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Tight Encapsulation of a “Naked” Chloride in an Imidotitanium Hexanuclear Host

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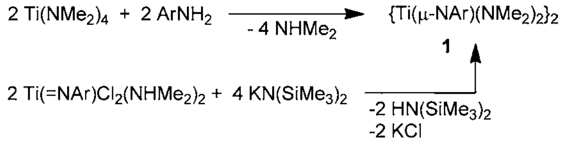
Ⓢ *Supporting Information*

ABSTRACT: Treating the imidotitanium dimer $[Ti(\mu\text{-}NAr)(NMe_2)_2]_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with excess Me_3SiCl affords the hexanuclear complex $[\{Ti({=}NAr)Cl_2\}_6(Cl)]^-[Q]^+$. The self-assembled hexameric cage arrangement encapsulates a chloride ion guest that provides evidence of new host–guest chemistry in this area, while the cationic part is composed of mixtures of the Q^+ cations $Me_2NHSiMe_3{}^+$ and $Me_2N(SiMe_3)_2{}^+$.

Imido complexes, and in particular group 4 imido complexes, have attracted intense interest because of their importance in understanding and developing stoichiometric or catalytic transformations.[1−4] Imido complexes are known for the majority of the d-block metals, and a wide range of substitution on the imido ligands has been demonstrated, which impacts the properties of the metal–nitrogen bond.[1,5b] Imido ligands have found practical applications as robust supporting (spectator) ligands, as reactive sites, or as ligands to known precursors to metal nitride materials.[2−4]

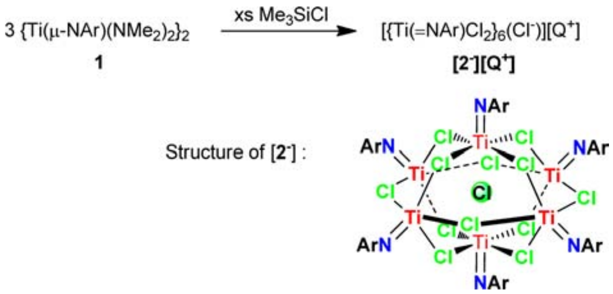
In previous articles, we have reported the one-pot synthesis [from $M(NMe_2)_4$, RNH_2, and Me_3SiCl],[5] coordination chemistry,[5a,b,6] and catalytic applications[2d,f,3h] of titanium(IV) and vanadium(IV) imido complexes of the general formula $M({=}NR)Cl_2(NHMe_2)_2$ (M = Ti, V). This has led us to study the mechanism of formation of these species and, in particular, the generation of the imido motifs by a transamination reaction between $Ti(NMe_2)_4$ and primary amines that we suggested is the initial step in the formation of $M({=}NR)Cl_2(NHMe_2)_2$ complexes.[7] A better understanding of this first step [also of relevance to imido generation in catalytic alkyne hydroamination with $Ti(NMe_2)_4$] led to the development of the synthesis of many new imido-bridged dinuclear species,[7] including unique dimer complexes with two *distinct* bridging μ-imido ligands, and *hetero*-bimetallic species bridged by μ-imido ligands.[8] Previously, as depicted in Scheme 1, we described the synthesis of the dimer complex $[Ti(\mu\text{-}NAr)(NMe_2)_2]_2$ (**1**) from a transamination reaction between $Ti(NMe_2)_4$ and $ArNH_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), and we stressed the point that $NHMe_2$ was very difficult to remove from this equilibrium reaction. Alternatively, **1** was prepared by deprotonation of coordinated $NHMe_2$ in $Ti({=}NAr)Cl_2(NHMe_2)_2$ with $KN(SiMe_3)_2$.[7] Here we present a new class of synthetic systems, composed of an unprecedented self-assembled hexanuclear cage molecule surrounded by terminal imidotitanium motifs and that encapsulates a chloride ion guest.

Scheme 1. Synthesis of Dimer 1[7]



As illustrated in Scheme 2, the treatment of a red toluene solution of **1** with excess Me_3SiCl (6 equiv per titanium) at ambient temperature led progressively to a green solution (within a few hours), and green crystals separated from the solution when left to stand overnight without stirring. The crystallization process was completed by the slow addition of pentane, and green crystals of $[\{Ti({=}NAr)Cl_2\}_6(Cl^-)][Q^+]$ ([**2**].[**Q**]) were separated by filtration followed by washing with portions of pentane (yield 82%).

Scheme 2. Synthesis of Hexanuclear Compound [2⁻]



The formulation for [**2**].[**Q**] was based on spectral and analytical data, as well as on a crystal structure determination (vide infra). ^{1}H NMR at 25 °C in dichloromethane-d_2 showed resonances attributable to 2,6-^{i}Pr$_2$C$_6$H$_3$ hydrogen atoms, together with unexpected smaller signals (in the $-NMe_2$ and $-SiMe_3$ regions) that could not be removed upon washing or after recrystallization.

