Synthesis and Reactivity of *N,N*-Dialkylcarbamato Complexes of Titanium(III) and Vanadium(III). Crystal and Molecular Structure of an Anionic Dimeric Titanium(III) Derivative

Daniela Belli Dell'Amico[a], **Fausto Calderazzo***[a], **Ugo Giurlani**[a] and **Giancarlo Pelizzi**[b]

Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa[a],
Via Risorgimento 35, I-56100 Pisa, Italy

Istituto di Chimica Generale ed Inorganica and Centro C.N.R. per la Strutturistica Diffrattometrica, Università di Parma[b],
Viale delle Scienze, I-43100 Parma, Italy

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The reaction of anhydrous trichlorides of titanium or vanadium with $HNiPr_2$ and CO_2 or the exchange reaction 1/2 $M_2(O_2CNiPr_2)_6$ + 3 $HNEt_2$ → 1/*n* $[M(O_2CNEt_2)_3]_n$ + 3 $NHiPr_2$ yielded the *N,N*-dialkylcarbamato derivatives 1, 2, 5 and 7. Further reaction of the uncharged dimeric complexes with $O_2CNR_2^-$ yielded the ionic derivatives $NH_2R_2[M_2(O_2CNR_2)_7]$ 3, 4 and 6. The equilibrium between uncharged dimeric complexes and anionic dimers has been observed spectroscopically in solution. The crystal and molecular structure of the titanium(III) derivative $NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]$ (3) has been solved by X-ray diffraction methods. In the dimeric carbamato-bridged anion, the titanium is hexacoordinated in a distorted pseudo-octahedral geometry. These complexes promptly react with protic substances such as hydrogen chloride and acetylacetone to give the corresponding titanium(III) and vanadium(III) complexes MCl_6^{3-} and $M(C_5H_7O_2)_3$, respectively. The diisopropyltitanium(III) derivative reacts with *p*-benzoquinone and 9,10-phenanthrenequinone to give 2:1 adducts of general formula $[Ti_2(O_2CNiPr_2)_6]$quinone, which are better regarded as phenolato and catecholato complexes of titanium(IV), respectively.

Synthese und Reaktivität von *N,N*-Dialkylcarbamato-Komplexen von Titan(III) und Vanadium(III). Kristall- und Molekülstruktur eines anionischen dimeren Titan(III)-Derivats

Bei der Reaktion von wasserfreiem $TiCl_3$ oder VCl_3 mit $HNiPr_2$ und CO_2 oder durch die Austauschreaktion 1/2 $M_2(O_2CNiPr_2)_6$ + 3 $HNEt_2$ → 1/*n* $[M(O_2CNEt_2)_3]_n$ + 3 $HNiPr_2$ entstanden die *N,N*-Dialkylcarbamato-Derivate 1, 2, 5 und 7. Weitere Reaktion der ungeladenen dimeren Komplexe mit $O_2CNR_2^-$ lieferte die ionischen Derivate $NH_2R_2[M_2(O_2CNR_2)_7]$ 3, 4 und 6. Das Gleichgewicht zwischen den ungeladenen dimeren Komplexen und den anionischen Dimeren wurde in Lösung spektroskopisch verfolgt. Die Kristall- und Molekülstruktur des Titan(III)-Derivats 3, $NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]$, wurde durch Röntgenstrukturanalyse bestimmt. In dem dimeren Carbamato-überbrückten Anion liegt das Titan hexakoordiniert in verzerrt pseudo-oktaedrischer Geometrie vor. Diese Komplexe reagieren rasch mit protischen Verbindungen wie HCl und Acetylaceton zu den entsprechenden Titan(III)- und Vanadium(III)-Komplexen MCl_6^{3-} bzw. $M(C_5H_7O_2)_3$. Das Diisopropyltitan(III)-Derivat gibt mit *p*-Benzochinon und 9,10-Phenanthrenchinon 2:1-Addukte der allgemeinen Formel $[Ti_2(O_2CNiPr_2)_6]$chinon, die als Phenolato- und Catecholato-Komplexe von Ti(IV) angesehen werden können.

N,N-Dialkylcarbamato complexes of transition elements of general formula $[M(O_2CNR_2)_n]_m$ are interesting under several respects: a) They belong to the general class of $[M(O_2C-X)_n]_m$ derivatives (X = O, R, H, OR) and therefore present interesting chemical and structural properties; b) they are useful starting materials for the preparation of metal complexes in nonaqueous media, which is particularly useful when hydrolytic processes are to be avoided; c) they contain the CO_2 unit bonded to both the metal and the NR_2 moiety, thus leading to a metal-assisted modification of the CO_2 reactivity[1].

A method of preparing these complexes[2] consists of assembling the O_2CNR_2 coordinating group around a transition metal cation by the simultaneous action of carbon dioxide and a secondary amine in a hydrocarbon solvent starting from an anhydrous metal halide. The alternative method[3] of preparing *N,N*-dialkylcarbamato complexes of transition elements is the formal insertion of carbon dioxide in between the metal-nitrogen bond of *N,N*-dialkylamido derivatives.

This paper reports the preparation of the titanium(III) and vanadium(III) complexes. Besides, it describes the first example of anionic complexes of this series, namely $[M_2(O_2CNR_2)_7]^-$, M = Ti, V. The crystal and molecular structure of $NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]$ has been studied by X-ray diffraction methods. Moreover, the NR_2 exchange reaction between $M_2(O_2CNiPr_2)_6$ complexes and $HNEt_2$ has been used as a preparative method. Part of this study has been communicated in a preliminary form[4].

Results and Discussion

In undertaking this study on *N,N*-dialkylcarbamato complexes of titanium(III) and vanadium(III), consideration was given to the fact that coordination chemistry of titanium(III) is still rather poor, as compared with other transition elements, and that interesting comparisons could be made between the titanium(III) and the vanadium(III) systems. Due to favourable solubility properties, the preparation of the *N,N*-dialkylcarbamato complexes of titanium(III) and vanadium(III) could be successfully carried out from the

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corresponding anhydrous trichlorides when the alkyl group was the isopropyl one. In such a case, the separation of the soluble reaction product from the substantially insoluble $HNiPr_2 \cdot HCl$ was possible through a simple filtration and the metal(III) complexes could be recovered from the solution either by evaporation to dryness of the solvent or by recrystallization at low temperature. The overall stoichiometry of the reaction leading to the *N,N*-dialkylcarbamato complexes is shown in equation (1). Although, in general, the behaviour of titanium(III) is similar to that of vanadium(III), substantial differences exist. By using the anhydrous trichlorides MCl_3 as starting materials, titanium was found to react slower with respect to vanadium, and temperatures as high as 80 °C were required in order to observe reasonable rates. This was rather surprising since, on the basis of simple electrostatic considerations, titanium(III) would be expected to react faster than vanadium(III), the ionic radius[5a)] of Ti^{3+} being 0.67 Å with respect to 0.64 Å of V^{3+}, indicating a slightly larger charge density on vanadium[6)].

$$2\,MCl_3 + 12\,HNR_2 + 6\,CO_2 \longrightarrow M_2(O_2CNR_2)_6 + 6\,NH_2R_2Cl \quad (1)$$

That some solid state effects connected with the MCl_3 species used in the reaction were responsible for the observed lower rates for titanium was suggested by the fact that, when the monomeric tetrahydrofuran adducts of titanium(III)[5b)] and vanadium(III)[5c)], $MCl_3(THF)_3$, were used for the reaction, the formation of the carbamato complexes occurred in both cases at room temperature and possibly titanium(III) was faster than vanadium(III), although no quantitative measurements were carried out.

