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 $W_2(\mu\text{-}Cl)_3Cl_6^{2-}$

Vladimir Kolesnichenko, Dale C. Swenson and Louis Messerle*

Department of Chemistry, The University of Iowa, Iowa City, IA 52242, USA. E-mail: lou-messerle@uiowa.edu

$(NR_4)W_2Cl_9$ 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]

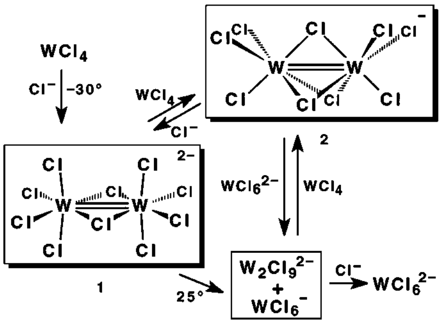
We recently developed new syntheses of powdered and crystalline $(WCl_4)_x$ and showed that its structure was a linear polymer of edge-sharing bioctahedra with alternating short (double bond) and long (no bond) W···W separations.[13] The unusually reactive powder form, prepared from Sn reduction of WCl_6 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]

$$3\,\mathrm{WCl_4} \xrightarrow[-(\mathrm{NR_4})\mathrm{WCl_6}]{3\,\mathrm{NR_4Cl}} \underset{\mathbf{3}}{(\mathrm{NR_4})_2[\mathrm{W_2}(\mu\text{-Cl})_3\mathrm{Cl_6}]} \xrightarrow{3\,\mathrm{NR_4Cl}} 3\,(\mathrm{NR_4})_2\mathrm{WCl_6} \quad (1)$$

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.

$$\begin{tikzcd}[column sep=small] \underset{\mathbf{1}}{3\,(\mathrm{NR_4})_2[\mathrm{W_2}(\mu\text{-Cl})_2\mathrm{Cl_8}]} \arrow[r] & \underset{\mathbf{3}}{2\,(\mathrm{NR_4})_2[\mathrm{W_2}(\mu\text{-Cl})_3\mathrm{Cl_6}]} + 2\,(\mathrm{NR_4})\mathrm{WCl_6} \arrow[d, "6\,\mathrm{WCl_4}"] \\ & \underset{\mathbf{2}}{6\,(\mathrm{NR_4})[\mathrm{W_2}(\mu\text{-Cl})_3\mathrm{Cl_6}]} \quad (2) \end{tikzcd}$$



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

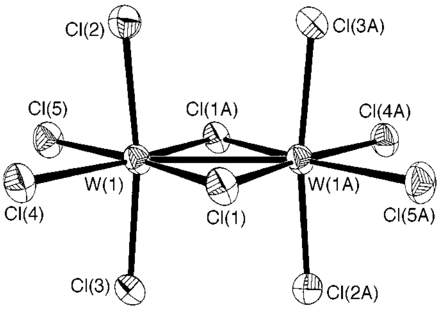


Fig. 1 Thermal ellipsoid plot of the molecular structure of the ditungsten anion portion of **1**

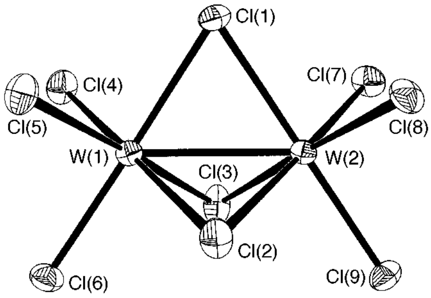


Fig. 2 Thermal ellipsoid plot of the molecular structure of the ditungsten anion portion of **2**

94.38(6)° and 93.98(6)°, respectively, and a Cl(2)···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···W separation of 3.814(2) Å and a Cl_μ–W–Cl_μ 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···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_μ–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 μ_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.

The support of Nycomed, Inc. and the University of Iowa Biosciences Initiative Research Program is gratefully acknowledged, as are the useful comments of a reviewer.

