Notes

Reduction of a Dimeric Tantalum(III) Compound in Acetonitrile Solution by Pulse Radiolysis†

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The reduction of the compound $[Ta_2Cl_6(4Me\text{-}py)_4]$ (4Me-py = 4-methylpyridine), having a metal–metal double bond, has been achieved by pulse radiolysis in dry oxygen-free acetonitrile. The reduction occurs by CH_3CN^- which leads to a transient species assigned to a tantalum dimer in a 2.5 oxidation state. The spectrum of this species has been established. It decays by a first-order process to give a new transient species which in turn decays more slowly by a second-order reaction.

The chemistry of molecular early transition-metal derivatives in low oxidation states (equal to or less than three) is recent compared to that of most other *d* elements. The importance of these oxidation states results from their involvement in homogeneous catalysis[1] or in small-molecule (CO, CO_2, or N_2)[2] or unsaturated-substrate[3] activation.

This work describes the pulse radiolysis of a tantalum compound having a metal–metal double bond $[Ta_2Cl_6(4Me\text{-}py)_4]$, where 4Me-py is 4-methylpyridine.[4] Previous attempts to reduce it chemically were unsuccessful, leading to insoluble or inert clusters,[5] as often observed for niobium or tantalum in low oxidation states; no intermediate step involving Ta^{II} or Ta^{I} could be detected. The electrochemical reduction of a niobium analogue, $[Nb_2Cl_6(PMe_2Ph)_4]$, was attempted in CH_2Cl_2. A two-electron transfer reaction was observed by polarography [well defined reduction step at −0.28 V *vs.* saturated calomel electrode (s.c.e.)] but transitory Nb^{II} was too unstable to be characterised, and coulometry proceeds by a four-electron transfer, probably leading to Nb^{I} which also could not be isolated.[6]

The pulse radiolysis technique allows one to obtain, from a solvent S, reducing species, e_s^- or S^-, which may be transferred to a solute at low concentration in the solution. The apparatus used was a Febetron 707, delivering 20-ns, 1.8-MeV electron pulses; the species generated were detected by absorption spectrophotometry and the dose absorbed by the solution was around 450 Gy. The solvent chosen, acetonitrile, is not commonly employed in such studies, compared to water[7] or alcohols.[8] However, unfortunately, tantalum(III) compounds are very sensitive to water and hydroxylic media, which degrade them to oxo compounds.[4,5] Other solvents, like tetrahydrofuran, which has been used in another case,[9] are not recommended here because they may promote decomposition reactions.[5]

The pulse radiolysis of CH_3CN is known[10] to produce two transient absorptions at 1 420 and 550 nm, tentatively assigned[10] to CH_3CN^- and $(CH_3CN)_2^-$ respectively. We have found that the decay of the former, followed at 1 500 nm in oxygen-free CH_3CN, is accelerated by the addition of the present tantalum compound in sub-millimolar concentrations. From the variation of the pseudo-first-order decay constant with concentration, the second-order rate constant for the reaction of CH_3CN^- with $[Ta_2Cl_6(4Me\text{-}py)_4]$ was found to be $(1.2 \pm 0.2) \times 10^{11}$ dm^3 mol^{-1} s^{-1}.

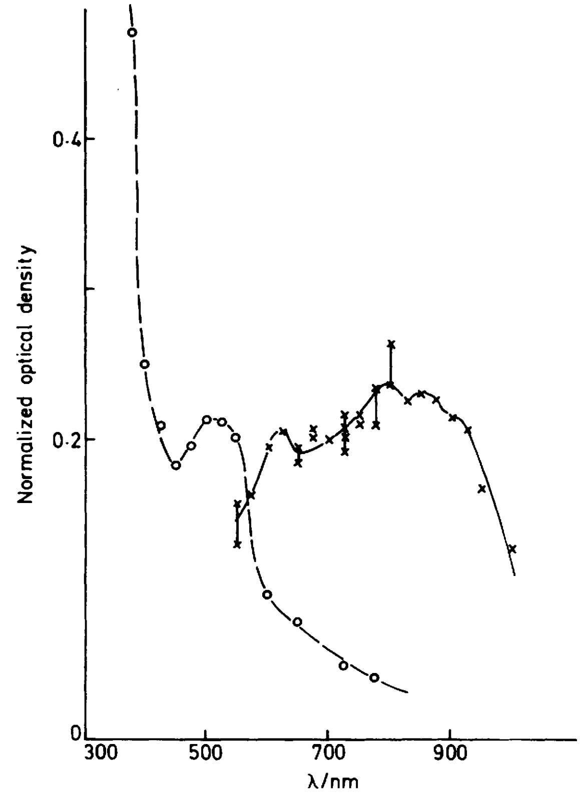

Figure. Electronic spectra obtained immediately after the pulse for CH_3CN solutions of $[Ta_2Cl_6(4Me\text{-}py)_4]$ (×) and 4-methylpyridine (O)