In addition to the neutral $M_2(O_2CNiPr_2)_6$ complexes, also the dimeric anionic $[M_2(O_2CNR_2)_7]^-$ were found in solution. To understand the observed facts, equilibria (2) and (4) and reaction (3) should be considered. For R = *i*Pr, equilibrium (2) is not much shifted to the right[7)], presumably due to steric reasons. Equilibrium (2) can in fact be regarded as an acid-base reaction and the presence of two bulky groups such as *i*Pr may hinder the formation of the carbamate.

$$CO_2 + 2\,HNR_2 \rightleftharpoons NH_2R_2[O_2CNR_2] \qquad R = Et, iPr \quad (2)$$

$$2\,MCl_3 + 6\,NH_2R_2[O_2CNR_2] \longrightarrow M_2(O_2CNR_2)_6 + 6\,NH_2R_2Cl \quad (3)$$

$$M_2(O_2CNR_2)_6 + [O_2CNR_2]^- \rightleftharpoons [M_2(O_2CNR_2)_7]^- \quad (4)$$

$M = Ti, V;\ R = iPr$

In this connection, it is interesting to note that in basic aqueous solutions of diisopropylamine no carbamate formation was observed[8)], presumably due to the competitive reaction of CO_2 with the less hindered OH^-. In the absence of water or of organic solvents, the formation of a CO_2-containing solid was reported[9)].

Reaction (3) merely expresses the concept that the formation of the titanium(III) and vanadium(III) complexes in these systems is a chloride-carbamato metathetical reaction. Equilibrium (4) has been definitely established in solution spectroscopically[10)]. In the case of the titanium(III) system, the uncharged complex has an IR absorption band in *n*-heptane (solvent where the equilibrium was studied) at 1580 cm^{-1}, while the anionic complex has a typical absorption band at 1610 cm^{-1}, see Table 1 and Figure 1. Although these bands are certainly stretching vibrations within the bonded carbamato group, it would be difficult to associate them with a specific bonding arrangement and they have been used in this context simply as analytical tools to distinguish one complex from the other.

Table 1. IR spectra of *N,N*-dialkylcarbamato complexes of titanium(III) and vanadium(III) [PCTFE = poly(chlorotrifluoroethylene)]

Compound		$\tilde{\nu}$ (cm^{-1})						Medium
$Ti_2(O_2CNiPr_2)_6$	**1**	1580m	1520m-s	1485m-s	1450m-s		1385m	C_2Cl_4
$V_2(O_2CNiPr_2)_6$	**2**	1590m	1510m-s	1490m-s	1450s		1385m	"
$[Ti_2(O_2CNiPr_2)_7]^-$ a)	**3**	1610m	1520vs	1485vs	1450s	1430s	1385m	PCTFE
$[Ti_2(O_2CNEt_2)_7]^-$ a)	**4**	1620m	1520vs	1460s	1440s		1380s	"
$[Ti(O_2CNEt_2)_3]_n$	**5**		1500vs	1460m	1430s		1375m	"
$[V_2(O_2CNiPr_2)_7]^-$ a)	**6**	1605m	1520vs	1485vs	1450s	1435s	1385m	"
$[V(O_2CNEt_2)_3]_n$	**7**		1500vs	1460w	1440s		1375w	"

a) The countercation is $[NH_2R_2]^{\bullet}$.

In general, it has been observed that the anionic species are favoured by low temperatures and high carbon dioxide pressures, in agreement with the presumably exothermic character of reactions (2) and (4). Depending on the operative conditions, both the neutral and the anionic complexes are present in the reaction mixtures. In the case of titanium(III), the separation of $Ti_2(O_2CNiPr_2)_6$ (**1**) from $NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]$ (**3**) can be easily carried out in view of their different solubility. The ionic compound is less soluble and at about 5 °C precipitates as a blue crystalline solid from its solutions. On the contrary, the neutral dimer is much more soluble and it can be recrystallized from its *n*-heptane solution at dry-ice temperature. Both the neutral and the anionic compounds have magnetic moments around 1.7 BM, thus indicating that no strong antiferromagnetic interactions occur between the two titanium(III) centres. In view of the cosiderable interest for coordination compounds of titanium(III) and since the anionic compound was unique among carbamato complexes of transition elements and in consideration, finally, of the fact that this was a key-product for understanding the structure of the other systems, it was decided to carry out an X-ray investigation of **3**.

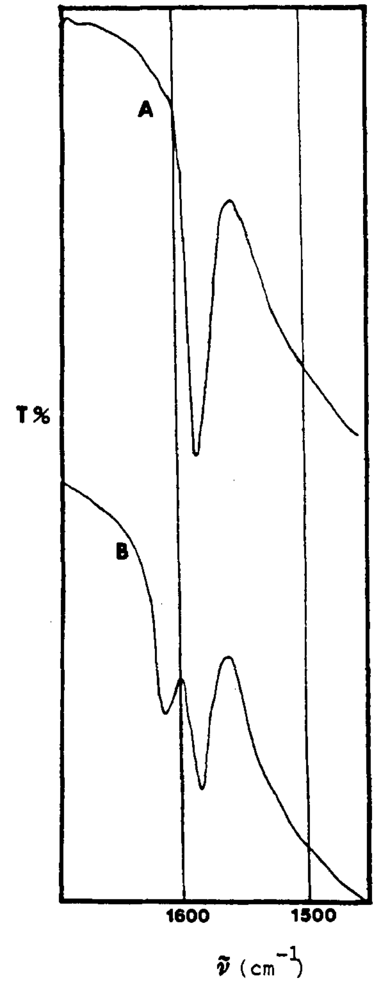


Figure 1. IR spectrum of the species pertaining to the equilibrium 1 $Ti_2(O_2CN\textit{i}Pr_2)_6$ + $[O_2CN\textit{i}Pr_2]^-$ $\rightleftarrows$ $[Ti_2(O_2CN\textit{i}Pr_2)_7]^-$ 3. Approximate concentrations: $[Ti_2(O_2CN\textit{i}Pr_2)_6]$, 9 × 10^{-3} M; $[NH\textit{i}Pr_2]$, 0.36 M; CaF_2 cell; 0.1 mm, *n*-heptane.
A) Solution of $Ti_2(O_2CN\textit{i}Pr_2)_6$ under CO_2; B) After addition of the amine

$M_2(O_2CN\textit{i}Pr_2)_6$
1: M = Ti
2: M = V

$NH_2R_2[Ti_2(O_2CNR_2)_7]$
3: R = *i*Pr
4: R = Et

$[M(O_2CNEt_2)_3]_n$
5: M = Ti
7: M = V

$NH_2\textit{i}Pr_2[V_2(O_2CN\textit{i}Pr_2)_7]$
6

The compound crystallizes with one $[Ti_2(O_2CN\textit{i}Pr_2)_7]^-$ anion and one $[NH_2\textit{i}Pr_2]^+$ cation in the asymmetric unit, see Figure 2a. A perspective view of the complex anion is presented in Figure 2b. One of the main points to note is that, although the molecule is not subject to any crystallographically imposed symmetry, its internal geometry corresponds nearly exactly to *m* symmetry, where the mirror plane can be taken as that containing the N(3), N(4), N(5), C(15), and C(29) atoms. The structural parameters of the two halves reflecting across the plane are, for the most part, identical within experimental error, as can be seen from the symmetry-related values collected in Table 2. Another interesting feature of the structure is the presence of three structurally distinct types of carbamato ligands: two monodentate, three bidentate bridging, and two terminal bidentate, **A**–**C**.

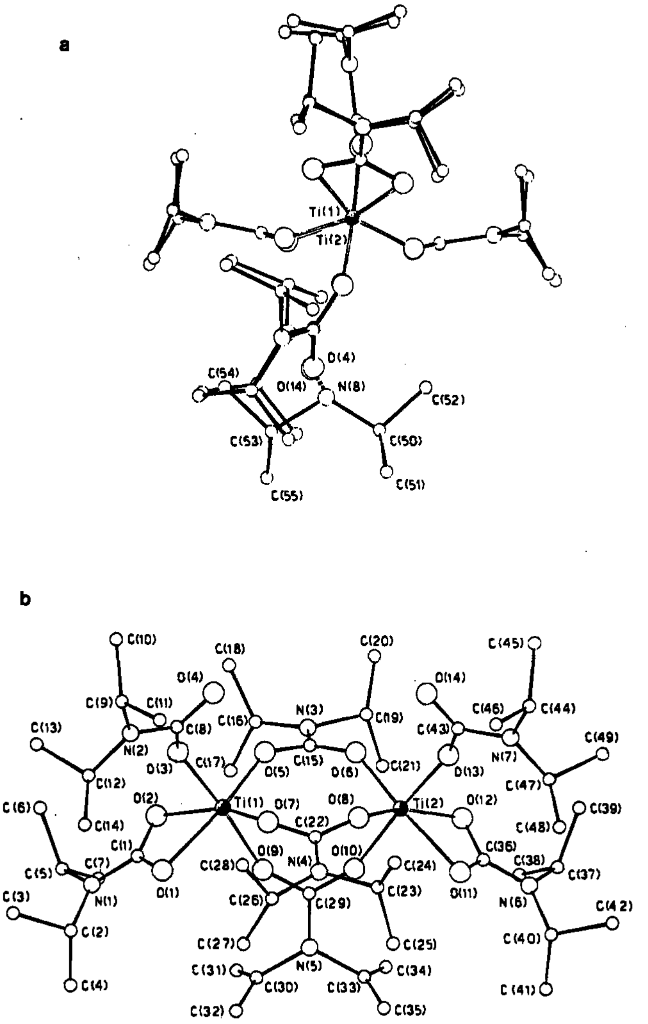
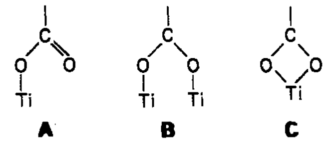


