The Oxidation of Tantalum with Ammonium Chloride as an Example of a Novel Route to Early Transitional Metal–Nitrogen Cluster Compounds. Synthesis and Crystal Structure of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$

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The oxidation of tantalum metal with ammonium chloride leads to dark-green single crystals of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$, a new imido-bridged tantalum-cluster compound with the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion.

There appears to be a growing preparative chemistry in which the ammonium ion, NH_4^+, plays a uniquely versatile role as a synthetic agent in solid-state reactions.[1,2] It is widely used as an acid owing to its active proton in the transformation of the basic rare earths (M_2O_3) to halides in the so called ammonium-halide routes.[3–6] The, formally, N^{3-} ion of NH_4^+ may also function as a reducing agent in external or internal redox reactions of which the latter are the most interesting. The reactions that occur in $(NH_4)_2[Pr(NO_3)_5(H_2O)_2]\cdot 2H_2O$ at four different temperatures between 280 and 450 °C may serve as one example.[7,8] Here the gases N_2, O_2, N_2O, NO and NO_2 are released leaving, finally, PrO_{2-x} behind. Another example is the thermal decomposition of $(NH_4)_3[RhCl_6]\cdot H_2O$ where an ammine ligand enters (is transferred to) the inner coordination sphere of Rh^{3+} releasing one equivalent of HCl. Electron transfer between N^{3-} and Rh^{3+} takes place some 30 °C higher (around 410 °C) in the so-formed $(NH_4)_2[Rh(NH_3)Cl_5]$.[9,10] Hence, the NH_3 'part' of NH_4^+ may act as a base. This is also true for the N^{3-} 'ion' itself which may be transferred to highly charged metal ions as is the case with $(NH_4)_3[Ta_2NCl_{10}]$ which forms upon reaction of tantalum with ammonium chloride at 380 °C.[11] In this reaction, Ta^0 is simultaneously oxidized by NH_4^+.

We have now observed that such reactions between ammonium halides and early transition metals are capable of the formation of cluster compounds. When an He-arc welded tantalum tube containing some NH_4Cl (not more than 150 mg for a tube of 8 mm outer diameter, 4 cm in length) is heated to 350 °C for two weeks, dark-green crystals of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$ (as the crystal structure determination has revealed†) grow from the tantalum wall. Yields are quantitative with respect to the amount of NH_4Cl used. As eqn. (1) may

$$17\,NH_4Cl + 5\,Ta \rightarrow (NH_4)_6[Ta_5(NH)_4Cl_{17}] + 9.5\,H_2 + 7\,NH_3 \qquad (1)$$

indicate, the NH_4^+ ions have a number of functions in this reaction. They act as an oxidizing agent, oxidizing Ta^0 to the oxidation state +3.8 thereby releasing hydrogen, as well as a base with the imide ions, NH^{2-}, bridging two tantalum atoms (see below), and, furthermore, as counter cations.

Most interestingly, this novel compound contains the, hitherto unknown, isolated anion $[Ta_5(NH)_4Cl_{17}]^{6-}$ (Fig. 1).

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† *Crystal data*: $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$, $M = 1675.73$, tetragonal, space group $I4/mmm$ (No. 139, $R_{int} = 0.013$), $Z = 2$, $a = 1340.71(9)$, $c = 1012.2(1)$ pm, $V_m = 548$ cm^3 mol^{-1}, $F(000) = 1447$, $\mu = 160.54$. No. of data measured 3762, no. of unique refelctions 555, no. of observed reflections with $|F_o| > 3\sigma|F_o|$ 522, no. of parameters 33. Diffraction data were collected on a Siemens-Stoe AED 2 diffractometer with graphite monochromated Mo-Kα radiation, ($\lambda = 71.07$ pm, ω-scan) at room temp. between $2 < \theta < 52°$. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects, ψ-scan for 24 reflections. The structure was solved by direct methods (SHELXS 86[15]) and Fourier techniques, and refined by full-matrix least-squares analysis (SHELX 76[16]). The final R value was 0.074 ($R_w = 0.055$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

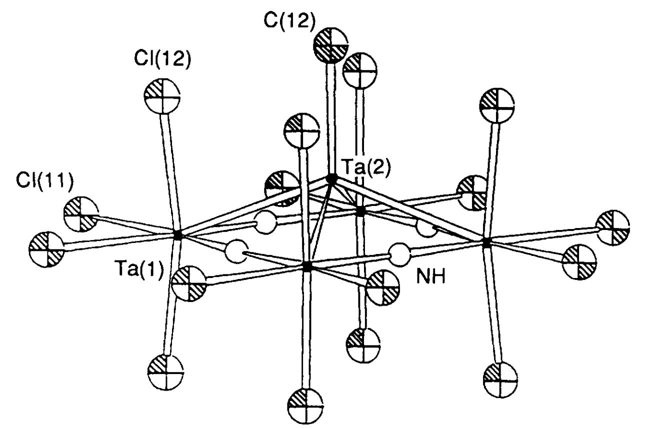

Fig. 1 The $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion in the crystal structure of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$. Selected bond distances (pm) and angles (°): Ta(1)–Ta(2) 293.5(2), Ta(1)–Cl(11) 260.7(5), Ta(1)–Cl(12) 240.0(9), Ta(1)–NH 195(2), Ta(2)–Cl(21) 234(3), Ta(1)–NH–Ta(1) 168.9(9)

Four tantalum atoms [Ta(1)] build the corners of a square with the nitrogen atoms of the four imide ions residing on its edges. The fifth tantalum atom is located at about 104 pm above the centre on the fourfold axis (space group *I4/mmm*) with four Ta(1)–Ta(2) distances of 294 pm. These distances compare very well with those in Ta_6Cl_{15} (292 pm).[12] The $[Ta_5(NH)_4]$ part is surrounded by seventeen chloride ions of which four times four are bound to Ta(1), eight in plane at 261 pm and eight out of plane at 240 pm. The seventeenth belongs to Ta(2) alone (d = 234 pm).

From X-ray structure determination, it is not possible to decide whether there is an imide or an oxide ligand located between the Ta(1) atoms. The IR absorption spectrum of $(NH_4)_6[Ta_5(NH)_4C_{17}]$ shows the bands of the free ammonium ion (ν_{as} 3200 cm^{-1}, δ_{as} 1405 cm^{-1}). If there is an imide ion coordinating to a tantalum atom, a deformation band around 1560 cm^{-1} should be visible (δ 1565 cm^{-1}).[13] To eliminate the bands of the ammonium ion, some NH_4Cl was mixed into the KBr pellet of the reference beam of a two beam instrument. There is no N–H deformation band at 1405 cm^{-1} left but a small N–H stretching band at 3220 cm^{-1} which is believed to be due to the imide ligand (ν 3224 cm^{-1}).[14] A comparison of the FTIR spectra of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$ and $(^{15}NH_4)_6[Ta_5(^{15}NH)_4Cl_{17}]$ (prepared analogously by oxidation of tantalum metal with $^{15}NH_4Cl$) shows a shift of some bands of 3–5 cm^{-1} to lower wave numbers for the ^{15}N compound.

The Ta_5 part of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$ is analogous in structure and electron count to the B_5 unit in B_5H_9. In each six electrons are provided for four Ta–Ta and B–B bonds, respectively. The new reduced tantalum imide-chloride may therefore be addressed as to contain a six-electron four-centre *nido* cluster. Less desirably, one might view $(NH_4)_6$-$[Ta_5(NH)_4Cl_{17}]$ as a mixed-valence compound with four Ta^{4+} in the base and one Ta^{1+} in the apex.

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