An X-ray structure determination (Figure 1) of the crystals obtained during the reaction unambiguously confirmed the presence of terminal arylimido ligands and revealed the complex to be the ion-separated hexanuclear compound $[(Cl^-)\subset\{Ti({=}NAr)Cl_2\}_6][(Me_3Si)_2NMe_2{}^+]$ with an anionic part composed of six terminal imidotitanium motifs that encapsulates a chloride ion (where ⊂ denotes encapsulation) and with a $[(Me_3Si)_2NMe_2]^+$

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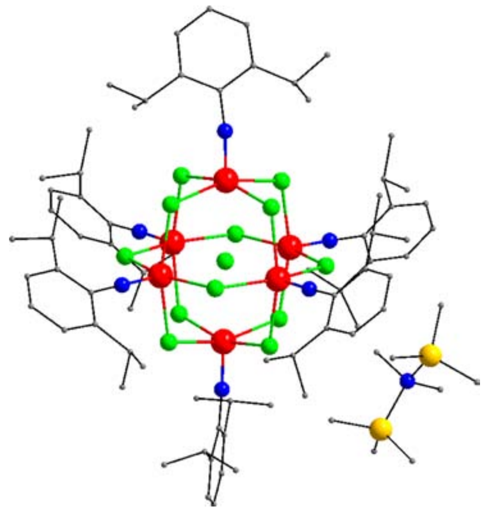

Figure 1. Molecular structure of ([**2**].[$(\mathbf{Me_3Si)_2NMe_2}$]). Legend: Ti, red; C, gray; N, blue; Cl, green; Si, yellow. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti···Cl range from 2.8093(13) to 2.8332(12); Ti−Cl range from 2.4383(12) to 2.4671(12); Ti−N range from 1.698(4) to 1.7001(4); Ti−N−C range from 169.7(3) to 178.9(3).

countercation. A closer inspection of the ^{1}H NMR spectra revealed the presence in solution of two different types of cations Q$^+$, $[(Me_3Si)_2NMe_2]^+$ and $[(Me_3Si)NHMe_2]^+$, in a relative ratio generally of about 4:1.[9]

The anionic $[(Cl^-)\subset\{Ti({=}NAr)Cl_2\}_6]$ host−guest assembly of **2** (Figure 1) is composed of a neutral, nearly D_3-symmetric, homometallic Ti_6Cl_{12} spherical cage (ave. Ti−Cl = 2.450 Å) with an internal diameter of ca. 5.6 Å and with six terminal arylimido ligands coordinated at its periphery to the six square-pyramidal titanium(IV) ions (ave. Ti−N = 1.699 Å; ave. Ti−N−C = 175.6°). The encapsulated Cl$^-$ ion is spatially trapped within the spherical neutral host cavity with weak Ti···Cl bonding (ca. 2.824 Å) trans to the imido groups of each metal center and counterbalanced by repulsive interactions with the 12 surrounding chlorine shells ($Cl_{shell}\cdots Cl_{guest}$ contact range of 3.395−3.428 Å). Overall, the anionic host−guest framework resembles that of the recently reported $[(BrCo)_6Ti_{15}O_{24}(O^iPr)_{18}(Br)]^-$, with a Br$^-$ ion encapsulated within a $Ti_{15}Co_6$ polyoxotitanate anion.[10a]