Figure 2. Views of $NH_2\textit{i}Pr_2[Ti_2(O_2CN\textit{i}Pr_2)_7]$ (**3**) with the numbering scheme used.
a) The cation-anion combination viewed along the titanium-titanium vector.
b) The $[Ti_2(O_2CN\textit{i}Pr_2)_7]^-$ anion



Each of the two independent titanium atoms has the same surrounding, the coordination sites being occupied by six oxygen atoms belonging to different carbamato groups: one of type **A**, three of type **B**, and two of type **C**. Accordingly, three types of Ti–O bond distances are observed which average as follows: **A** 1.981, **B** 1.991, **C** 2.117 Å. All the individual values are quite reasonable and agree with those quoted in the literature for six-coordinated titanium(III) bonded to oxygen donor atoms[11]. A satisfactory description of the titanium environment can be achieved by examining the bond angles at the metal centres (Table 2) as well as the least-squares planes calculations of Table 3. From the tabulated data it can be deduced that the coordination geometry for each titanium can be regarded as a slightly tetragonally distorted octahedron in which two oxygen atoms from ligand as in **B** and two from the ligand as in **C** span the equatorial positions, while the third oxygen atom from the ligand (**B**) and the one from ligand as in **A** are axial. The four donor atoms in the equatorial set are almost coplanar with no atom deviating by more than 0.08 Å from the mean least-squares plane passing through them and with the metal atom displaced from the plane by only 0.05 Å. The distortion from a regular octahedral geometry is due primarily to the constraints brought about by the type **C** carbamato ligand, which, owing to its small bite, comprises an angle of only 62.2° (av.) at the metal atom. This narrowing is accompanied by a significant widening of the other equatorial angles which are opened from the idealized value of 90° to 96 – 104° and by a remarkable bending (ca. 2° from the expected 180°) of the two *trans* angles. The axial ligands are ca. 2.0 Å from the equatorial plane and deviate from 180° by approximately 5°. Within the dimeric anion, the Ti(1)···Ti(2) distance is 4.30 Å, thus showing that no metal-metal interaction is occurring, which is in agreement with the magnetic moment of 1.84 BM found for this compound. It is interesting to note that titanium(III) was predicted to have a magnetic moment slightly higher than the spin-only value (1.73 BM) due to spin-orbit coupling[12]; thus, the value we find appears to be perfectly consistent with the presence of two magnetically diluted titanium(III) centres in the system. Bond distances and angles for the carbamato groups can be regarded as normal as they are in the ranges observed for this type of ligands in transition metal complexes[2,3]. In each carbamato group the O_2CN moiety is very close to planarity (maximum deviation 0.03 Å). The Ti – O angles

Table 2. Selected bond distances (Å) and bond angles (deg) for $NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]$ (3) with e.s.d.'s in parenthesis

Ti(1)-O(1)	2.114(5)	Ti(2)-O(11)	2.089(6)
Ti(1)-O(2)	2.141(7)	Ti(2)-O(12)	2.125(6)
Ti(1)-O(3)	1.986(7)	Ti(2)-O(13)	1.977(7)
Ti(1)-O(5)	1.962(7)	Ti(2)-O(6)	1.957(7)
Ti(1)-O(7)	1.987(7)	Ti(2)-O(8)	1.984(7)
Ti(1)-O(9)	2.039(7)	Ti(2)-O(10)	2.019(7)
C(1)-O(1)	1.28(1)	C(36)-O(11)	1.30(1)
C(1)-O(2)	1.26(1)	C(36)-O(12)	1.28(1)
C(1)-N(1)	1.38(1)	C(36)-N(6)	1.33(1)
C(8)-O(3)	1.28(1)	C(43)-O(13)	1.26(1)
C(8)-O(4)	1.25(1)	C(43)-O(14)	1.26(1)
C(8)-N(2)	1.40(2)	C(43)-N(7)	1.39(1)
C(15)-O(5)	1.27(1)	C(15)-O(6)	1.27(1)
C(15)-N(3)	1.33(1)		
C(22)-O(7)	1.25(1)	C(22)-O(8)	1.25(1)
C(22)-N(4)	1.31(1)		
C(29)-O(9)	1.25(1)	C(29)-O(10)	1.27(1)
C(29)-N(5)	1.35(1)		
N(1)-C(2)	1.50(2)	N(6)-C(40)	1.49(1)
N(1)-C(5)	1.48(2)	N(6)-C(37)	1.48(1)
N(2)-C(9)	1.49(2)	N(7)-C(44)	1.49(2)
N(2)-C(12)	1.52(2)	N(7)-C(47)	1.49(2)
N(3)-C(16)	1.49(2)	N(3)-C(19)	1.58(2)
N(4)-C(26)	1.45(2)	N(4)-C(23)	1.52(2)
N(5)-C(30)	1.48(1)	N(5)-C(33)	1.48(2)
N(8)-C(50)	1.50(1)	N(8)-C(53)	1.54(1)
O(3)-Ti(1)-O(9)	175.2(3)	O(10)-Ti(2)-O(13)	175.7(3)
O(1)-Ti(1)-O(2)	62.0(3)	O(11)-Ti(2)-O(12)	62.4(2)
O(2)-Ti(1)-O(5)	96.4(3)	O(12)-Ti(2)-O(6)	96.7(3)
O(5)-Ti(1)-O(7)	104.2(3)	O(6)-Ti(2)-O(8)	101.3(3)
O(7)-Ti(1)-O(1)	97.4(3)	O(8)-Ti(2)-O(11)	99.8(3)
O(1)-Ti(1)-O(5)	157.7(3)	O(11)-Ti(2)-O(6)	158.2(3)
O(2)-Ti(1)-O(7)	159.4(4)	O(12)-Ti(2)-O(8)	162.1(3)
Ti(1)-O(1)-C(1)	89.7(6)	Ti(2)-O(11)-C(36)	91.4(6)
Ti(1)-O(2)-C(1)	88.9(7)	Ti(2)-O(12)-C(36)	90.6(6)
Ti(1)-O(3)-C(8)	140.7(7)	Ti(2)-O(13)-C(43)	147.2(7)
Ti(1)-O(5)-C(15)	143.1(7)	Ti(2)-O(6)-C(15)	142.0(6)
Ti(1)-O(7)-C(22)	143.3(7)	Ti(2)-O(8)-C(22)	144.4(7)
Ti(1)-O(9)-C(29)	145.0(7)	Ti(2)-O(10)-C(29)	152.1(7)
O(1)-C(1)-O(2)	119(1)	O(11)-C(36)-O(12)	116(1)
O(1)-C(1)-N(1)	119(1)	O(11)-C(36)-N(6)	122(1)
O(2)-C(1)-N(1)	122(1)	O(12)-C(36)-N(6)	122(1)
O(3)-C(8)-O(4)	125(1)	O(13)-C(43)-O(14)	124(1)
O(3)-C(8)-N(2)	116(1)	O(13)-C(43)-N(7)	118(1)
O(4)-C(8)-N(2)	119(1)	O(14)-C(43)-N(7)	118(1)
O(5)-C(15)-O(6)	120(1)		
O(5)-C(15)-N(3)	120(1)	O(6)-C(15)-N(3)	120(1)
O(7)-C(22)-O(8)	122(1)		
O(7)-C(22)-N(4)	120(1)	O(8)-C(22)-N(4)	118(1)
O(9)-C(29)-O(10)	122(1)		
O(9)-C(29)-N(5)	119(1)	O(10)-C(29)-N(5)	119(1)
C(1)-N(1)-C(2)	119(1)	C(36)-N(6)-C(40)	119(1)
C(1)-N(1)-C(5)	121(1)	C(36)-N(6)-C(37)	121(1)
C(8)-N(2)-C(9)	121(1)	C(43)-N(7)-C(44)	122(1)
C(8)-N(2)-C(12)	119(1)	C(43)-N(7)-C(47)	119(1)
C(15)-N(3)-C(16)	121(1)	C(15)-N(3)-C(19)	117(1)
C(22)-N(4)-C(26)	124(1)	C(22)-N(4)-C(23)	121(1)
C(29)-N(5)-C(30)	120(1)	C(29)-N(5)-C(33)	119(1)
C(50)-N(8)-C(53)	116.8(8)		
N(8)-C(50)-C(52)	107(1)	N(8)-C(53)-C(54)	104(1)
N(8)-C(50)-C(51)	112(1)	N(8)-C(53)-C(55)	111(1)
C(51)-C(50)-C(52)	113(1)	C(55)-C(53)-C(54)	113(1)