With higher concentrations (2×10^{-3}—5×10^{-3} mol dm^{-3}) of complex we established the spectrum of a transient species (Figure). It comprises several bands and shoulders at 620, 790, 860, and 930 nm, with corresponding absorption coefficients ε 1 020, 1 170, 1 150, and 1 030 dm^3 mol^{-1} cm^{-1} (calculated with a CH_3CN^- radiolysis yield of 1.03[10]). We verified that irradiation of 4-methylpyridine alone in CH_3CN led to an entirely different spectrum (Figure), showing that CH_3CN^-

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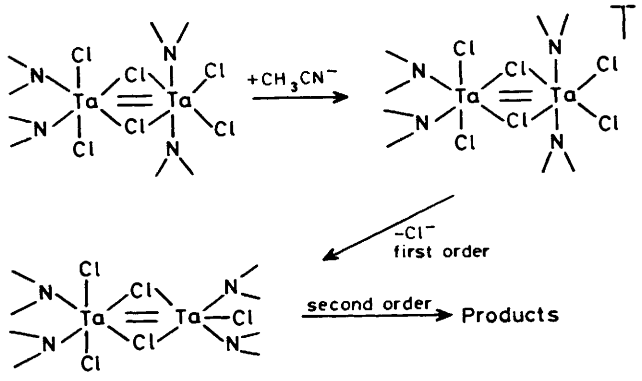
† *Non-S.I. units employed*: eV ≈ 1.60×10^{-19} J; G = 10^{-4} T.

transfers its electron directly to the metal, without an intermediate step using the ligand, as is sometimes reported for other compounds.[11] The very high electron-transfer rate constant is characteristic of a diffusion-controlled process, and the spectrum corresponds, very probably, to a primary product, which we may write as $[Ta_2Cl_6(4Me\text{-}py)_4]^-$. This species disappears by a fast first-order reaction ($k = 1.5 \times 10^5\ s^{-1}$) in 30 μs leading to a second compound which decays more slowly by a second-order reaction (at 600 nm, $2k/\varepsilon l$ is estimated as $4 \times 10^3\ s^{-1}$; for our apparatus, $l = 2.5$ cm).

When the CH_3CN solution was saturated with CH_3Cl, a good scavenger for reducing species, no transient absorption was observed in the visible–i.r. region, indicating that the tantalum transient, detected in argon-saturated CH_3CN, does arise from reaction with CH_3CN^-.

In order to provide some confirmation of the species proposed above, we subjected a CH_3CN solution of $[Ta_2Cl_6(4Me\text{-}py)_4]$, rapidly frozen to liquid-nitrogen temperature, to γ-irradiation from a ^{60}Co source (2 400 Gy). The tantalum dimer being a diamagnetic molecule a one-electron addition should lead to a paramagnetic adduct, giving an e.s.r. signal. The detection was followed from 77 to 130 K. Immediately after the irradiation and at 77 K, we observed an e.s.r. signal at $g_{av.} = 2.0055$, which may be attributed to one or several radicals. With increasing temperature, a new broad and reasonably intense signal appears (peak width ≈ 1 250 G) centred at $g = 2.17$, assignable to a metallic species, despite the lack of hyperfine structure (explainable by the important tantalum quadrupolar moment and the fact that frozen CH_3CN is a polycrystalline matrix). We report this preliminary result as a confirmation of the electron transfer from CH_3CN^- to $[Ta_2Cl_6(4Me\text{-}py)_4]$, giving $[Ta_2Cl_6(4Me\text{-}py)_4]^-$. The product so formed would then lose a chloride by a first-order reaction to give $[Ta_2Cl_5(4Me\text{-}py)_4]$, itself disappearing by disproportionation (second-order reaction). The reaction mechanism proposed is shown below.



The transitions observed in the visible region for the first observed species are probably *d–d* ones, because no change occurs in the spectrum when 4-methylpyridine is added to the solution (a charge-transfer metal-to-ligand absorption ought to be increased in intensity by such an addition). To support this hypothesis, Xα theoretical calculations were attempted. The agreement between the experimental and calculated transition energy is very good.[12] The transitions have *d–d* character. Furthermore, the extra electron seems to be rather delocalized on the two metallic sites, in spite of the disymmetric ligand arrangement around each tantalum, suggested by analogy with $[W_2Cl_6(4Me\text{-}py)_4]$ or $[Ta_2Cl_6(PMe_3)_4]$.[13,14]

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