Labile \textit{triangulo}-Trititanium(II) and -Trivanadium(II) Clusters

Triangular trinuclear clusters have stimulated considerable theoretical interest$^1$ and produced elegant synthetic chemistry,$^2-^4$ since they can be regarded as the basic building blocks of many high-nuclearity polyhedral clusters. A cluster compound contains, by definition, a network of metal-metal bonds that define the coordination polyhedron. However, theoretical work has demonstrated that in \textit{triangulo} clusters the presence of at least three bridging ligands is a very important factor for the stability of the $M_3$ skeleton.$^1$ Therefore, the obvious conclusion important to synthetic chemists is that $M$-$M$ bonds can be rather weak in these species.

We have now prepared cationic \textit{triangulo}-trititanium(II) and -trivanadium(II) clusters with the dual purpose of (i) making an entry into the nonexistent cluster chemistry of divalent vanadium and titanium and possibly (ii) testing the ability of these divalent metals to form $M$-$M$ bonds [debated in the case of V(II)$^5$ and extremely rare in the case of Ti(II)$^6$]. The choice of trans-\textit{(TMEDA)$_2$MCl$_2$} ($M = \text{Ti, V}$; \textit{TMEDA} = $N,N,N',N'$-tetramethylethylene diamine) as starting materials was determined by their versatility in disproportionation, ligand replacement and clusterization reactions.$^9$

As shown in Scheme I, the reaction of trans-\textit{(TMEDA)$_2$MCl$_2$}

\begin{equation}
\text{trans-\textit{(TMEDA)$_2$MCl$_2$}} \rightarrow \text{Scheme I}
\end{equation}

with NaNP$_2$ and VCl$_3$(THF)$_3$, able to selectively abstract one of the bridging ligands, proceeds instantaneously at room temperature, leading to the formation of the trinuclear cationic \textit{(TMEDA)$_2$MCl$_2$}$^+$ ($M = \text{Ti, V}$).$^{10}$ The lower stability of trans-\textit{(TMEDA)$_2$VCl$_2$} with respect to the vanadium analogue has so far prevented the preparation of a wider series of titanium derivatives. It is noteworthy that while the same trinuclear frame has been obtained in the case of vanadium upon treatment with TiCl$_3$(THF)$_2$ and YCl$_3$(THF)$_3$, reaction with other salts [ZnCl$_2$(THF)$_2$, AlCl$_3$(THF)$_3$] capable of forming complex di-

\begin{equation}
\text{trans-\textit{(TMEDA)$_2$MCl$_2$}} \rightarrow \text{Scheme I}
\end{equation}

References:


of bond distances (Å) and angles (deg) are as follows: T11–T12 = 2.761 (4), T11–T13 = 2.770 (4), T12–T13 = 2.762 (4), T11–C11 = 2.474 (5), T11–C13 = 2.470 (5), T11–N1 = 2.317 (11), N1–T11–N2 = 78.5 (4), N1–T11–C11 = 92.7 (3), C11–T11–C13 = 87.37 (16). (b) ORTEP drawing of [(TMEDA)₂V₂Cl₄]⁺ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: V₂–V₃ = 3.145 (6), V₂–V₄ = 3.159 (5), V₃–V₄ = 3.158 (5), V₂–C₁₇ = 2.499 (7), V₂–C₁₅ = 2.510 (7), V₂–N₃ = 2.20 (2); N₃–V₂–C₁₇ = 97.4 (5), C₁₆–V₂–C₁₇ = 162.3 (7), C₁₅–V₂–C₁₇ = 84.8 (2), V₂–C₁₁–V₃ = 70.2 (2), V₂–C₁₅–V₃ = 77.5 (2).

anions yielded different products having the well-known structure [(L)₂V₂Cl₄]⁺.¹¹ The reaction with NaNPh₂ appears to be of a different nature. With both metals, the formation of the trimeric species is accompanied by a partial disproportionation reaction and consequent formation of a mixed-valence species. In the case of vanadium, the formation of the anion [V(NPh₂)₄]⁻ is rather straightforward.¹² However, the formation of the dimetallic anion [N₅V₂(Ti[(η⁵-C₅H₅)PhN]₂)Cl₂][(N,N'-bidentate)] in the case of 1 suggests that the reaction proceeds via a complicated disproportionation mechanism involving the formation of zerovalent species.

The structures of 1 and 3 have been determined by X-ray analysis.¹³ The trinuclear structure of the [M₃Cl₅(TMEDA)]⁺ cation is basically the same in the Ti and V derivatives (parts a and b of Figure 1, respectively) and is defined by the three metallic centers and three coplanar bridging chlorine atoms. The remaining two μ₃-chlorine atoms are symmetrically placed above and below the molecular plane. The M–Cl distances are slightly different in the two compounds probably as a result of the different electronic configurations of the two metals [ranging from 2.456 (5) to 2.503 (5) Å and from 2.496 (7) to 2.537 (8) Å for 1 and 3 respectively]. Furthermore, while the M–Cl distances formed by the axial (μ⁴-) and equatorial (μ₃-) chlorine atoms are quite comparable in 1 [Ti₁–Cl₁ = 2.474 (5) Å, Ti₁–Cl₃ = 2.470 (5) Å], a marked difference can be observed in the vanadium derivative 3 [V₂–Cl₁₆ = 2.496 (7) Å, V₂–Cl₁₇ = 2.526 (8) Å]. The [N₅V₂(Ti[(η⁵-C₅H₅)PhN]₂)Cl₂][(N,N'-bidentate)] anion in complex 1 (Figure 1) consists of a tetracoordinated titanium atom placed in the center of a slightly distorted tetrahedron defined by the nitrogen atoms of four amido groups (N–Ti–N angles ranging from 100.4 to 125.8°). Two rings from two different amido groups are parallel and are attached to one titanium atom, formally zerovalent, forming a (η⁵-arene)₂Ti sandwich. No special features were observed for the VCl₄(TMEDA)⁻ anion of 3, which possesses a normal octahedral geometry (Figure 1S).

