

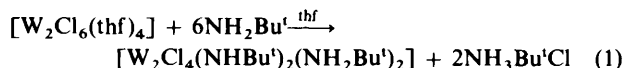
Preparation, Characterisation, and X-Ray Crystal Structure of $[W_2Cl_4(NHBU^t)_2(NH_2BU^t)_2] \cdot \dagger$ A Triply-bonded Ditungsten Compound containing t-Butylamido Ligands

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Treatment of the dimer $[W_2Cl_6(thf)_4]$ (thf = tetrahydrofuran) with excess t-butylamine caused the replacement of two chlorines by t-butylamido ligands and the formation of the new dimer $[W_2Cl_4(NHBU^t)_2(NH_2BU^t)_2]$ which was characterised by n.m.r. spectroscopy and a single-crystal X-ray structure determination. The molecule has 222 (D_2) symmetry, with disordering of the amide and amine ligands, and an eclipsed structure with strong $Cl \cdots H-N$ intermolecular bonding. The $W \equiv W$, $W-Cl$, and $W-N$ distances are 2.288(3), 2.352(5), and 2.11(2) Å respectively.

The chemistry of dinuclear compounds of molybdenum and tungsten containing metal-metal triple bonds has been developed extensively during the last ten years.^{1,2} This work has centred mainly on the M_2X_6 dialkylamido and alkoxo compounds, $[M_2(NR_2)_6]$, $[M_2Cl_2(NR_2)_4]$, $[M_2(OR)_6]$ (R = alkyl) etc., which adopt staggered, ethane-like geometries (A).¹ Recently, the number of compounds known to contain the triply bonded M_2^{6+} unit (M = Mo or W) in which the metal atoms are four-co-ordinate (B) has increased due to the isolation of the alkoxo derivatives $[M_2(OR)_6L_2]$ (L = phosphine or amine),^{1,3} $[M_2(OR)_4\{R'C(O)CHC(O)R''\}_2]$,⁴ and $[M_2(OR)_4(O_2CX)_2]$ (X = OR,⁵ Ph,⁶ or NMe_2).⁷ The conformations adopted by these complexes depend on steric interactions between ligands across the metal-metal bond, with staggered geometries being most common, eclipsed geometries occurring when the metal-metal bond is spanned by a bridging ligand or a hydrogen bond.³

We have found that treatment of $[W_2Cl_6(thf)_4]$ [formed *in situ* by the reduction of WCl_4 with Na-Hg in tetrahydrofuran (thf)⁸] with t-butylamine gives an orange-brown solution from which orange, crystalline $[W_2Cl_4(NHBU^t)_2(NH_2BU^t)_2]$ (1) can be isolated in ca. 80% yield [equation (1)]. This is in contrast to



the reaction between MoX_3 and $NHMe_2$ which has been shown to give the quadruply-bonded Mo^{II} complexes $[Mo_2X_4(NHMe_2)_4]$ (X = Cl or Br).^{9,10}

The ¹H n.m.r. spectrum of (1) contained two Bu^t resonances as singlets at δ 1.08 and 1.27, an AB pattern due to the diastereotopic NH_2 protons of co-ordinated NH_2BU^t with δ_A 3.77, δ_B 4.18, $^2J(HH) = 12.8$ Hz, and a singlet at δ 12.40 due to $NHBU^t$. Evidence for the presence of these ligands was also found in the i.r. spectrum of (1), with $\nu(NH)$ at 3 305w, 3 240w, and 3 202m, and $\delta(NH_2)$ at 1 554m, 1 545 (sh) cm^{-1} . Two quaternary carbon resonances at δ 54.28 and 61.47 with two CH_3 resonances at δ 31.04 and 33.08 in the ¹³C n.m.r. spectrum also indicated that two types of NBU^t were present in the molecule. An X-ray crystal structure analysis was carried out to determine the structure of (1) and a diagram of the molecule is shown in the Figure. Bond lengths and angles are given in Table 1.

† Tetrachlorobis(t-butylamido)bis(t-butylamine)ditungsten(II) ($3W-W$).

Supplementary data available (No. SUP 56489, 2 pp.): thermal parameters, hydrogen atom parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