Table 3. Weighted least-squares planes for **3**[a)]

1) $0.3990x - 0.4918y - 0.7739z = -12.3887$
O(1), O(5), O(2), O(7)
O(1) 0.058(6), O(5) 0.045(7), O(2) – 0.064(7), O(7) – 0.051(7), Ti(1) – 0.047(2), O(3) – 2.032(7), O(9) 1.988(7) Å

2) $-0.1314x + 0.7870y - 0.6028z = 4.4054$
O(1), O(5), O(3), O(9)
O(1) – 0.172(7), O(5) – 0.173(7), O(3) 0.166(7), O(9) 0.180(7), Ti(1) 0.206(2), O(2) – 1.834(7), O(7) 2.189(7) Å

3) $-0.8764x - 0.4573y - 0.1510z = -11.9493$
O(3), O(9), O(2), O(7)
O(3) 0.132(7), O(9) 0.127(7), O(2) – 0.127(7), O(7) – 0.204(9), Ti(1) 0.202(3), O(1) – 1.792(6), O(5) 2.159(7) Å

4) $-0.8711x + 0.4461y - 0.2051z = 2.6516$
O(6), O(11), O(8), O(12)
O(6) – 0.038(6), O(11) – 0.050(6), O(8) 0.061(8), O(12) 0.038(7), Ti(2) 0.053(3), O(10) – 1.965(7), O(13) 2.028(7) Å

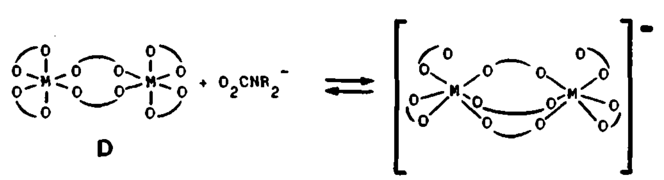
5) $-0.3413x - 0.8415y - 0.4188z = -14.6614$
O(6), O(11), O(10), O(13)
O(6) 0.189(7), O(11) 0.177(7), O(10) – 0.211(7), O(13) – 0.195(7), Ti(2) – 0.185(2), O(8) – 2.169(7), O(12) 1.839(7) Å

6) $0.4263x + 0.4289y - 0.7964z = 2.6773$
O(10), O(13), O(8), O(12)
O(10) – 0.117(7), O(13) – 0.122(7), O(8) 0.156(8), O(12) 0.091(6), Ti(2) – 0.194(2), O(6) – 2.147(7), O(11) 1.768(6)

[a)] The atoms defining the planes and the distances from the planes are given below the equation of the plane. The planes are relative to an orthogonal system of axes.

range from 88.9(7) to 91.4(6)° for type **C** ligands and from 140.7(7) to 152.1(7)° for type **A** and type **B** ligands. As a result of the bridging action of the type **B** carbamato groups, two puckered eight-membered chelate rings are formed (total puckering amplitude[13]: 0.737(5) Å for Ti(1)O(5)C(15)-O(6)Ti(2)O(8)C(22)O(7); 1.466(7) Å for Ti(1)O(9)C(29)O(10)-Ti(2)O(8)C(22)O(7)). The diisopropylammonium cation is hydrogen bonded to the anion through its nitrogen atom to the two uncoordinated oxygen atoms of the monodentate carbamato ligands [N(8)···O(4) 2.72(1) Å; N(8)···O(14) 2.67(1) Å], see Figure 2a.

A comparison of IR spectra of $[Ti_2(O_2CN\textit{i}Pr_2)_7]^-$ and $[V_2(O_2CN\textit{i}Pr_2)_7]^-$, see Experimental Part and Table 1, strongly suggests that the two systems are isostructural. The same kind of reasoning applies to the molecular structures of $M_2(O_2CN\textit{i}Pr_2)_6$ complexes of titanium(III) and vanadium(III) (**1**, **2**), whose IR spectra, see Table 1, are substantially identical. Knowing the molecular structure of the $[Ti_2(O_2CN\textit{i}Pr_2)_7]^-$ anion is helpful for suggesting possible structures for the uncharged dimeric species. Titanium(III) and vanadium(III) are frequently hexacoordinated, although in some cases pentacoordination is also known[14]. In order to achieve the hexacoordination in a dimeric structure (as shown by molecular mass determination in benzene solution), the metal will use bridging carbamato groups of type **B**, similar to those encountered in the molecular structure of the anion. By taking into consideration that a dimeric structure with four carbamato groups would be perhaps crowded and unlikely, the most reasonable suggestion is that the uncharged dimer has structure **D** with two carbamato bridges and two terminal bidentate $O_2CN\textit{i}Pr_2$ groups per titanium. However, the point has already been raised that the latter arrangement is highly strained and thus it is quite likely that the conversion from the uncharged dimer to the complex anion, see equilibrium (4), is mainly dominated by the stringent requirement of relieving the strain associated with the presence of two terminally bidentate carbamato ligands in the uncharged dimer, to give the established structure of the anion.



Reaction (1) between $TiCl_3$ (or VCl_3) and $HNEt_2$ in the presence of CO_2, although it occurred rapidly even at room temperature[15], is not a good preparative method for the *N*,*N*-diethylcarbamato derivatives; in fact, the reaction products (NH_2Et_2Cl and $[M(O_2CNEt_2)_3]_n$) are both very slightly soluble in the hydrocarbon used for the reaction and they cannot be easily separated. An alternative method of preparation, which does not appear to have been used earlier, consists of treating the readily soluble diisopropyl derivative with $HNEt_2$ under CO_2 at room temperature. Although stoichiometrically this is a NR_2 exchange, it has been shown that the reaction does not occur in the absence of CO_2. Recovery of the slightly soluble ethyl derivative and its separation from the isopropyl complex was then a simple matter. No products of partial exchange could be detected. Both the lower solubility of the final transition metal complex and the higher stability of $NH_2Et_2[O_2CNEt_2]$ with respect to the isopropyl analogue, are presumably responsible for the successful exchange in equation (5).

$$\underset{\mathbf{1}}{{}^1/_2\, Ti_2(O_2CN\textit{i}Pr_2)_6} + 3\, HNEt_2 \xrightarrow{CO_2} \underset{\mathbf{5}}{1/n\, [Ti(O_2CNEt_2)_3]_n} + 3\, HN\textit{i}Pr_2 \qquad (5)$$

That reaction (5) occurs only in the presence of CO_2 resembles what has been found earlier[18] in the $W(NMe_2)_3(O_2{}^{13}CNMe_2)_3/CO_2/HN(CD_3)_2$ system, in which high $HN(CD_3)_2/CO_2$ molar ratios up to 5 led to complete inhibition of the exchange reactions. By taking our case as an example, the observed exchange is more likely governed by equilibria (6) and (7), with the latter being predominating. At room temperature and atmospheric pressure, the $CO_2/HNEt_2$ molar ratio observed in gasvolumetric experiments is slightly higher than 0.5[2a], thus suggesting that some diethylcarbamic acid might be present in solution.

$$CO_2 + HNEt_2 \rightleftharpoons HOC(O)NEt_2 \qquad (6)$$

$$HOC(O)NEt_2 + HNEt_2 \rightleftharpoons NH_2Et_2[O_2CNEt_2] \qquad (7)$$

Thus, electrophilic attack by diethylcarbamic acid on the titanium(III) carbamato complex appears to be the most likely pathway to the NR_2 exchange process, although other possibilities cannot be excluded. In this connection, it is relevant that electrophilic attack on the metal-coordinated oxygen of *N*,*N*-dialkylcarbamato complexes of transition elements has been reported earlier[1].

