsten is obtained. All attempts to separate pure $[W(NMe_2)_3]_n$ from this mixture by vacuum sublimation and fractional recrystallization have failed. Chromatographic techniques employing dehydrated Florisii also failed since $[W(NMe_2)_3]_n$ was selectively destroyed on the support.

Though pure $[W(NMe_2)_3]_n$ has not been isolated, spectroscopic properties of the mixture were informative with regard to the nature of $[W(NMe_2)_3]_2$. In the mass spectrum a strong parent ion, $W_2(NMe_2)_6^+$, and several other $W_2$-containing ions are observed. $^1H$ NMR studies reveal a single resonance at $\delta$ 3.44 ppm from TMS at room temperature and above, and two resonances with equal intensities at $\delta$ 2.46 and 4.39 ppm at −40° and below. This behavior is directly analogous to that observed for $Mo_2(NMe_2)_6$ and corresponds to the temperature-dependent rate of proximal and distal methyl exchange.[9] Thus, all the physical data indicated the dinuclear, diamagnetic nature of $[W(NMe_2)_3]_n$ and thus suggested the presence of a W-W triple bond, rather than the presence of bridging dimethylamido ligands. Crystallographic examination of crystalline samples obtained from the $[W(NMe_2)_3]_2$-$W(NMe_2)_6$ mixture was then undertaken.

A crystalline sample, obtained from THF, contained crystals of pure $W(NMe_2)_6$[8] as well as single crystals having a mixed composition of $W(NMe_2)_6$ and $W_2(NMe_2)_6$ in a ratio of 1:2. The structure of this mixed species was solved and refined.[12] The unit cell contains two molecules of $W_2(NMe_2)_6$ with the tungsten atoms lying on a crystallographic threefold axis and a single molecule of $W(NMe_2)_6$ occupying a position of $\bar{3}$ symmetry. The $W(NMe_2)_6$ molecule shows crystallographic disorder arising from two orientations of the $NMe_2$ group about the W-N axis. The refined dimensions of this structure agree satisfactorily with those previously obtained for pure $W(NMe_2)_6$.[8]

The $W_2(NMe_2)_6$ molecules are ordered and have the structure shown in Figure 1. Important averaged dimensions are: W-W = 2.294 (1) Å, W-N = 1.96 (1) Å, $N_1$-C = 1.46 (2), Å, $N_2$-C = 1.45 (2) Å, and W-W-N = 103.9 (4)°; the $WNC_2$ groups are essentially planar with angles at the nitrogen atoms of 111 (1)° for C-N-C, 117 (1)° for distal W-N-C, and 132 (1)° for proximal W-N-C.

The structure is thus similar to that of $Mo_2(NMe_2)_6$[10] but has a metal-metal bond which is longer by 0.08 Å. The W-W triple bond is similar in length to the only other unbridged triple bond between metal atoms of the third transition series that has so far been reported,[13] viz., the Re≡Re bond in $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$ which has a length of 2.293 (2) Å. Further study of both of the $M_2(NMe_2)_6$ compounds is in progress.[14]

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## Modification of Firefly Luciferase with a Luciferin Analog. A Red Light Producing Enzyme

*Sir:*

Light production in the firefly appears to involve the sequence of reactions outlined in Chart I, as determined by in vitro studies.[1,2] Luciferase activity is measured by light emission, and in the normal assay (pH 7.9) the enzyme produces the familiar yellow-green light emission.[2] Proton losses occur at steps b and e, and basic residues on the enzyme are presumably involved in these ionizations. If two different bases are involved, it should be possible, in principle, to block the second one (Chart I, step e) to form an enzyme capable of only red light emission (process f, Chart I).[3] In the presence of protons (pH 5.5 to ~7) and heavy metals (acting reversibly) firefly luciferase produces red light,[4] and possibly these species block the second site by reducing its basicity. We now report on the use of an inhibitor of luciferase that produces a red light emitting enzyme by alkylation.

Enzymes have been chemically modified with reagents that range from those that bear little resemblance to native substrates to those that are patterned after the substrate.[5] Inhibitors in the latter category are more likely to modify the active site of the enzyme.[6] In most cases of derivatization, a major part of the reactive substrate becomes attached to the enzyme. The appending of a large group to the active site probably accounts for the observation that most modified enzymes prepared in this way are inactive.[7,8] Within the past few years, the use of inhibitors that deliver a small group to the enzyme has been reported. Methyl 4-