

## Synthesis and Crystal Structure of the First Titanium Halide with Isolated Octahedral Clusters, $[\text{Ti}_6\text{C}]\text{Cl}_{14}$

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$[\text{Ti}_6\text{C}]\text{Cl}_{14}$  is obtained as black, single crystals through metallothermic reduction of titanium(III) chloride with sodium in the presence of a carbon source and crystallizes isostructurally with  $[\text{Zr}_6\text{C}]\text{Cl}_{14}$  and  $[\text{Nb}_6\text{C}]\text{Cl}_{14}$ .

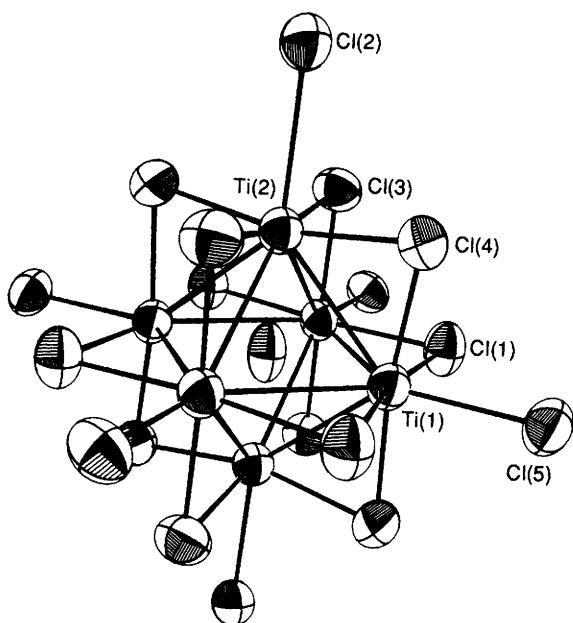
Cluster compounds of the early transition metals (M) have been studied extensively.<sup>1–5</sup> Most frequently, these compounds contain isolated or condensed  $\text{M}_6$  octahedra. Depending on their electron count, these octahedra can be empty, e.g. as in  $\text{Ta}_6\text{I}_{14}$ ,<sup>6</sup> or filled by an interstitial atom as in  $[\text{Zr}_6\text{C}]\text{Cl}_{14}$ .<sup>7</sup> Di-, tri-, tetra-, and penta-nuclear clusters are, however, also known, e.g. in  $\text{ZrI}_3$ ,<sup>8</sup>  $\text{Nb}_3\text{Br}_8$ ,<sup>9</sup>  $\text{CsNb}_4\text{Cl}_{11}$ ,<sup>10</sup>  $(\text{NH}_4)_6[\text{Ta}_5(\text{NH})_4]\text{Cl}_{17}$ ,<sup>11</sup> (compressed tetragonal pyramid) and  $\text{Rb}[\text{Pr}_5(\text{C}_2)]\text{Cl}_{10}$ ,<sup>12</sup> (trigonal bipyramid). The tendency for cluster formation increases going down within a group and peaks for groups 5 and 6 paralleling the increase of the enthalpy of sublimation of the metals, consequently clusters are rare in 3d metal chemistry. Only scandium is known to form isolated and condensed  $\text{Sc}_6$  clusters, stabilized by an interstitial atom. With its neighbour titanium, condensed octahedral clusters have been observed in chalcogenides, e.g. in  $\text{TiO}$ ,<sup>13</sup> and  $\text{Ti}_4\text{Te}_5$ ,<sup>14</sup> and triangular clusters in binary and ternary halides such as  $\text{Ti}_7\text{Cl}_{16}$ ,<sup>15</sup> and  $\text{KTi}_4\text{Cl}_{11}$ .<sup>16</sup> The first octahedral interstitially stabilized titanium cluster has now been isolated:  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$ .

$[\text{Ti}_6\text{C}]\text{Cl}_{14}$ † was first obtained by metallothermic reduction of titanium trichloride with sodium (equimolar amounts) in the presence of a carbon source (paraffin) at fairly low temperatures (440–550 °C). The yield of  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$  is approximately 30–50%, by-products are  $\text{Na}_3\text{TiCl}_6$ ,  $\text{TiCl}_2$  and  $\text{NaCl}$  as identified from X-ray powder diffraction patterns. Good quality black single crystals with metallic lustre were obtained after 120 days at 525 °C under anhydrous, anaerobic condi-

tions, under argon. Conproportionation reactions under comparable conditions ( $\text{Ti}:\text{TiCl}_3:\text{C} = 1:2:1/3$ ; 520 °C; 61 days) were not successful. We suspect that  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$  is only metastable being obtained under kinetically favourable conditions at a fairly low temperature. For all syntheses tantalum containers jacketed with evacuated silica tubes were used.<sup>17</sup>

