Labile triangulo-trititanium(II) and -trivanadium(II) clusters

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Labile triangu-lo-Tritinanium(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 triangu-lo 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 triangu-lo-tritinanium(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 clusterification\(^5\) reaction.\(^5\) We have now prepared cationic triangu-lo-tritinanium(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 clusterification\(^5\) reaction.\(^5\) As shown in Scheme I, the reaction of trans-(TMEDA)\(_2\)MCl\(_2\) with NaNP\(_2\) and VCl\(_3\)(THF), able to selectively abstract one chlorine atom, proceeds instantaneously at room temperature, leading to the formation of the trimetallic catonic [(TMEDA)\(_2\)MCl\(_5\)]\(^+\) (M = Ti, V).\(^10\) The lower stability of trans-(TMEDA)\(_2\)VCl\(_5\) 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 trimetallic frame has been obtained in the case of vanadium upon treatment with TiCl\(_3\)(THF)\(_2\) and YCl\(_3\)(THF)\(_2\), reaction with other salts [ZnCl\(_2\)(THF)\(_2\), AlCl\(_3\)(THF)\(_2\)] capable of forming complex di-


(10) I was prepared as follows. Solid NaH (0.34 g, 13.7 mmol) was added to a solution (−60 °C) of Ph$_2$NH (2.3 g, 13.6 mmol) in THF (70 mL). The addition of (TMEDA)$_2$TiCl$_3$ (2.28 g, 6.6 mmol) turned the color deep brown. The mixture was stirred for 2 h at −30 °C and at room T for 10 h. After evaporation of the solvent in vacuo, the solid residue was recrystallized from ether (50 mL), yielding deep brown-red crystals of 1 (1.16 g, 0.77 mmol). Anal. Calcd (found) for C$_{10}$H$_{18}$N$_2$(OTf)$_2$: C, 55.97 (55.85); H, 9.98 (9.83); Cl, 11.80 (11.77); Ti, 15.94 (15.91). 2 was prepared as follows. THF solution (150 mL) of neat Ph$_2$NH (2.7 g, 16 mmol) was treated with NaH (0.40 g, 16 mmol). The mixture was stirred and warmed for 30 min. The addition of trans-(TMEDA)$_2$VCl$_3$ (2.8 g, 7.8 mmol) to the resulting mixture turned the color to deep red. Stirring was continued for 14 h. The solvent was removed in vacuo and the solid residue recrystallized from toluene (40 mL) containing 10 mL of THF. Olive-green crystals of 1 separated upon cooling at −30 °C (yield 0.83 g, 6.61 mmol, 31%). Anal. Calcd (found) for C$_{29}$H$_{34}$N$_2$VCl$_7$: C, 62.97 (62.37); H, 6.27 (6.40); N, 9.68 (9.83); Cl, 12.65 (12.28); V, 14.54 (14.55). 3 was prepared as follows. A suspension of VCl$_3$(TMEDA) (3.12 g, 8.8 mmol) in THF (200 mL) was treated with solid VCl$_3$(THF)$_2$ (1.46 g, 3.9 mmol). The color turned purple and a gray microcrystalline solid formed during the 6 h of stirring. The gray solid was filtered and extracted with boiling THF, yielding greenish gray crystals of 3 (2.10 g, 2.1 mmol, 73%). Anal. Calcd (found) for C$_{29}$H$_{34}$N$_2$VCl$_7$: C, 29.18 (29.27); H, 6.48 (6.64); N, 11.34 (11.26); V, 20.65 (20.47); Cl, 32.35 (32.57).
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), Ni-T11-N2 = 78.5 (4), N1-Ti1-C11 = 92.7 (3), C11-Ti1-C13 = 87.37 (16). (b) ORTEP drawing of [(TMEDA)2VCl3]+ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: V2-V3 = 3.159 (5), V2-V4 = 3.158 (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-C17-V3 = 70.2 (2), V2-C15-V3 = 77.5 (2).

Figure 1. (a) ORTEP drawing of [(TMEDA)2TiCl3]+ showing the labeling scheme. Selected values 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), Ni-T11-N2 = 78.5 (4), N1-Ti1-C11 = 92.7 (3), C11-Ti1-C13 = 87.37 (16). (b) ORTEP drawing of [(TMEDA)2VCl3]+ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: V2-V3 = 3.159 (5), V2-V4 = 3.158 (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-C17-V3 = 70.2 (2), V2-C15-V3 = 77.5 (2).

Figure 2. ORTEP drawing of [N,N'-[Ti([η⁶-C₆H₆]PhN)]₂Ti(NPh₂)₂]⁺ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: Ti4-N7 = 1.990 (11), Ti4-N8 = 2.008 (10); N7-Ti4-N8 = 100.4 (4), N8-Ti4-N10 = 125.8 (4). For possible electronic structures of electron-poor trinuclear clusters see (a) Young, C. G. Coord. Chem. Rev. 1989, 96, 89. (b) Muller, A.; Joster, R.; Cotton, F. A. Angew. Chem., Int. Ed. Engl. 1980, 19, 875.
the formation of Ti-Ti single bonds.\(^6\) Furthermore, the magnetic moment of 1 (\(\mu_{\text{eff}} = 1.81 \mu_B\)), although difficult to interpretate 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 3 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 trinuclear Ti(II) frame can reasonably be expected to be diamagnetic. By way of contrast, the V-V distances in the isostructural trivananadium 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 (\(\mu_{\text{eff}} = 3.01 \mu_B\)) 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.\(^1\) 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 trinuclear frames was easily achieved with both 1 and 3 via simple treatment with pyridine at room temperature, forming the mononuclear (pyridine)\(_2\)MCi\(_3\) [M = Ti,\(^{3+}\) V\(^{7+}\)] 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 1S) of the [VCl\(_6\)(TMEDA)]\(^3+\) 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.

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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.\(^1,3\) 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 or 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, exhibits a net magnetic moment below 15 K, the highest 3D ordering temperature reported so far for a molecular compound characterized by a canted spin structure.

Reaction of a 2:1 molar ratio of sodium 4-imidazoleacetate (Sigma) and ferrous acetate tetrahydrate in deoxygenated methanol for 12 h affords white microcrystals of [Fe(4-imidazoleacetate)\\(_2\)]2CH\(_2\)OH (1) in 92% yield. Colorless single crystals suitable for X-ray diffraction study were obtained by slow interdiffusion of deoxygenated methanolic solutions of sodium.