Crystal, Molecular, and Electronic Structure of $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$: a Metal–Metal Single Bond between Eight-co-ordinate Tantalum Atoms

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The crystal structure of the title complex shows an MCl_4M bridge across a weak Ta–Ta interaction and eight-fold co-ordination about each metal centre; an electronic structure calculation supports the existence of a σ metal–metal bond.

To date, heavier group 5 d^1 transition metal complexes have shown six- and eight-fold co-ordination geometries for monomeric species [*e.g.* $NbCl_4L_2$, $TaCl_4(diars)_2$[1] (diars = *o*-$Me_2AsC_6H_4AsMe_2$)] and some evidence of weak metal–metal bonding in polymeric octahedral species (*e.g.* $NbCl_4$, Nb–Nb distances of 3.029 and 3.794 Å).[2]

During work involving reactions of $TaCl_5$ with various lithium reagents in the presence of PMe_3, we have often observed the formation of small amounts of an insoluble red-brown crystalline product for which analyses were poor but showed that reduction from Ta^V had occurred. The complex did not form when $TaCl_5$ was kept for long periods in the presence of PMe_3–solvent or when a reducing agent such as zinc or magnesium metal was added and was apparently formed only as a reduction side product when the lithium reagent was present. As the insolubility suggested a polymeric material with the possibility of a metal–metal interaction, the structure was determined by a single-crystal *X*-ray study.

Crystal data: $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$, $C_{12}H_{36}Cl_8P_4Ta_2$, $M = 949.88$, cubic, $a = 16.4000(4)$ Å, $U = 4410.94$ Å^3, space group *Im*3, $Z = 6$, $D_c = 2.144$ g cm^{-3}, $F(000) = 2047.63$, $\mu(\text{Mo-}K_\alpha) = 61.15$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å. Intensity data were recorded on a Nonius CAD4 diffractometer with

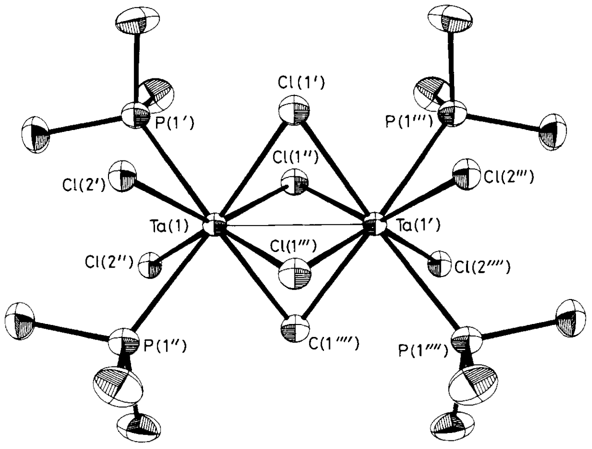

Figure 1. Molecular structure of $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$. Important bond lengths (Å) and angles (°): Ta(1)–Cl(1) 2.544(2), Ta(1)–Cl(2) 2.497(2), Ta(1)–P(1) 2.677(3), Ta(1)–Ta(1′) 2.830(1), Ta(1)–Cl(1)–Ta(1′) 67.6(1), P(1)–Ta(1)–Cl(1) 79.8(1), P(1)–Ta(1)–Cl(2) 72.1(0), Cl(2)–Ta(1)–Cl(1) 79.4(1), Cl(1′)–Ta(1)–Cl(1″) 72.5(1), Cl(1′)–Ta(1)–Cl(1‴) 71.4(1), P(1′)–Ta(1)–P(1″) 114.1(1), Cl(2′)–Ta(1)–Cl(2″) 113.6(1), Cl(1′)–Ta(1)–Cl(1⁗) 112.4(1).

