# Syntheses and structures of $W_2(\mu\text{-Cl})_3Cl_6^-$ and $W_2(\mu\text{-Cl})_2Cl_8^{2-}$, new $d^2$–$d^2$ confacial and edge-sharing bioctahedral ditungsten compounds, and a convenient synthesis of $W_2(\mu\text{-Cl})_3Cl_6^{2-}$

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**$(NR_4)W_2Cl_9$ and $(NR_4)_2W_2Cl_{10}$, prepared by addition of $NR_4Cl$ (R = alkyl) to $(WCl_4)_x$ powder in $CH_2Cl_2$, have confacial [W=W, 2.689(1) Å] and edge-sharing bioctahedral [W=W, 2.792(1) Å] structures, respectively, as $NBnEt_3^+$ salts, and convert with added $NR_4Cl$ to $(NR_4)_2W_2Cl_9$ and $(NR_4)WCl_6$ and eventually $(NR_4)_2WCl_6$; $(NR_4)W_2Cl_9$ can be converted to $(NR_4)_2W_2Cl_{10}$ by $NR_4Cl$ at −30 °C.**

High symmetry confacial [$M_2(\mu\text{-L})_3L_6$, $D_{3h}$; L = ligand] and edge-sharing [$M_2(\mu\text{-L})_2L_8$, $D_{2h}$] bioctahedral complexes are known for many transition metals and are of considerable importance for understanding metal–metal single and multiple bonding.[1] The effect of orbital population on M–M distance can be understood by studying isostructural compounds with various d-electron counts. Confacial bioctahedral congeners with differing d-electron counts are known for few metals (*e.g.* Re,[2] W). For tungsten, $W_2(\mu\text{-Cl})_3Cl_6^{3-}$ ($d^3$–$d^3$; one of the first[3] metal–metal bonded compounds to be recognized[4] as such) and $d^2$–$d^3$ $W_2(\mu\text{-Cl})_3Cl_6^{2-}$ have been reported.[5,6] The W–W distance in the former, which has been studied theoretically,[7] is a short 2.409(7)–2.4329(6) Å,[6,8,9] (depending on cation), and increases[6] by 0.12 Å upon oxidation to $W_2(\mu\text{-Cl})_3Cl_6^{2-}$. While there are many preparations[10] of $W_2(\mu\text{-Cl})_3Cl_6^{3-}$, few are known for the dianion;[5,6,11] $W_2(\mu\text{-Br})_3Br_6^{2-}$ is also known.[12]

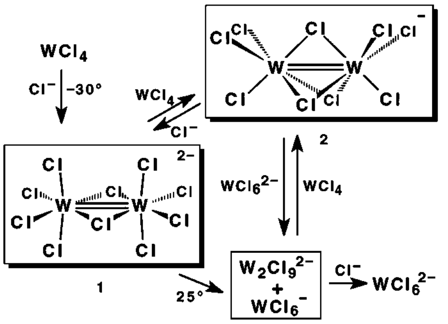
We recently developed new syntheses of powdered and crystalline $(WCl_4)_x$ and showed that its structure was a linear polymer of edge-sharing bioctahedra with alternating short (double bond) and long (no bond) W···W separations.[13] The unusually reactive powder form, prepared from Sn reduction of $WCl_6$ in $ClCH_2CH_2Cl$, reacts with $NR_4Cl$ to give the new chloroditungstates $W_2(\mu\text{-Cl})_2Cl_8^{2-}$ **1** and $W_2(\mu\text{-Cl})_3Cl_6^-$ **2** as well as $W_2(\mu\text{-Cl})_3Cl_6^{2-}$ **3**. We report synthetic and structural details.

The reaction of $NR_4Cl$ ($R_4$ = $BnEt_3$, $BnBu_3$, $Bu_4$) with $(WCl_4)_x$ leads to scission of dinuclear fragments, disproportionation, and then comproportionation depending on stoichiometry and temperature. At 25 °C, reaction of $(WCl_4)_x$ with one equiv. of $NBnEt_3Cl$ (a cation which facilitates product separation) in $CH_2Cl_2$ leads to $(NBnEt_3)_2(W_2Cl_9)$ [**3**; 96% isolated yield, eqn. (1)]† and $(NBnEt_3)WCl_6$. The mixture is comproportionated by $NBnEt_3Cl$ to $(NBnEt_3)_2WCl_6$ [94% yield, eqn. (1)]. UV–VIS spectra of products matched literature data.[11,14]