In addition, one of the most abundant species in negative-ion fast-atom-bombardment mass spectrometry at m/z 1799 (theoretical m/z 1799.09) is the host−guest anion **2** and suggests a stable confinement of the chloride ion inside a robust[11] $\{Ti({=}NAr)Cl_2\}_6$ framework. Indeed, attempts to remove or exchange the chloride in **2** by a different halide (Br$^-$ or I$^-$) proved not to be possible.[12] A space-filling view (see the Supporting Information) allowed one to estimate the volume within the hexanuclear cage at ca. 3.1 Å^3 (when removing the encapsulated halogenide), which is most certainly too small to accommodate encapsulation of larger Br$^-$ or I$^-$ ions. The novel cluster entity appears to be a thermodynamic sink under the conditions in which it forms. Importantly, examples of metal-based inorganic hosts of this type are very rare.[10] Considering the tight encapsulation of the Cl$^-$ ion inside the Ti_6Cl_{12} cavity, rather than simply being incorporated into a preformed hexanuclear cavity, it is quite probable that the formation of **2** is dependent on anion templating of hypothetical $\{Ti(NAr)Cl_2\}$ subunits around a Cl$^-$ ion.[13] A complementary experiment strongly supports this hypothesis: as depicted in Scheme 3, we treated a dichloromethane suspension of $TiCl_3(NMe_2)$ with 1 equiv of $ArNH_2$, which likely proceeds via the intermediacy of $[Ti({=}NAr)Cl_3]$-$[NH_2Me_2]$. Within hours, the reaction produced yellow crystals of a new compound, $[\{Ti({=}NAr)Cl_2\}_3(Cl)_3]_2[\{Ti({=}NAr)Cl_2\}_2(Cl)_3][NH_2Me_2]_9$ ([**3**]$_2$[**4**][$\mathbf{NH_2Me_2}$]$_9$; see Figure 2), composed of two trinuclear terminal imido-containing motifs (with the structure resembling half of the structure of **2**) that cocrystallized with one parent dinuclear unit (with structure resembling one-third of the structure of **2**) and nine dimethylammonium cations (the cation originates from protonation of liberated $NHMe_2$ due to transamination of the $-TiNMe_2$ bond with $ArNH_2$). In this system, the formation of one dimethylammonium per titanium center very likely prevents further aggregation to the hexanuclear structure by stabilizing trinuclear **3** and dinuclear **4** motifs. Bond distances and angles in these motifs are very similar to those in hexanuclear **2** (ave. Ti−N = 1.695 Å; ave. Ti−N−C = 175.2°; ave. Ti−Cl = 2.483 Å). In the trinuclear species, the additional Cl$^-$ ion is located trans to the three imido groups of each metal center with weak Ti−Cl bonding (ca. 2.82 Å).

Scheme 3. Synthesis of Trinuclear and Dinuclear Compounds 3 and 4 from $TiCl_3(NMe_2)$

$$TiCl_3(NMe_2) + ArNH_2 \xrightarrow[CH_2Cl_2]{} \{[Ti({=}NAr)Cl_3]^-[NH_2Me_2)]^+\}$$

$$\xrightarrow{\text{crystallization}} \underset{\mathbf{[3][NH_2Me_2]_3}}{2\,[\{Ti({=}NAr)Cl_2\}_3(Cl)_3][NH_2Me_2]_3} + \underset{\mathbf{[4][NH_2Me_2]_3}}{[\{Ti({=}NAr)Cl_2\}_2(Cl)_3][NH_2Me_2]_3}$$

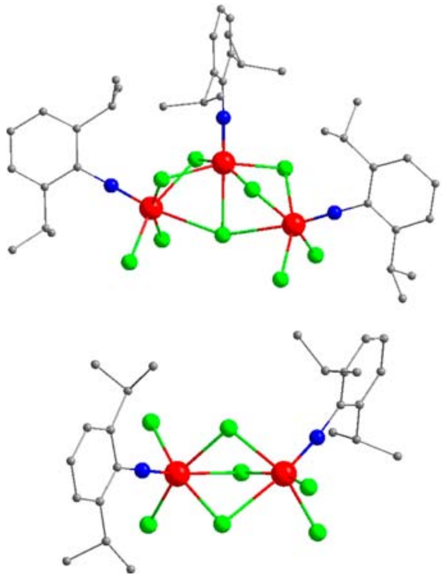

Figure 2. Molecular structure of parts of [**3**]$_2$.[**4**].[$\mathbf{NH_2Me_2}$]$_9$. Top: [**3**]. Bottom: [**4**]. Legend: Ti, red; C, gray; N, blue; Cl, green. Hydrogen atoms, dimethylammonium cations, one molecule of **3**, and toluene molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): for **3**, Ti···Cl$^-$ range from 2.719(2) to 2.8866(14) Å, Ti−Cl range from 2.3846(16) to 2.5238(14), Ti−N range from 1.690(4) to 1.702(4), and Ti−N−C range from 169.0(4) to 179.4(4); for **4**, Ti−Cl range from 2.4124(18) to 2.7623(15), Ti−N 1.694(4), and Ti−N−C 173.5(3).

Interestingly, using Me_3SiBr in place of Me_3SiCl in the reaction with **1** afforded the bromide-encapsulated compound $[\{Ti({=}NAr)Br_2\}_6(Br^-)][Q^+]$ (**5**). Furthermore, preliminary studies demonstrated that the formation of a hexameric stucture such as in **2** is not limited to Ar− substituents. Indeed, the treatment of the *μ-tert*-butylimido congener $[Ti(\mu\text{-N}^tBu)(NMe_2)_2]_2$ with Me_3SiCl afforded in a similar way the hexanuclear anion $[\{Ti(=N^tBu)Cl_2\}_6(Cl^-)]$ (**6**).[14]