The structures of the products of general formula $[M(O_2CNR_2)_3]_n$ strongly depend on the nature of the group R. While with R = *i*Pr the products are dimeric ($n = 2$), **1**, **2**, for R = Et much higher molecular complexities are to be envisaged, in view of the low solubility in hydrocarbons. It is quite reasonable to assume that the less sterically demanding ethyl groups may induce the formation of polynuclear structures with all-bridging carbamato groups of type **B**.

All of the carbamato complexes reported in this paper are promptly attacked by diluted sulfuric acid: this reaction has been actually used for the quantitative determination of the combined carbon dioxide. By operating in a hydrocarbon medium, the reaction of $M_2(O_2CN\textit{i}Pr_2)_6$ (**1**, **2**) with dry HCl led to the formation of the hexachlorotitanate(III) and the hexachlorovanadate(III) anions, according to equation (8).

The MCl_6^{3-} anions of titanium(III) and vanadium(III) are not stable in aqueous solution and the pyridinium derivatives[19a] have been prepared either by melting pyHCl with MCl_3 or by treating pyHCl with MCl_3 in chloroform.

These reactions were not successful for the preparation of the alkylammonium derivatives. In agreement with earlier findings[19a)], the hexachlorometallate(III) anions undergo prompt solvolysis by MeCN with formation of the anionic bis-acetonitrile adducts, as shown in equation (9). The adducts were identified from their visible spectrum[19a,b)].

$$\tfrac{1}{2}\,M_2(O_2CN\mathit{i}Pr_2)_6 + 6\,HCl \longrightarrow (NH_2\mathit{i}Pr_2)_3[MCl_6] + 3\,CO_2 \qquad (8)$$

1: M = Ti
2: M = V

$$[MCl_6]^{3-} + 2\,MeCN \longrightarrow 2\,Cl^- + [M(Cl)_4(MeCN)_2]^- \qquad (9)$$

$$\mathbf{1},\mathbf{2} + 6\,C_5H_8O_2 \longrightarrow 6\,HN\mathit{i}Pr_2 + 6\,CO_2 + 2\,M(C_5H_7O_2)_3 \qquad (10)$$

$C_5H_8O_2 = CH_3COCH_2COCH_3$

Attack of the *N,N*-dialkylcarbamato complexes can occur with a weak acid such as acetylacetone to give the corresponding β-diketonato complexes, see equation (10).

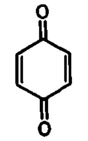
Although in such a case a proton attack on the metal-coordinated *N,N*-dialkylcarbamato group appears to be the most likely pathway, preliminary coordination of the β-diketone to the metal, followed by the proton transfer, cannot be excluded. The literature reports[20)] the somewhat related case of acetylacetone reacting with (diethylamido)titanium(III) to give tris(acetylacetonato)titanium(III).

The *N,N*-dialkylcarbamato derivatives of titanium(III) are sensitive to oxygen and are readily oxidized by mild oxidants such as iodine. The reaction with dry oxygen was studied but found to yield untractable materials. On the contrary, the potentially bi-electronic oxidants *p*-benzoquinone and 9,10-phenanthrenequinone gave reproducable results, the titanium(III)/quinone molar ratio used being 2, and excess amounts of the quinone eventually present in the reaction mixture were recovered unchanged. The stoichiometries of these reactions are as indicated in equations (11) and (12). The substances are red (adduct with *p*-benzoquinone) or violet, moderately soluble in hydrocarbon solvents.

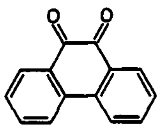
$$\mathbf{1}\ Ti_2(O_2CN\mathit{i}Pr_2)_6 + p\text{-}C_6H_4O_2 \longrightarrow Ti_2(O_2CN\mathit{i}Pr_2)_6 \cdot C_6H_4O_2 \qquad (11)$$

$$\mathbf{1} + 9{,}10\text{-Phquin} \longrightarrow Ti_2(O_2CN\mathit{i}Pr_2)_6 \cdot Phquin \qquad (12)$$

p-$C_6H_4O_2$ =



9,10-Phquin =



While the uncoordinated quinones have IR CO stretching vibrations around 1680 cm^{-1} (*p*-benzoquinone[21)], 1674s and 1662s cm^{-1} in $CHCl_3$; 9,10-phenanthrenequinone[22)], 1684 cm^{-1} *in CCl_4) the substances obtained by these reactions* do not show any infrared band above 1570 cm^{-1}, thus showing that a considerable reduction of the CO bond order has occurred upon complexation to titanium. In the case of metal complexes of *ortho*-quinones[23)] a lowering of about 50 cm^{-1} has been suggested to be indicative of a simple coordination, while the one-electron transfer (semiquinone ligand) and the two-electron transfer (diphenolato ligand) are characterized by a decrease of the CO stretching by about 200 and 500 cm^{-1}, respectively. In view of the diamagnetism of the complexes and of the 2:1 titanium/quinone stoichiometry observed, we suggest that these adducts should formally be regarded as titanium(IV) derivatives of the corresponding diphenolato ligands. The IR spectra are not very helpful in this case, since absorptions due to carbamato ligand may interfere: however, an inspection of the IR data (see Experimental Part) shows that all of the observed absorptions (provided coincidences are not present) should be attributed to the carbamato ligand and thus the CO stretching vibrations of the coordinated phenolato should be below 1360 cm^{-1}. Concerning structures, the product obtained from 9,10-phenanthrenequinone may have a structure similar to the $[Ti_2(O_2CN\mathit{i}Pr_2)_7]^-$ anion, with the $C_{14}H_8O_2$ group replacing one of the bridging carbamato groups. A similar structure for the product of the reaction with *p*-benzoquinone appears to be less likely, in view of the small available room between the two titanium centres (4.30 Å) to accomodate a $C_6H_4O_2$ bridging unit.

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Experimental

All operations were carried out unter prepurified nitrogen or carbon dioxide, as specified. Solvents were dried by conventional methods prior to use. Commercially available (Aldrich) $TiCl_3$ and VCl_3 were used, the former being washed with *n*-heptane prior to use. The THF adducts $TiCl_3(THF)_3$[24)] and $VCl_3(THF)_3$[25)] were prepared according to the literature. – IR spectra: Perkin-Elmer model 283B instrument equipped with grating. – Visible spectra: Carlo Erba Spectra Comp 601. – Magnetic susceptibilities: Faraday method, magnetic balance calibrated with $CuSO_4 \cdot 5\,H_2O$. – Molecular weights: Cryoscopy in benzene.

Bis-μ-(diisopropylcarbamato-O,O')-bis(diisopropylcarbamato-O)bis(diisopropylcarbamato-O,O')dititanium (**1**)

a) *From $TiCl_3$:* Anhydrous $TiCl_3$ (6.41 g; 41.6 mmol) was introduced under CO_2 into a flask containing *n*-heptane (200 ml), and diisopropylamine (37.75 g; 374 mmol) was then added. The mixture was stirred for 8 h under CO_2 at atmospheric pressure at 80°C and then rapidly cooled down to room temperature; the blue solution was filtered and the filtrate was evaporated to dryness. The blue residue (14.2 g, 71% yield of **1** with satisfactory analytical data) was further purified by dissolution in 100 ml of *n*-heptane under nitrogen. The solution cooled down to −78°C separated a deep blue crystalline solid which was isolated by filtration and dried in vacuo at −78°C. During this operation, the crystals collapsed while the solid was releasing *n*-heptane (39.7% yield based on initial titanium). The blue product is well soluble in the common organic solvents, is quickly oxidized by air, and hydrolized by moisture. Molecular mass determinations by cryoscopy in benzene showed the compound to be dimeric. Magnetic susceptibility is $\chi_{Ti}^{corr} = 1130 \times 10^{-6}$ cm^3 · mol^{-1} (per mol of titanium, diamagnetic correction = -320×10^{-6} cm^3 · mol^{-1}), corresponding to μ_{eff} = 1.64 BM. The

IR spectrum of the compound in C_2Cl_4 solution is in Table 1. The spectrum in poly(chlorotrifluoroethylene), PCTFE, is identical.