$$3\,WCl_4 \xrightarrow[-(NR_4)WCl_6]{3\,NR_4Cl} \underset{\mathbf{3}}{(NR_4)_2[W_2(\mu\text{-Cl})_3Cl_6]} \xrightarrow{3\,NR_4Cl} 3\,(NR_4)_2WCl_6 \quad (1)$$

$$\begin{array}{l} \underset{\mathbf{1}}{3\,(NR_4)_2[W_2(\mu\text{-Cl})_2Cl_8]} \longrightarrow \underset{\mathbf{3}}{2\,(NR_4)_2[W_2(\mu\text{-Cl})_3Cl_6]} + 2\,(NR_4)WCl_6 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow {\scriptstyle 6\,WCl_4} \\ \qquad\qquad\qquad\qquad\qquad\qquad \underset{\mathbf{2}}{6\,(NR_4)[W_2(\mu\text{-Cl})_3Cl_6]} \quad (2) \end{array}$$

The reaction between $(WCl_4)_x$ and $NBnEt_3Cl$ in $CH_2Cl_2$ at −30 °C yields $(NBnEt_3)_2[W_2(\mu\text{-Cl})_2Cl_8]$ **1** which crystallizes along with undissolved $(WCl_4)_x$. Upon warming to 25 °C, **1** redissolves and disproportionates to **3** and $(NBnEt_3)WCl_6$ [eqn. (2)], thus establishing that **1** is an intermediate in eqn. (1). With additional $(WCl_4)_x$, **3** and $(NR_4)WCl_6$ comproportionate to emerald green $(NBnEt_3)[W_2(\mu\text{-Cl})_3Cl_6]$ [**2**; eqn. (2)]. Compound **2** can be prepared conveniently‡ in one step (90% isolated yield) by combining $(WCl_4)_x$ with 0.5 equiv. $NBnEt_3Cl$ in $CH_2Cl_2$ at 25 °C, and can be converted§ back to **1** (95% isolated yield) at −30 °C by $NBnEt_3Cl$ in $CH_2Cl_2$; isolation is possible because of the low solubility of the $NBnEt_3^+$ salt. We believe that **1** and **2** have not been observed in previous studies[5,6,14] because they disproportionate in solution (**1**) or in the presence of $Cl^-$ (**2**). Compound **2** is reduced to **3** by either $(NBnEt_3)_2WCl_6$ or $Cp_2Fe$ in $CH_2Cl_2$. Scheme 1 summarizes the principal transformations.



Scheme 1

The syntheses of **1**, **2**, and **3** are facilitated by the use of $(WCl_4)_x$ powder.[13] Reactions of $(WCl_4)_x$, as prepared by reduction of $WCl_6$ with red phosphorus, $W(CO)_6$, or Sb,[13] with $NR_4Cl$ proceed more slowly and lead to lower purity materials because the lower solubility of these $(WCl_4)_x$ materials results in an excess of $NR_4Cl$ in the early stages of the reactions.

Single crystals of $(NBnEt_3)_2[W_2(\mu\text{-Cl})_2Cl_8]\cdot 3CH_2Cl_2$ **1** were obtained from −35 °C $CH_2Cl_2$ solution. The solid-state structure¶ of the centrosymmetric ditungstate portion of **1** (Fig. 1) consists of an edge-sharing bioctahedron with a W(1)–W(1A) distance of 2.792(1) Å, a W(1)–Cl(1)–W(1A) angle of 71.88(6)°, and a Cl(1)–W(1)–Cl(1A) angle of 108.12(6)°. The crystallographically independent axial Cl(2) and Cl(3) in each bioctahedral hemisphere are bent away from Cl(3A) and Cl(2A) with Cl(2)–W(1)–W(1A) and Cl(3)–W(1)–W(1A) angles of