$[\text{Ti}_6\text{C}]\text{Cl}_{14}$  crystallizes isostructurally with  $\text{Nb}_6\text{Cl}_{14}$ ,<sup>20</sup> although the  $\text{Ti}_6$  cluster is centred by an interstitial carbon atom, as is also the case in  $[\text{Zr}_6\text{C}]\text{Cl}_{14}$ . As Fig. 1 shows, the  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$  units in  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$  are surrounded by eighteen chlorine atoms, of which twelve are capping the edges of the octahedron ( $\text{Cl}^{\text{e}}$ ) and six are located at the corners ( $\text{Cl}^{\text{a}}$ ). According to the matrix effect as described by Corbett,<sup>3</sup> the  $\text{Ti}_6$  octahedron is compressed in the fourfold axis direction, so that the  $\text{Ti}(2)\text{--Ti}(2)$  distance is 20.7 pm shorter than the perpendicular  $\text{Ti}(1)\text{--Ti}(1)$  distance.  $\text{Ti}\text{--Ti}$  distances range between 299.95(15) and 309.83(13) pm for the 12 edges of the  $\text{Ti}_6$  octahedron with an average of 303.1 pm. They compare, therefore, quite well with the mean distances in  $\text{Ti}_7\text{Cl}_{16}$  ( $\bar{d} = 295.4$  pm),  $\text{KTi}_4\text{Cl}_{11}$  ( $\bar{d} = 295.5$  pm) and  $\text{TiO}$  ( $\bar{d} = 294.9$  pm). The  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$  clusters are cubic closest packed. Two-dimensional infinite  $[\text{Ti}_6\text{C}]\text{Cl}_{12}\text{Cl}_{4/2}^{\text{a}}$  layers are formed through connection of the  $[\text{Ti}_6\text{C}]\text{Cl}_{18}$  units parallel to (010) by four  $\text{Cl}^{\text{a}}$  atoms. Additionally, there are weak interactions between these layers, so that the total interconnectivity can be described as  $[\text{Ti}_6\text{C}]\text{Cl}_{10}\text{Cl}_{2/2}^{\text{a}}\text{Cl}_{2/2}^{\text{a}}\text{Cl}_{4/2}^{\text{a}}$ .

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**Fig. 1** The  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$  unit in the crystal structure of  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$ . Selected atomic distances (pm):  $\text{Ti}(1)\cdots\text{C}(1)$ , 217.71(9);  $\text{Ti}(1)\cdots\text{Cl}(1)$ , 238.40(18);  $\text{Ti}(1)\cdots\text{Cl}(3)$ , 239.92(15);  $\text{Ti}(1)\cdots\text{Cl}(4)$ , 240.49(16);  $\text{Ti}(1)\cdots\text{Cl}(2)$ , 246.92(17);  $\text{Ti}(1)\cdots\text{Cl}(5)$ , 253.18(12);  $\text{Ti}(1)\cdots\text{Ti}(2)$ , 299.95(15);  $\text{Ti}(1)\cdots\text{Ti}(1)$ , 301.41(14);  $\text{Ti}(1)\cdots\text{Ti}(1)$ , 305.94(12);  $\text{Ti}(1)\cdots\text{Ti}(1)$ , 309.83(13);  $\text{Ti}(1)\cdots\text{Ti}(1)$ , 435.43(13);  $\text{Ti}(2)\cdots\text{C}(1)$ , 207.39(13);  $\text{Ti}(2)\cdots\text{Cl}(3)$ , 237.32(17);  $\text{Ti}(2)\cdots\text{Cl}(4)$ , 237.83(16);  $\text{Ti}(2)\cdots\text{Cl}(2)$ , 290.57(24);  $\text{Ti}(2)\cdots\text{Ti}(2)$ , 414.78(19).

### Footnote

† Crystal data:  $[\text{Ti}_6\text{C}]\text{Cl}_{14}$ ,  $M = 795.75$ , orthorhombic, space group  $Cmca$  (No. 64,  $R_{\text{int}} = 0.014$ ,  $Z = 4$ ,  $a = 1345.92(11)$ ,  $b = 1224.58(6)$ ,  $c = 1095.76(5)$  pm,  $V = 1806.02(19)$  Å<sup>3</sup>,  $D_c = 2.9266$  g cm<sup>-3</sup>,  $F(000) = 1504$ ,  $\mu = 45.884$  cm<sup>-1</sup>, Number of data measured 6972, number of unique reflections 1574, number of observed reflections with  $|F_0| \geq 2\sigma |F_0|$  1475, 54 parameters. Diffraction data were collected on a Siemens-Stoe AED 2 diffractometer with graphite monochromated  $\lambda(\text{Mo-K}\alpha) = 71.07$  pm,  $\omega$ - $2\theta$ -scan at room temp. to  $2\theta_{\text{max}} = 63^\circ$ . Intensity data were corrected for Lorentz and polarisation effects, empirical absorption correction,  $\Psi$ -scan for 20 reflections,  $\Delta\Psi = 10^\circ$ . The structure was solved by a combination of direct methods (SHELXS 86<sup>18</sup>) and Fourier techniques, and refined by full-matrix least-squares analysis (SHELX 76<sup>19</sup>). The final  $R$  value was 0.058 ( $R_w = 0.040$ ). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe. See Information for Authors, Issue No. 1.

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