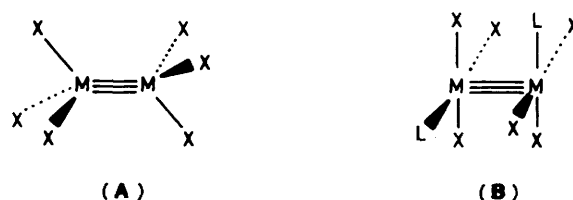


Table 1. Bond lengths (Å) and angles (°) for $[W_2Cl_4(NHBU^t)_2(NH_2BU^t)_2]$

(a) Bond lengths			
N(1)-W(1)	2.108(15)	Cl(1)-W(1)	2.352(5)
W(1)-W(1a)	2.288(3)	C(11)-C(10)	1.439(27)
C(10)-N(1)	1.478(20)	C(13)-C(10)	1.517(28)
C(12)-C(10)	1.445(21)		
(b) Bond angles			
Cl(1)-W(1)-N(1)	89.0(5)	C(10)-N(1)-W(1)	131.8(14)
Cl(1)-W(1)-W(1a)	102.4(1)	N(1)-W(1)-W(1a)	98.0(3)
C(11)-C(10)-N(1)	109.4(17)	C(12)-C(10)-N(1)	107.6(15)
C(12)-C(10)-C(11)	111.2(20)	C(13)-C(10)-N(1)	103.4(17)
C(13)-C(10)-C(11)	112.8(19)	C(13)-C(10)-C(12)	112.0(21)

Each tungsten is approximately square planar with *trans* chlorines and *trans* NBU^t groups and the two WCl_2N_2 units are eclipsed with nitrogen atoms opposite chlorines. The NBU^t groups are disordered with a $W-N$ distance [2.108(15) Å], between those previously reported for $W-NR_2$ (1.98 Å)¹¹ and $W-NHR_2$ (2.28 Å)¹ (R = Me). The $W-W$ distance [2.288(3) Å] is somewhat shorter than similar alkoxo compounds¹ which is consistent with the lesser degree of ligand-to-metal π donation expected when alkoxo groups are replaced by chlorines. $W-Cl$ distances [2.352(5) Å] are slightly longer than in $[W_2Cl_4(NMe_2)_4]$.¹² The eclipsed geometry can be explained by $Bu^tNH \cdots Cl$ hydrogen bonding across the $W \equiv W$ bond ($N \cdots Cl$ 3.12 Å) which also causes shielding of the NH proton because of the diamagnetic anisotropy of the metal-metal triple bond.¹³⁻¹⁵

By carrying out ¹⁵N INEPT experiments using values of $^1J(NH)$ obtained from the 400-MHz ¹H n.m.r. spectrum of (1), a ¹⁵N resonance at δ 66.1 was observed and assigned to NH_2BU^t by virtue of its multiplicity in the non-refocused spectrum. A resonance which could unequivocally be assigned to $NHBU^t$ was not observed. This resonance is to be expected in the region

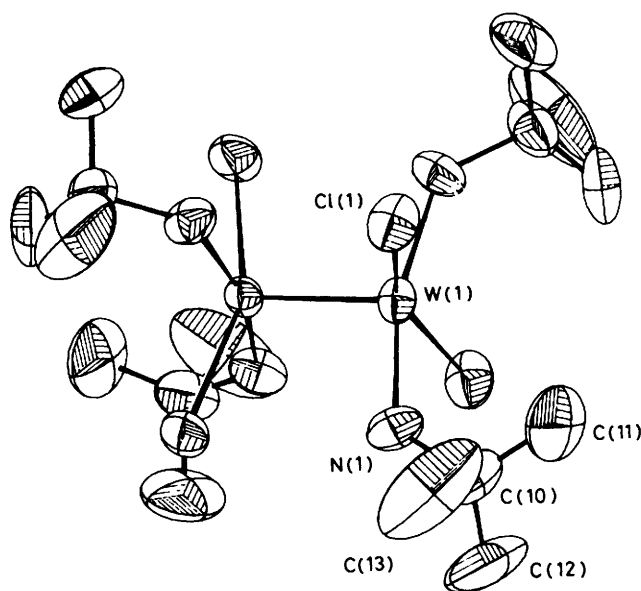


Figure. Molecular structure of $[\text{W}_2\text{Cl}_4(\text{NHBU})_2(\text{NH}_2\text{BU})_2]$

between those found for imido ligands and co-ordinated NH_2Bu^1 .^{16,*}

Previous attempts to isolate $[\text{W}_2\text{Cl}_n(\text{NR}_2)_{6-n}]$ ($\text{R} = \text{Me}$ or Et) compounds for $n > 2$ have been unsuccessful, insoluble polymeric solids and $[\text{W}_2\text{Cl}_2(\text{NR}_2)_4]$ being obtained.¹² This would suggest that the presence of NH_2Bu^1 is preventing polymerisation of $[\text{WCl}_2(\text{NHBU})]$ and further attempts to synthesise $[\text{W}_2\text{Cl}_n(\text{NR}_2)_{6-n}]$ with $n > 2$ in the presence of phosphine or amine ligands might be successful. When a $[\text{H}_8]$ toluene solution of (1) in a sealed n.m.r. tube was heated, the AB pattern due to co-ordinated NH_2Bu^1 (which at 80 MHz and ambient temperature is slightly broad) gradually broadened and collapsed into a single peak which, by 100 °C had started to sharpen up again to a singlet at δ 3.88. This is probably due to breaking of the hydrogen bonds between the two halves of the molecule and rotation about the $\text{W}=\text{W}$ bond. In this situation the NH_2Bu^1 protons become equivalent. Under these conditions, no polymerisation was observed, and the original spectrum was restored upon cooling the sample to ambient temperature.