$C_{42}H_{84}N_6O_{12}Ti_2$ Calcd. CO_2 27.5 Ti 10.0 mol. mass 961.0
Found CO_2 27.2 Ti 10.0 mol. mass 994

b) *From $TiCl_3(THF)_3$:* Adduct $TiCl_3(THF)_3$ (2.25 g; 6.07 mmol) was introduced under CO_2 into a flask containing 100 ml of *n*-heptane and treated with diisopropylamine (5.5 g; 54.4 mmol). The mixture was stirred for 6 h at room temperature. Then the blue solution was separated from NH_2iPr_2Cl by filtration and evaporated to dryness to give the blue **1** as the solid residue (71% yield).

Diisopropylammonium Tris-μ-(diisopropylcarbamato-O,O')-bis-(diisopropylcarbamato-O)bis(diisopropylcarbamato-O,O')dititanate (3)

a) *From $TiCl_3$:* A solution of diisopropylamine (36.57 g; 362 mmol) was syphoned into a 500 ml stainless-steel autoclave containing anhydrous $TiCl_3$ (6.20 g; 40.2 mmol). The autoclave was loaded with CO_2 (40 atm at room temperature) and stirred for 12 h at 80°C and then for additional 12 h at room temperature. The reaction mixture was collected from the autoclave into a glass vessel by using the internal gas pressure both as a protecting atmosphere and as the extruder of the suspension. After filtration under CO_2 to eliminate NH_2iPr_2Cl, the blue solution was cooled down to 5°C; the blue crystals so obtained were separated by filtration, briefly dried in vacuo (2.3 g, 9.3%) and used for the X-ray diffractometric experiment. The compound is soluble in saturated and aromatic hydrocarbons and other organic solvents; however, it is readily decomposed unless it is kept under CO_2 in the presence of an excess of the amine (vide infra). It is readily decomposed by air and moisture. Magnetic susceptibility: $\chi_{Ti}^{corr} = 1420 \times 10^{-6}\,cm^3 \cdot mol^{-1}$ (diamagnetic correction = $-415 \times 10^{-6}\,cm^3 \cdot mol^{-1}$), corresponding to $\mu_{eff} = 1.84$ BM. The IR spectrum of the compound (PCTFE mull) is in Table 1.

$C_{55}H_{114}N_8O_{14}Ti_2$ (1207.4) Calcd. CO_2 25.5 Ti 7.9
Found CO_2 25.5 Ti 7.8

b) *From* **1**: A cylindrical glass container with **1** (1.03 g; 1.07 mmol) and diisopropylamine (1.94 g; 19.2 mmol) in *n*-heptane (40 ml) was introduced under CO_2 in a stainless-steel autoclave; CO_2 was then compressed up to 40 atm at room temperature. The autoclave was maintained at 5°C without stirring for a week. Then the gas was vented and the glass container was extracted from the autoclave: the blue crystals suspended in the liquid phase were collected by filtration under CO_2 (0.4 g, 31%). Satisfactory analytical results were obtained and the IR spectrum in PCTFE was superimposable to that of the product obtained according to prodecure a).

IR spectroscopic evidence of equilibrium (13) in solution has been obtained in the following manner.

$$\underset{\mathbf{1}}{Ti_2(O_2CNiPr_2)_6} + NH_2iPr_2[O_2CNiPr_2] \rightleftharpoons \underset{\mathbf{3}}{NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]} \qquad (13)$$

The neutral dimer **1** (0.09 mmol) was dissolved in *n*-heptane (10 ml) under nitrogen and the IR spectrum was measured. The solution was then saturated with CO_2 at atmospheric pressure: the solution, before and after saturation with CO_2, showed a band at 1580 cm^{-1} typical of **1**. The introduction of diisopropylamine (0.37 g; 3.66 mmol) caused some colour change and the IR spectrum measured after 1 h stirring at room temperature showed a new band at 1610 cm^{-1} due to the ionic carbamato complex **3**. Furthermore, a solution of **3** (0.15 g; 0.12 mmol) in *n*-heptane under nitrogen, aftet 30 min stirring at room temperature, showed the presence of the 1580 cm^{-1} band, in addition to the original one at 1610 cm^{-1}. The latter disappeared after 1 h stirring and it could not be restored by substituting the gas with CO_2[10].

X-Ray Analysis of $NH_2iPr_2[Ti_2(O_2CNiPr_2)_7]$ (3): A suitable crystal of dimensions (mm) 0.26 × 0.49 × 0.73 was selected and then mounted in a glass capillary for atmosphere protection. The subsequent diffraction experiment was carried out at room temperature on a Siemens AED single-crystal computer-controlled diffractometer. The setting angles of 20 intense reflections ($19 < \Theta < 33°$) were used to determine by least-squares fit accurate cell parameters and their standard deviations. Crystal data are as follows[26]: $C_{55}H_{114}N_8O_{14}Ti_2$, $M = 1207.4$, monoclinic, $a = 23.741(9)$, $b = 22.730(7)$, $c = 13.359(6)$ Å, $\beta = 99.06(4)°$, $U = 7119(5)$ Å^3, $Z = 4$, $D_c = 1.126\,g \cdot cm^{-3}$; Cu-$K_\alpha$ radiation ($\lambda = 1.54178$ Å); μ(Cu-K_α) = 23.79 cm^{-1}, $F(000) = 2624$. The data collection was performed with the Cu-K_α radiation by the Θ-2Θ scan technique, within the limits $3 < \Theta < 60°$. Inspection of systematic absences uniquely determined the space group as $P2_1/a$. A total of 11818 reflections in the quadrant $+h+k+l$ were collected without any significant change in the intensity of a standard reflection which was periodically measured during the experiment. After removal of redundant data and space group forbidden data, the number of unique data was 10730, of which 4643 were considered observed at the $I > 2\sigma(I)$ level. The intensities were measured with the profile technique and corrected for Lorentz and polarization effects. The positions of the two independent titanium atoms were determined by using Patterson calculations and the remainder of the structure was located through an alternating sequence of least-squares cycles and difference Fourier syntheses. The full-matrix least-squares refinement with individual isotropic thermal parameters for all non-hydrogen atoms led to $R = 0.1518$. Conversion to anisotropic parameters gave $R = 0.0924$.

At this point a scan of the observed data indicated that the weaker reflections were badly measured, showing large values of $F_o - F_c$. So, it seemed reasonable to adopt for the unobserved reflections the more stringent rejection criterion of $F_o < 3\sigma(F_o)$. Continuing refinement omitting 877 reflections together with further 17 reflections suffering for a poor agreement between F_o and F_c reduced R to 0.0805. This rather high value may be the result of the poor quality of the crystal, which is probably contaminated by its twins as well as of its weak diffracting power. It can be added that, after the structure determination had been completed, a further data set was collected with Mo-K_α radiation by using a different sample, but the data from this crystal could not be refined below an R factor of 0.1045. Because of the large number of variables, the atoms were subdivided into four groups, which were refined in alternate cycles. The hydrogen atoms were ignored. The data-to-variable ratio was 5.3:1. Attempts to correct for absorptions were made, but did not lead to appreciable results. The data were weighted with $w = 1/[\sigma^2(F_o) + 0.011297\,F_o^2]$ in the last stages of refinement. Peaks of the final difference Fourier map were not greater than 0.42 e Å^{-3} and were located near the propyl carbon atoms. Analytical expressions for the scattering factors were those of SHELX-76[27], except those for titanium which were taken from ref.[28]. Real and imaginary anomalous dispersion corrections to the atomic scattering factors were included[28]. The final values of the positional parameters are published[4]; selected bond distances and angles are in Table 2[29].