In summary, this work has provided access to new base-free hexanuclear imidotitanium complexes with an original structure and encapsulation of a Cl^- anion guest within the hexanuclear cage unit, which reveals the potential for imidotitanium in host−guest chemistry. Furthermore, the fact that the titanium atoms in **2** are not coordinated to any bases is extremely rare[15] and promises potential access to new base-free complexes or compounds that are inaccessible from other known imido synthons [such as well-known dimethylamine or pyridine adducts $Ti(=NR)Cl_2L_n$ ($L = NHMe_2$, Py)].[16,17] Work is now in progress to explore the potential applications of [**2**].[**Q**].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis and characterization of complexes [**2**].[**Q**], $[\mathbf{3}]_2.[\mathbf{4}].[\mathbf{NH_2Me_2}]_9$, [**5**].[**Q**], and [**6**].[**Q**], a CIF file, and tables of atomic coordinates, bond distances, and bond angles for the X-ray crystal structures of [**2**].$[\mathbf{(Me_3Si)_2NMe_2}]$ and $[\mathbf{3}]_2.[\mathbf{4}].[\mathbf{NH_2Me_2}]_9$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(9) The proton in the cation $[(Me_3Si)NHMe_2]^+$ very likely results from difficulties in having very pure precursor **1** (which often contains traces of $NHMe_2$ or −NHAr amido byproducts; see ref 7); indeed, when using a sample containing a higher amount of such impurities, we crystallized a small amount of compound [**2**].$[\mathbf{NH_2Me_2}]$ with a $NH_2Me_2^+$ countercation.

(10) For related encapsulation of halides in polyoxoanions, see: (a) Lv, Y.; Willkomm, J.; Steiner, A.; Gan, L.; Reisner, E.; Wright, D. S. *Chem. Sci.* **2012**, *3*, 2470−2473. (b) Sakai, Y.; Yoza, K.; Kato, C. N.; Nomiya, K. *Chem.—Eur. J.* **2003**, *9*, 4077−4083. (c) Sakai, Y.; Yoza, K.; Kato, C. N.; Nomiya, K. *Dalton Trans.* **2003**, 3581−3586.

(11) The hexanuclear structure is, nevertheless, broken by strong donor molecules, and the compound is decomposed in the presence of air/moisture.

(12) We observed no evidence for halogen exchange with LiI (1−5 equiv), $^nBu_4NI$ (5 equiv), PPh_3CH_3Br (5 equiv), and Me_3SiBr (20 equiv) or halogen abstraction with $NaBPh_4$ (1−6 equiv) and $AgBF_4$ (1 equiv) in reactions with [**2**][**Q**] and conducted in dichloromethane-d_2 at room temperature for 1 week [in certain cases, under forcing conditions (50 °C), decomposition to unidentified species occurred]. The cationic part, however, could in some cases be exchanged by other cations such as ammonium or phosphonium.

(13) A crossover experiment between equimolar amounts of **1** and the dimethyl-substituted analogue $[Ti(\mu\text{-NAr}')(NMe_2)_2]_2$ ($Ar' = 2,6\text{-}Me_2\text{-}C_6H_3$) with excess Me_3SiCl afforded green crystals of the general composition $[(Cl^-)\subset\{Ti_6(=NAr)_2(=NAr')_4Cl_{12}\}][Q]$ but which is probably composed of a mixture of $\{Ti_6(=NAr)_x(=NAr')_yCl_{12}\}$ clusters (with $x = 0{-}6$ and $y = 6{-}0$). So far, we were unable to fully resolve the structure because of statistical disorder between the Ar and Ar′ substituents. However, weak spatial correlations between the ^{i}Pr and Me protons were evidenced by NOESY NMR experiments and confirm the presence of both types of imido ligands within the same compound constructed from $\{Ti(NAr)Cl_2\}$ and $\{Ti(NAr')Cl_2\}$ elementary subunits.

(14) For both **5** and **6**, the hexanuclear arrangement with encapsulation of a halogen atom was confirmed by an X-ray diffraction study.

(15) The only known example of base-free imidotitanium dichloride is an octanuclear species, $[Ti(\mu\text{-NSiMe}_3)Cl_2]_8$, obtained from $TiCl_4$ and $(Me_3Si)_2NH$ or $(Me_3Si)_3N$. See: (a) Bettenhausen, R.; Milius, W.; Schnick, W. *Chem.—Eur. J.* **1997**, *3*, 1337−1341. (b) Schlichenmaier, R.; Strähle, R. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1526−1529.

(16) We have already reported that vanadium analogue complexes of **2** are useful precursors for the preparation of rare vanadium phosphine complexes $V(=NAr)Cl_2(PR_3)_2$ (see ref 6a).

(17) Complex **2** was recently used for the synthesis of new N-heterocyclic carbene complexes (see ref 6b) and new phosphine complexes (see ref 18).

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