The *t*-butylamido compound (1) is potentially a useful starting material for the preparation of other tungsten-tungsten bonded compounds and the chemistry of this molecule is under investigation.

Experimental

All manipulations were carried out in a dry, inert (N_2) atmosphere using standard Schlenk techniques. Solvents were dried and distilled from sodium benzophenone ketyl. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 577 spectrophotometer. N.m.r. spectra were recorded on a Bruker WH400 spectrometer at 400 MHz (^1H), 100 MHz (^{13}C), and 40.6 MHz (^{15}N). Hydrogen-1 spectra were also recorded at 80 MHz on a Bruker WP80 spectrometer.

Tetrachlorobis(t-butylamido)bis(t-butylamine)ditungsten(II).—*t*-Butylamine (4.6 cm³, 43.6 mmol) was added to a stirred

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for $[\text{W}_2\text{Cl}_4(\text{NHBU})_2(\text{NH}_2\text{BU})_2]$

Atom	x	y	z
W(1)	634(0.5)	634(0.5)	0
N(1)	1 643(10)	-18(15)	1 605(15)
C(10)	2 642(12)	357(14)	2 243(20)
C(11)	2 891(14)	1 369(15)	1 632(29)
C(12)	3 439(12)	-405(18)	1 879(30)
C(13)	2 421(18)	394(29)	3 896(21)
Cl(1)	15(4)	1 813(3)	1 806(4)

solution of $[\text{W}_2\text{Cl}_6(\text{thf})_4]$ prepared by reduction of WCl_4 (4.73 g, 14.52 mmol) with one equivalent of Na-Hg (0.4%) in tetrahydrofuran (100 cm³). After 14 h the solution was filtered and the solvent removed under reduced pressure. The residue was extracted with hot hexane (50 cm³) and the solvent stripped from the filtrate to give the product as an orange crystalline solid. Yield 4.53 g, 78%. I.r. (Nujol): 3 305w, 3 240w, 3 202m, 2 710w,br, 2 600w,br, 2 508w, 2 070w,br, 1 606w, 1 554m, 1 545 (sh), 1 397w, 1 344w, 1 266w, 1 210s, 1 130s, 1 024w, 968w, 896w, 793w, 743m, 600w,br, 451w, 347w, and 314s cm⁻¹ {Found: C, 24.2; H, 5.3; Cl, 18.8; N, 6.90. $[\text{W}_2\text{Cl}_4(\text{NHBU})_2(\text{NH}_2\text{BU})_2]$ requires C, 24.0; H, 5.30; Cl, 17.75, N, 7.00%}.

X-Ray Crystallography.—The crystal used for the X-ray study was sealed under argon in a glass capillary. Cell dimension and intensity data were measured using a CAD4 diffractometer in a manner previously described in detail.¹⁸

Crystal data. $\text{C}_{16}\text{H}_{22}\text{Cl}_4\text{NW}_2$, $M = 800.05$, tetragonal, $a = b = 12.764(2)$, $c = 9.008(1)$ Å, $U = 1 467.6$ Å³, space group $P4_22_2$, $Z = 2$, $D_c = 1.810$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.710 69$ Å, $\mu(\text{Mo-K}\alpha) = 78.56$ cm⁻¹, 1 302 unique reflections measured ($1.5 < 2\theta < 25^\circ$) of which 1 010 were considered observed [$I > 1.5\sigma(I)$].

The structure was solved *via* the heavy-atom method and refined by least squares. The unique tungsten atom lies on a two-fold axis ($x, x, 0$) and the molecule as a whole has crystallographic 222 symmetry, which requires disordering of the amide and amine groups. All non-hydrogen atoms were assigned anisotropic thermal parameters; methyl hydrogens were inserted in idealised positions and assigned one overall, refined isotropic thermal parameter. Attempts to locate and refine the amine/amide hydrogens were unsuccessful. The final R and R' values were 0.0347 and 0.0350, and the weighting scheme $w = 1/[\sigma^2(F_o) + 0.0003F_o^2]$ gave acceptable agreement analyses. Final atomic positional parameters are given in Table 2.

Acknowledgements

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* The compound $[\text{W}(\text{NBu}^1)_2(\text{NHBU})_2]$ ¹⁷ has ^{15}N resonances at δ 365.1 and 143.5 due to $N\text{Bu}^1$ and $N\text{HBU}^1$ respectively (D. C. Bradley and R. J. Errington, unpublished work).

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