Tris(diethylcarbamato)titanium, $[Ti(O_2CNEt_2)_3]_n$ (5): Anhydrous $TiCl_3$ (5.99 g; 38.8 mmol) in *n*-heptane (150 ml) was treated with diisopropylamine (35.27 g; 349 mmol) under CO_2 at atmospheric pressure ($p_{CO_2} + p_{solvent}$). After 8 h stirring at 80°C, the suspension was filtered and the solvent and the excess of diisopropylamine were removed under reduced pressure. The residue, consisting of $Ti_2(O_2CN\textit{i}Pr_2)_6$ (**1**), was added of *n*-heptane (50 ml) and diethylamine (25.40 g; 348 mmol) under CO_2 at atmospheric pressure. An immediate formation of a pale blue precipitate was observed upon addition of diethylamine. The mixture was stirred for 12 h at room temperature. The solid was then filtered unter CO_2, washed with *n*-heptane, and dried under reduced pressure (6.2 g, 40% yield with respect to $TiCl_3$). The product is nearly insoluble in all common organic solvents, including CH_3CN and CH_2Cl_2; it is soluble in hot DMF with formation of a blue solution. It is readily oxidized by air and promptly decomposed by diluted sulfuric acid with quantitative evolution of CO_2. The IR spectrum of the product as PCTFE mull is in Table 1. NEt_2 was determined as amine after hydrolysis.

$C_{15}H_{30}N_3O_6Ti$ (396.3)	Calcd.	CO_2 33.3 NEt_2 55.3 Ti 12.1
	Found	CO_2 32.3 NEt_2 55.8 Ti 12.1

An attempt to prepare **5** from **1** (0.40 g; 0.42 mmol) in *n*-heptane (20 ml) in the presence of a large excess of diethylamine (3.51 g; 48.1 mmol) *under nitrogen* failed (about 12 h stirring at room temperature).

Diethylammonium Tris-μ-(diethylcarbamato-O,O')-bis(diethylcarbamato-O)bis(diethylcarbamato-O,O')dititanate (**4**): The filtrate from the preparation described above of compound **5** was evaporated to dryness, *n*-heptane (20 ml) was then added to the residue and the resulting solution was kept under CO_2 at 5°C for a week. The deep blue crystalline **4** precipitated and was collected by filtration and dried in vacuo (1.6 g, 8.5%). The compound is more soluble than **5** in saturated hydrocarbon solvents and is rapidly decomposed by air. An IR spectrum of the product as PCTFE mull is in Table 1. The formation of **4** was also evidenced spectroscopically by treating a suspension of **5** with $NHEt_2$ and CO_2 at atmospheric pressure in *n*-heptane.

$C_{39}H_{82}N_8O_{14}Ti_2$ (982.9	Calcd.	CO_2 31.3 Ti 9.7
	Found	CO_2 31.3 Ti 9.7

Bis-μ-(diisopropylcarbamato-O,O')-bis(diisopropylcarbamato-O)bis(diisopropylcarbamato-O,O')divanadium (**2**)

a) *From VCl_3:* Anhydrous VCl_3 (8.05 g; 51.2 mmol) was suspended in *n*-heptane (150 ml); diisopropylamine (46.5 g; 460 mmol) was then added to the solution under CO_2 at atmospheric pressure and the mixture was stirred for 8 h at 80°C. The mixture, which consisted of a brown liquid phase and a colourless solid ($NH_2\textit{i}Pr_2Cl$) was filtered under nitrogen. The filtered solution was evaporated to dryness and the brown residue was found to be analytically pure **2**. A molecular mass determination established that the compound is dimeric in benzene solution. The product is well soluble in most organic solvents and it is oxidized readily by air and decomposed by moisture and by diluted sulfuric acid with quantitative evolution of carbon dioxide. Magnetic susceptibility $\chi_M^{corr} = 3070 \times 10^{-6}$ $cm^3 \cdot mol^{-1}$ (diamagnetic correction $= -320 \times 10^{-6} cm^3 \cdot mol^{-1}$), corresponding to $\mu_{eff} = 2.70$ BM. The IR spectrum of **2** in C_2Cl_4 solution is in Table 1.

$C_{42}H_{84}N_6O_{12}V_2$	Calcd.	CO_2 27.3 V 10.5 mol. mass 967.0
	Found	CO_2 27.0 V 10.5 mol. mass 932

b) *From $VCl_3(THF)_3$:* The adduct $VCl_3(THF)_3$ (2.47 g; 6.61 mmol) in *n*-heptane (100 ml) was treated with diisopropylamine (6.00 g; 59.4 mmol) under CO_2 at atmospheric pressure for 12 h at room temperature. After filtration, the carbamato complex **2** was obtained as analytically pure product (2.2 g, 68%) by evaporation to dryness of the solution under reduced pressure.

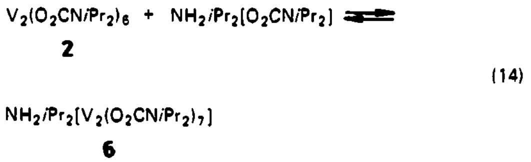
Diisopropylammonium Tris-μ-(diisopropylcarbamato-O,O')-bis(diisopropylcarbamato-O)bis(diisopropylcarbamato-O,O')divanadate (**6**)

a) *From VCl_3:* A solution of diisopropylamine (28.7 g; 284 mmol) in *n*-pentane (150 ml) was syphoned into a stainless-steel autoclave containing VCl_3 (4.97 g; 31.6 mmol). Carbon dioxide was then pressurized at 40 atm at room temperature and the autoclave content was stirred for 2 days at room temperature. The reaction mixture was discharged from the autoclave by the technique specified above for the titanium complex **3** and filtered under carbon dioxide. The brown-green solution was evaporated to dryness under reduced pressure and the residue was treated with *n*-pentane (30 ml) under CO_2. The suspension was filtered and the green complex **6** was collected by filtration and dried in vacuo (1.6 g, 8.1%). The compound is decomposed by air and moisture, while diluted sulfuric acid gave quantitative evolution of combined carbon dioxide. Magnetic susceptibility: $\chi_M^{corr} = 3440 \times 10^{-6} cm^3 \cdot mol^{-1}$ (diamagnetic correction $= -415 \times 10^{-6} cm^3 \cdot mol^{-1}$), corresponding to $\mu_{eff} =$ 2.86 BM (at 20.0°C).

$C_{55}H_{114}N_8O_{14}V_2$ (1213.4)	Calcd.	CO_2 25.4 V 8.4
	Found	CO_2 25.3 V 8.4

b) *From* **2**: A solution of $V_2(O_2CN\textit{i}Pr_2)_6$ (1.37 g; 1.42 mmol) and diisopropylamine (0.57 g; 5.6 mmol) in *n*-pentane (50 ml) was introduced by suction into a stainless-steel autoclave (110 ml capacity). Carbon dioxide was then compressed to 40 atm at room temperature and the content of the autoclave was then stirred for 24 h at room temperature; the gas was vented and the solution transferred into a flask and evaporated to dryness under reduced pressure. By addition of *n*-pentane (10 ml) a suspension was obtained from which compound **6** was recovered by filtration and drying in vacuo (0.6 g, 33%).

Spectroscopic (IR and VIS) evidences of the interconversion (14) was obtained in the following manner.



$$\underset{\mathbf{2}}{V_2(O_2CN\textit{i}Pr_2)_6} + NH_2\textit{i}Pr_2[O_2CN\textit{i}Pr_2] \rightleftharpoons \underset{\mathbf{6}}{NH_2\textit{i}Pr_2[V_2(O_2CN\textit{i}Pr_2)_7]} \qquad (14)$$

By operating under nitrogen, compound **2** (0.12 g; 0.12 mmol) was dissolved in 12 ml of *n*-heptane. The IR spectrum showed the typical band of the dimeric carbamato complex at 1590 cm^{-1}. Nitrogen was evacuated from the flask and CO_2 at atmospheric pressure was introduced. No change of the IR spectrum was noted. Upon addition of diisopropylamine (0.1 g; 1.0 mmol), a new band at 1605 cm^{-1} due to the $[V_2(O_2CN\textit{i}Pr_2)_7]^-$ anion was observed. The **2** ⇄ **6** interconversion can be evidenced by the change of colour of the solution: starting from **2** the initial brown colour of the solution turned gradually green upon addition of the amine under carbon dioxide. The visible spectrum, initially showing bands at 430, 490 and 680 nm, was substantially modified both in the intensity and in the wavelength.