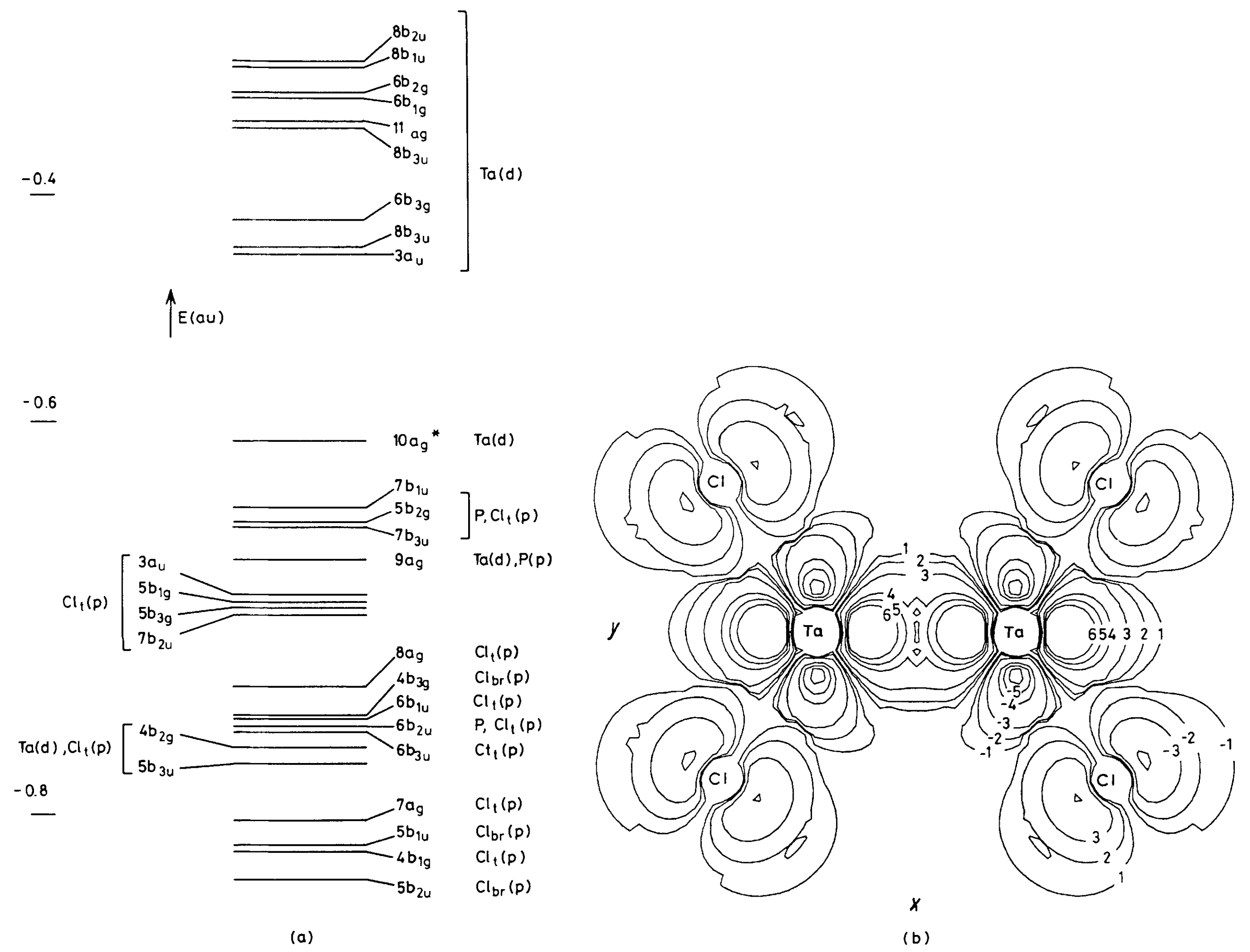

Figure 2. (a) SCF-X_α-Scattered wave orbital energies for $[Ta_2Cl_4(\mu\text{-}Cl)_4(PH_3)_4]$. (* = highest occupied molecular orbital.) (b) Contour plot of the metal–metal bonding MO, $10a_g$, in the xy plane of the molecule. [Contours ±1, ±2, ±3, ±4, ±5, ±6 represent contours at ±0.01, ±0.02, ±0.04, ±0.08, ±0.10, ±0.12 (atomic units) respectively.]

Mo-K_α radiation, and corrected for Lorentz, polarisation, and absorption effects. The structure was solved from Patterson and electron density syntheses and refined by full-matrix least-squares (all non-hydrogen atoms anisotropic) to an R-value of 0.0306 for 691 reflections with $F_o > 3\sigma(F_o)$. All hydrogen atoms were located.†

The structure (Figure 1) contains two tantalum(IV) metal centres bridged by four chlorine atoms with each metal centre containing two terminal chlorines and two PMe_3 groups. The co-ordination geometry about each tantalum centre is a regular square antiprism with *mm* symmetry imposed by the space group. Of particular interest are the four highly symmetrical chlorine bridges, each with a Ta–Cl bond length of 2.544(2) Å, being slightly longer than the terminal Ta–Cl [2.497(2) Å]. Metal–metal bonding has not previously been defined by X-ray analysis for two Ta^{IV} centres, but the Ta–Ta separation in the complex of 2.830(1) Å is intermediate between that found in the $[Ta_6Cl_{12}]^{2+}$ ion[3] (Ta–Ta distance 2.96 Å) where the bond order is 2/3, and the tantalum(III) complexes $[TaCl_3(PMe_3)_2]_2$[4] (Ta–Ta distance 2.721 Å), $Ta_2Cl_6(tht)_3$[5] (tht = tetrahydrothiophene, Ta–Ta distance 2.681 Å), and $Ta_2Cl_6(PhC{\equiv}CPh)(thf)_2$[6] (thf = tetrahydrofuran, Ta–Ta distance 2.677 Å) where bond orders of 2 have been defined. The structural features shown by the complex include both eight-fold co-ordination about each tantalum atom and what we believe is the first example of a symmetrical $M(\mu\text{-}Cl)_4M$ bridge across a metal–metal bond involving two d^1, Ta^{IV}, metal centres.‡

A SCF-X_α-scattered wave calculation[7,8] of the electronic structure of the complex $[Ta_2Cl_4(\mu\text{-}Cl)_4(PH_3)_4]$ (D_{2h} symmetry)§ supports the existence of a σ metal–metal interaction between the d orbitals of the two tantalum atoms leading to a doubly occupied bonding molecular orbital, $10a_g$, and an empty antibonding molecular orbital, $8b_{3u}$, 2.5 eV

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ An unsymmetrical $Ta(\mu\text{-}H)_2(\mu\text{-}Cl)_2Ta$ bridge has been reported in $Cl_2(Me_3P)_2Ta(\mu\text{-}H)_2(\mu\text{-}Cl)_2Ta(PMe_3)_2Cl_2$: A. P. Sattelberger, R. B. Wilson, Jr., and J. C. Huffman, *J. Am. Chem. Soc.*, 1980, **102**, 7113.

§ The co-ordinates used in the calculation were identical to those of the structure of $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ with protons replacing methyl groups of the phosphine [r(P–H) = 1.4177 Å].

higher in energy, Figure 2(a). In the co-ordinate system chosen for the calculation the $10a_g$ metal–metal bonding orbital is comprised of tantalum $d_{x^2-y^2}$ and d_{z^2} waves and terminal chlorine p waves [populations:[9] Ta(x^2-y^2), 0.542; Ta(z^2), 0.112; Cl_t(p), 0.12], Figure 2(b). The complex thus shows characteristics of both high and low valent tantalum chemistry, *i.e.* > six-fold co-ordination for Ta^{IV} and Ta^{V} and metal–metal bonding in Ta^{III}.

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