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, λ/nm (ε/dm³ 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, β = 108.38(3)°, V = 2324.9(8) Å³, T = 213 K, space group $P2_1/n$, Z = 2, μ = 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, β = 94.80(3)°, V = 2442.3(9) Å³, T = 213 K, space group $P2_1/c$, Z = 4, μ = 10.398 mm⁻¹, 4672 reflections measured, 3819 independent reflections, $R1$ = 0.0500, $wR2$ = 0.0987. CCDC 182/968.

1 (*a*) F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd edn. Clarendon Press, Oxford, 1993, p. 3; (*b*) F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, 1972, **6**, 161; (*c*) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3821; (*d*) S. Shaik, R. Hoffmann, C. R. Fisel and R. H. Summerville, *J. Am. Chem. Soc.*, 1980, **102**, 4555; (*e*) W. C. Trogler, *Inorg. Chem.*, 1980, **19**, 697; (*f*) F. A. Cotton and X. Feng, *Int. J. Quantum Chem.*, 1996, **58**, 671.

2 G. A. Heath, J. E. McGrady, R. G. Raptis and A. C. Willis, *Inorg. Chem.*, 1996, **35**, 6838.

3 (*a*) O. Olsson, *Ber. Dtsch. Chem. Ges.*, 1913, **46**, 566; (*b*) O. Olsson, *Z. Anorg. Allg. Chem.*, 1914, **88**, 1914.

4 (*a*) C. Brosset, *Ark. Chem., Miner. Geol. A*, 1935, **12**, no. 4; (*b*) C. Brosset, *Nature*, 1935, **135**, 874.

5 R. Saillant and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 1969, **91**, 2174.

6 F. A. Cotton, L. R. Falvello, G. N. Mott, R. R. Schrock and L. G. Sturgeoff, *Inorg. Chem.*, 1983, **22**, 2621.

7 (*a*) R. Stranger, S. A. Macgregor, T. Lovell, J. E. McGrady and G. A. Heath, *J. Chem. Soc., Dalton Trans.*, 1996, 4485; (*b*) J. E. McGrady, T. Lovell and R. Stranger, *Inorg. Chem.*, 1997, **36**, 3242.

8 W. H. Watson, Jr. and J. Waser, *Acta Crystallogr.*, 1958, **11**, 689.

9 K. R. Dunbar and L. E. Pence, *Acta Crystallogr., Sect. C*, 1991, **47**, 23.

10 (*a*) H. B. Jonassen, A. R. Tarsey, S. Cantor and G. F. Helfrich, *Inorg. Synth.*, 1957, **5**, 139; (*b*) R. A. Laudise and R. C. Young, *Inorg. Synth.*, 1960, **6**, 149; (*c*) E. A. Heintz, *Inorg. Synth.*, 1963, **7**, 142; (*d*) R. C. Young, *J. Am. Chem. Soc.*, 1932, **54**, 4515; (*e*) R. Uzel and R. Pribil, *Coll. Czech. Chem. Commun.*, 1938, **10**, 330; (*f*) O. Collenberg and J. Backer, *Z. Electrochem.*, 1924, **30**, 230; (*g*) R. Saillant, J. L. Hayden and R. A. D. Wentworth, *Inorg. Chem.*, 1967, 6, 1497.

11 W. H. Delphin and R. A. D. Wentworth, *Inorg. Chem.*, 1973, **12**, 1914.

12 J. L. Templeton, R. A. Jacobsen and R. E. McCarley, *Inorg. Chem.*, 1977, **16**, 3320.

13 V. Kolesnichenko, D. C. Swenson and L. Messerle, *Inorg. Chem.*, 1998, **37**, 3257.

14 T. B. Scheffler and C. L. Hussey, *Inorg. Chem.*, 1984, **23**, 1926.

15 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

16 F. A. Cotton and C. E. Rice, *Acta Crystallogr., Sect. B*, 1978, **34**, 2833.

17 E. Hey, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1984, **508**, 86.

18 J. Jensen and L. Messerle, unpublished results.

Received in Bloomington, IN, USA, 26th May 1998; 8/03903H