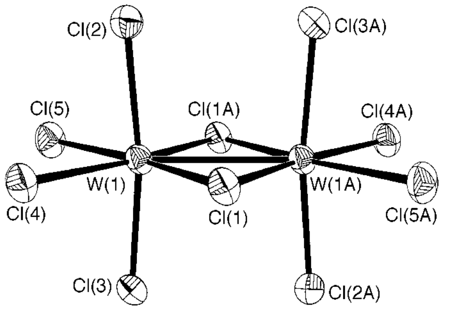


**Fig. 1** Thermal ellipsoid plot of the molecular structure of the ditungsten anion portion of **1**

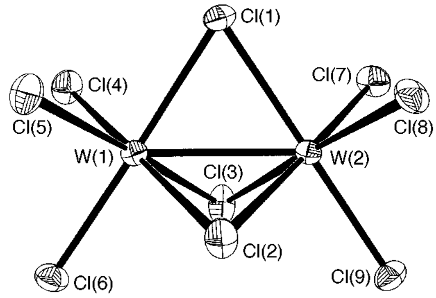


**Fig. 2** Thermal ellipsoid plot of the molecular structure of the ditungsten anion portion of **2**

94.38(6)° and 93.98(6)°, respectively, and a Cl(2)$\cdots$Cl(3A) non-bonded distance which is appreciably closer [3.131(3) Å] than twice the Cl van der Waals (VDW) radius of 1.70–1.90 Å.[15]

The anion in **1** is similar to that of the W=W bonded portion of $(WCl_4)_x$, and can be formally viewed as the scission of that edge-sharing bioctahedral portion of the polymeric structure[13] and addition of two $Cl^-$ endcaps. The W=W distance in crystalline $(WCl_4)_x$ is 2.688(2) Å, with W–Cl–W bridge angles of 69.4(2)° and bent-back axial Cl [W–W–Cl(axial), 94.99(12)°]. The axial Cl in each bioctahedral hemisphere of $(WCl_4)_x$ are also closer [3.085(10) Å] than twice the Cl VDW radius. There is no similarity between the structures of **1** and $W_2Cl_{10}$ [*i.e.* $W_2(\mu\text{-}Cl)_2Cl_8$] which has a long W$\cdots$W separation of 3.814(2) Å and a $Cl_\mu$–W–$Cl_\mu$ angle of 81.5(1)°.[16]

The only other Group 6 $M_2(\mu\text{-}Cl)_2Cl_8^{2-}$ compound is edge-sharing bioctahedral $(PPh_4)_2[Mo_2Cl_{10}]$,[17] with no Mo–Mo bond (Mo$\cdots$Mo, 3.80 Å). The reason(s) for the substantial differences between $Mo_2(\mu\text{-}Cl)_2Cl_8^{2-}$ and $W_2(\mu\text{-}Cl)_2Cl_8^{2-}$ **1** are presently unknown, though the difference in degree of metal–metal bonding parallels that for $Mo_2(\mu\text{-}Cl)_3Cl_6^{3-}$ and $W_2(\mu\text{-}Cl)_3Cl_6^{3-}$.

Single crystals of $(NBnEt_3)[W_2(\mu\text{-}Cl)_3Cl_6]$ **2** were obtained from cooled (−35 °C) $CH_2Cl_2/CHCl_3$ solutions. Single-crystal X-ray diffractometry[‖] confirmed that the anion portion of **2** possesses a confacial bioctahedral structure (Fig. 2) with a W(1)–W(2) distance of 2.696(3) Å and an acute W(1)–Cl(μ)–W(2) average angle of 66.6(1)° which is smaller than the bridge angle of 70.53° for an idealized confacial bioctahedron. The W–W distance and W–$Cl_\mu$–W angles are consistent with a formal W(1)–W(2) double-bonding ($a_1'^2e'^2$) interaction.

The W–W distance in $W_2(\mu\text{-}Cl)_3Cl_6^{n-}$ ($n$ = 3, 2, 1) thus increases from 2.409(7) to 2.4329(6) Å for $n$ = 3, to 2.540(1) Å for $n$ = 2, and to 2.696(3) Å for $n$ = 1 (compound **2**), as would be expected from σ-bond weakening with increasing nuclear charge and/or the decrease in formal bond order from 3 to 2.5 to 2.[6] The UV–VIS data for **2** correspond to those reported[11] for $(Bu_4N)_2(W_4Cl_{17})$, whose structure was not determined. The analytical accuracy, as the authors noted, did not rule out an alternative formulation such as $NBu_4(W_2Cl_9)$. It is interesting that $W_4Cl_{17}^{2-}$ was reported[11] to react with excess $Cl^-$ to give products including $W_2Cl_9^{2-}$, as does **2**.