Tris(diethylcarbamato)vanadium, $[V(O_2CNEt_2)_3]_n$ (**7**): Anhydrous VCl_3 (5.10 g; 32.4 mmol) was added to a solution of diisopropylamine (29.5 g; 292 mmol) in *n*-heptane (150 ml), the mixture was saturated with carbon dioxide at atmospheric pressure and stirred at room temperature for 24 h while the internal pressure of the flask was maintained at the original value by connecting it to the CO_2 supplier from time to time. The mixture was then filtered and the filtrate was evaporated to dryness under reduced pressure. The solid residue was added to *n*-heptane (50 ml) and the brown solution, after being filtered under nitrogen, was treated with diethylamine (21.3 g; 292 mmol) under carbon dioxide for about 12 h at room temperature. A green solution and the green $[V(O_2CNEt_2)_3]_n$ were obtained, the latter as a solid in suspension, which was collected by filtration and then dried in vacuo (6.0 g, 46%). The compound is substantially insoluble in the common organic solvents, it is promptly hydrolized upon contact with moisture and it is decomposed by diluted sulfuric acid with quantitative evolution of the combined carbon dioxide. Magnetic susceptibility $\chi_V^{corr} = 2990 \times 10^{-6}\ cm^3 \cdot mol^{-1}$ (diamagnetic correction $= -220 \times 10^{-6}\ cm^3 \cdot mol^{-1}$), corresponding to $\mu_{eff} = 2.67$ BM (at 22.6°C). The IR spectrum as PCTFE mull is in Table 1.

$C_{15}H_{30}N_3O_6V$ (399.4) Calcd. CO_2 33.1 V 12.7
Found CO_2 32.6 V 12.6

Reaction of **1** *with HCl, Equation (8):* By operating under nitrogen, $Ti_2(O_2CN\mathit{i}Pr_2)_6$ (1.15 g; 1.20 mmol) was dissolved in *n*-heptane (50 ml) and then treated with dry HCl. The treatment with HCl was repeated several times. Upon contact with the reagent, a blue precipitate was observed, which rapidly turned light-brown, while the solution became substantially colourless. The solid was filtered and dried in vacuo (0.9 g, 68.5% yield of $(NH_2\mathit{i}Pr_2)_3[TiCl_6]$ based on initial titanium). The light-brown solid was extremely reactive to air and moisture and dissolved in acetonitrile to give a colourless precipitate ($NH_2\mathit{i}Pr_2Cl$) and a blue solution whose visible spectrum (λ_{max} = 670 nm, 14900 cm^{-1}) was assigned to the $[TiCl_4(MeCN)_2]^-$ anion[19a].

$C_{18}H_{48}Cl_6N_3Ti$ (567.2) Calcd. Cl 37.5 Ti 8.4
Found Cl 37.4 Ti 8.3

Reaction of **2** *with HCl, Equation (8):* Under conditions similar to those in the reaction with **1**, the vanadium(III) complex **2**, (1.05 g; 1.09 mmol) in 50 ml of *n*-heptane was treated with dry HCl. The ionic $(NH_2\mathit{i}Pr_2)_3[VCl_6]$ was isolated as a pink-violet solid (73% yield). By treatment with acetonitrile, a colourless precipitate of $NH_2\mathit{i}Pr_2Cl$ and a yellow-brown solution were obtained, the latter showing absorption bands at 710 and 490 nm (14000 and 20400 cm^{-1}, respectively), in agreement with the spectrum reported in the literature[19b] for the $[VCl_4(MeCN)_2]^-$ anion.

$C_{18}H_{48}Cl_6N_3V$ (570.3) Calcd. Cl 37.3 V 8.9
Found Cl 36.8 V 8.8

Reaction between **1** *or* **2** *and Acetylacetone, Equation (10):* Acetylacetone (1.21 g; 12.1 mmol) was added under nitrogen to a solution of **1** (1.93 g; 2.01 mmol) in *n*-heptane (25 ml). A fast gas evolution occurred upon stirring at room temperature and was over in about 0.5 h. Solvent was removed under reduced pressure and the solid residue was sublimed at about 150°C/0.05 Torr (1.0 g, 70%). The product was analytically identified as $Ti(C_5H_7O_2)_3$ and found to have an IR spectrum superimposable to that of an authentic sample prepared according to a known procedure[30]. The reaction between **2** and acetylacetone was carried out in a similar manner with analogous results, the product of the reaction being analytically consistent with and spectroscopically identical to $V(C_5H_7O_2)_3$[31].

Reaction of **1** *with p-Benzoquinone, Equation (11):* By operating under nitrogen, 50 ml of a solution of *p*-benzoquinone (0.63 g; 5.83 mmol) in 20 ml of toluene was slowly added to a solution of **1** (1.40 g; 1.46 mmol) in 30 ml of the same solvent. The initially blue solution of the titanium complex turned deep red. Addition of *n*-heptane (20 ml) precipitated the red adduct $Ti_2(O_2CN\mathit{i}Pr_2)_6C_6H_4O_2$ (0.9 g; 60.5%). This compound is rapidly hydrolized in air, it is slightly soluble in hydrocarbon solvents, well soluble in tetrahydrofuran. The IR spectrum (PCTFE mull) has bands at 1550 vs, 1485 s, 1380 m and 1355 vs cm^{-1}.

$C_{48}H_{88}N_6O_{14}Ti_2$ (1069.1) Calcd. C 53.9 H 8.3 N 7.9
Found C 53.4 H 8.2 N 7.7

Reaction of **1** *with 9,10-Phenanthrenequinone, Equation (12):* By operation under nitrogen, the solution of **1** (0.85 g; 0.88 mmol) in *n*-heptane (10 ml) was added dropwise to a suspension of 9,10-phenanthrenequinone (0.18 g; 0.87 mmol) in the same solvent (20 ml). The violet adduct $Ti_2(O_2CN\mathit{i}Pr_2)_6C_{14}H_8O_2$ precipitated: it was recovered by filtration and dried in vacuo (0.6 g, 58%). The product is moderately soluble in hydrocarbons. The IR spectrum (PCTFE mull) in the 1600 – 1350 cm^{-1} region has bands at 1570 sh, 1550 s, 1535 s, 1490 vs, 1450 sh, 1390 m and 1360 vs cm^{-1}. As nujol mull, below 1350 cm^{-1}: 1295 m, 1260 w, 1200 m, 1160 s, 1075 m, 1055 m, 1030 m, 970 w, 930 w, 900 w, 870 w, 815 m, 790 m, 750 m, 720 m, 675 w and 615 s cm^{-1}.

$C_{56}H_{92}N_6O_{14}Ti_2$ (1169.2) Calcd. CO_2 22.6 Ti 8.2
Found CO_2 22.1 Ti 8.2

CAS Registry Numbers

1: 107440-47-1 / **2**: 107440-46-0 / **3**: 106879-07-6 / **4**: 106879-09-8 / **5**: 106912-82-7 / **6**: 106879-11-2 / **7**: 106912-80-5 / $(NH_2\mathit{i}Pr_2)_3[TiCl_6]$: 107440-48-2 / $(NH_2\mathit{i}Pr_2)_3[VCl_6]$: 107440-49-3 / $Ti(C_5H_7O_2)_3$: 14284-96-9 / $V(C_5H_7O_2)_3$: 13476-99-8 / $Ti_2(O_2CN\mathit{i}Pr_2)_6C_{14}H_8O_2$: 107452-91-5 / $Ti_2(O_2CN\mathit{i}Pr_2)_6C_6H_4O_2$: 107452-92-6 / $NH\mathit{i}Pr_2$: 108-18-9 / CO_2: 124-38-9 / $TiCl_3(THF)_3$: 18039-90-2 / $NHEt_2$: 109-89-7 / $VCl_3(THF)_3$: 19559-06-9 / $C_6H_4O_2$: 106-51-4 / $C_{14}H_8O_2$: 84-11-7

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