The difference between the M–M distances observed in the two cations is striking. The fairly short Ti–Ti bonding distances (average Ti–Ti = 2.764 Å) observed in 1 might be consistent with

![Figure 1. ORTEP drawing of [(TMEDA)₂Ti₂Cl₅]⁺ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: T11–T12 = 2.861 (4), T11–T13 = 2.770 (4), T12–T13 = 2.762 (4), T11–C11 = 2.474 (5), T11–C13 = 2.470 (5), T11–N1 = 2.317 (11), N1–T11–N2 = 78.5 (4), N1–T11–C11 = 92.7 (3), C11–T11–C13 = 87.37 (16).](image-a)

![Figure 2. ORTEP drawing of [N₅V₂(Ti[(η⁵-C₅H₅)PhN]₂)Cl₂][(N,N'-bidentate)] showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: T14–N7 = 1.990 (11), T14–N8 = 2.008 (10), N7–T14–N8 = 100.4 (4), N8–T14–N10 = 125.8 (4).](image-b)
the formation of Ti-Ti single bonds. Furthermore, the magnetic moment of 1 \( \mu_B = 1.81 \mu_B \), although difficult to interpret because of the multivalent and polymeric nature of these compounds, is consistent with the presence of one unpaired electron per molecule. Considering that the anionic fragment of 1 contains one titanium atom bonded to the four amido groups which is probably a \( \text{d}^1 \) Ti(III), and another which is likely a diamagnetic \( \text{d}^4 \) Ti(0) atom, the trimetallic Ti(II) frame can reasonably be expected to be diamagnetic. By way of contrast, the V-V distances in the isostructural trivanadium aggregate 3 [ranging from 3.145 (6) to 3.159 (5) Å] are considerably longer and likely not in agreement with the presence of a V-V bond. Assuming a normal \( \text{d}^3 \) high-spin configuration for the octahedral \( \text{VCl}_6(\text{TMEDA}) \) fragment, the magnetic moment of 3 \( \mu_{\text{eff}} = 5.01 \mu_B \) indicates that the vanadium atoms of the trinuclear unit should possess a low-spin electronic configuration with less than one unpaired electron per vanadium atom.

There is no doubt that somehow the different electronic configuration of the two metals \( \text{d}^2 \) against \( \text{d}^3 \) should be responsible for the different M-M distances in these two electron-poor clusters. However, in our opinion the low-spin configuration of each vanadium atom in 3 (with two coupled electrons and no V-V bond) makes the existence of a Ti-Ti bond in 1 doubtful, in spite of the short "bonding" distance.

Consistent with this rationale, the cleavage of the trimetallic frames was easily achieved with both 1 and 3 via simple treatment with pyridine at room temperature, forming the mononuclear \( \text{(pyridine)}_3\text{MC}_6[R = \text{Ti}, V] \) as deep blue and deep red crystalline solids, respectively.

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Supplementary Material Available: Tables listing crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for 1 and 3, an ORTEP diagram (Figure 15) of the [\( \text{VCl}_4(\text{TMEDA}) \)]\(^+\) anion in 3, and a fully labeled ORTEP for the cation 3 (32 pages); tables of observed and calculated structure factors for 1 and 3 (70 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Ottawa
Ottawa, Ontario K1N 6N5, Canada

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[Fe(4-imidazoleacetate)]\( _2 \)2CH\(_2\)OH: A 2D Antiferromagnetic Iron(II) System Exhibiting 3D Long-Range Ordering with a Net Magnetic Moment at 15 K

Cooperative magnetic phenomena are well-known in solid-state materials but rare in molecular systems. Although substantial efforts have focused on the preparation of ferro- or ferrimagnetic molecular compounds exhibiting long-range magnetic ordering during the past few years, the transition temperature of the ferromagnetic molecular compounds reported so far is extremely low.\(^1\)\(^2\) On the other hand, some antiferromagnetic substances exhibit weak ferromagnetism at low temperature resulting from a canting of the spins.\(^3\) Although uncommon, such a situation may occur either in linear chain systems when magnetic interactions between next nearest neighbors occur in two- or three-dimensional materials.\(^4\) Among this class of compounds, the layered complexes of 1,2,4-triazole with divalent metal thiocyanates,\(^5\) although exhibiting canted spin structures quite similar to that reported in this work, are characterized by low ordering temperature (3–6 K) and hidden canting. The title compound, [Fe(4-imidazoleacetate)]\( _2 \)2CH\(_2\)OH\(^6\) (4) in 92% yield,\(^7\) for crystals suitable for X-ray diffraction study\(^8\) were obtained by slow interdiffusion of deoxygenated methanolic solutions of sodium

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