The mechanism of formation of **1**, **2**, and **3** from chloride attack on $(WCl_4)_x$, the solid-state and solution magnetochemistry of **1** and **2** (which exhibits a surprisingly low moment of $\leqslant$ 1.3 $\mu_B$ in solution by the Evans method), theoretical studies using the GAMESS program,[18] and the reactivity of the new ditungsten(IV) perchloroanions are under investigation.

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## Notes and References

† Synthesis of **3**: a stirred mixture of 0.500 g (1.535 mmol) $WCl_4$ and 0.350 g (1.537 mmol) $NBnEt_3Cl$ in 10 mL $CH_2Cl_2$ converted in 10 min from a gray suspension to a deep purple-brown suspension with microcrystals, and eventually to a deep blue-purple precipitate in a green-brown solution. After several days, the precipitate was filtered off, washed with $CH_2Cl_2$ until the wash became light blue-purple, and dried *in vacuo*. Weight = 0.525 g (96% yield). The UV–VIS spectrum ($CH_2Cl_2$) matched those of known $W_2Cl_9^{2-}$ salts. Anal: W, 33.7; Cl, 29.01. Calc. for $(NBnEt_3)_2W_2Cl_9$: W, 34.32; Cl, 29.78%. The supernatant was cooled to −30 °C for one day and a first crop of the brown crystalline product was isolated by filtration for analysis and dried *in vacuo*; weight 0.110 g (37% yield) $(NBnEt_3)WCl_6$. Anal: W, 31.2; Cl, 36.43. Calc. for $(NBnEt_3)WCl_6$: W, 31.22; Cl, 36.12%.

‡ Synthesis of **2**: a stirred mixture of $WCl_4$ (1.00 g, 3.07 mmol), $NBnEt_3Cl$ (0.350 g, 1.54 mmol), and $CH_2Cl_2$ (15 mL) gave a deep blue-green solution after 10–30 min. After one day, the deep blue-green solution was filtered and rotary-evaporated to a viscous oil, which crystallized to 1.218 g dark emerald-green product (90% yield). Anal: W, 41.1; Cl, 35.58. Calc. for $(NBnEt_3)W_2Cl_9$: W, 41.83; Cl, 36.29%. UV–VIS, $\lambda$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 650 (825), 530 (370), 360 (shoulder), and 305 (22600). MS (FAB, negative ion mode, $m/z$): 687 (M$^+$, base peak for $W_2Cl_9^-$ isotope pattern).

§ Synthesis of **1** *via* $Cl^-$ addition to $W_2Cl_9^-$: pre-cooled (−30 °C) solutions of 0.052 g (0.228 mmol) $NBnEt_3Cl$ in 2 mL of $CH_2Cl_2$ and 0.200 g (0.228 mmol) $(NBnEt_3)(W_2Cl_9)$ in 4 mL of $CH_2Cl_2$ were mixed. Deep purple-brown microcrystals formed immediately. After aging at −30 °C for 1 day, the crystals were filtered off cold, washed with cold $CH_2Cl_2$ (*ca.* 5 mL) and dried *in vacuo*. Weight = 0.257 g (95% yield). Anal: W, 30.8. Calc. for $(NBnEt_3)_2W_2Cl_{10}\cdot CH_2Cl_2$: W, 30.85%.

¶ Crystallographic data for **1**: $C_{29}H_{50}Cl_{16}N_2W_2$, $[(NBnEt_3)_2(W_2Cl_{10})\text{-}(CH_2Cl_2)_3]$, $M$ = 680.81, monoclinic, $a$ = 14.620(3), $b$ = 15.430(3), $c$ = 10.860(2) Å, $\beta$ = 108.38(3)°, $V$ = 2324.9(8) Å$^3$, $T$ = 213 K, space group $P2_1/n$, $Z$ = 2, $\mu$ = 5.889 mm$^{-1}$, 5553 reflections measured, 4053 independent reflections, $R1$ = 0.0451, $wR2$ = 0.0918.

‖ Crystallographic data for **2**: $C_{13}H_{22}Cl_9NW_2$, $M$ = 879.07, monoclinic, $a$ = 8.910(2), $b$ = 15.350(3), $c$ = 17.920(4) Å, $\beta$ = 94.80(3)°, $V$ = 2442.3(9) Å$^3$, $T$ = 213 K, space group $P2_1/c$, $Z$ = 4, $\mu$ = 10.398 mm$^{-1}$, 4672 reflections measured, 3819 independent reflections, $R1$ = 0.0500, $wR2$ = 0.0987. CCDC 182/968.

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