Preparation of New Dialkylamido Complexes of Metals of the Titanium and Vanadium Triads Stabilised by Terdentate Chelating Ligands; *X*-ray Structure of $Cl_2VN(CH_2CH_2NEt_2)_2$

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The use of chelating amido ligands enables the preparation of a range of new tractable ternary derivatives of electropositive transition metals including unusual oxidation states of previously poor accessibility for compounds of this nature.

Dialkylamido complexes of metals in the Ti and V triads are common and readily prepared,[1] especially in their higher oxidation states. Complexes containing multidentate amido ligands are, however, rare. A few examples are known with bidentate ligands but for ligands containing three or more donors, the only reported examples[2] are those of hybrid amidophosphines.

As part of a project to study organometallic compounds of electropositive transition metals stabilised by chelating multidentate ligands, we have been investigating the chemistry of group IV and V transition metals with the terdentate amido ligand $-N(CH_2CH_2NEt_2)_2$ (L, derived from 3,9-diethyl-3,6,9-triazaundecane[3]). Herein we present some preliminary results on readily prepared amido metal halide complexes of Ti, Zr, V, and Nb† and the *X*-ray crystal structure of $Cl_2VN(CH_2CH_2NEt_2)_2$, only the second example of a crystallographically characterised dialkylamidovanadium complex and the first one containing other anionic ligands available for substitution and other transformations.

For the titanium complex, the e.s.r. spectrum is consistent

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† All the compounds mentioned here are represented in Scheme 1. They are crystalline, air-sensitive, soluble in hydrocarbons and other non-polar solvents and satisfactory analytical data have been obtained. Elemental analyses (C, H, and N) were obtained from Butterworth Laboratories Ltd., Teddington, U.K.

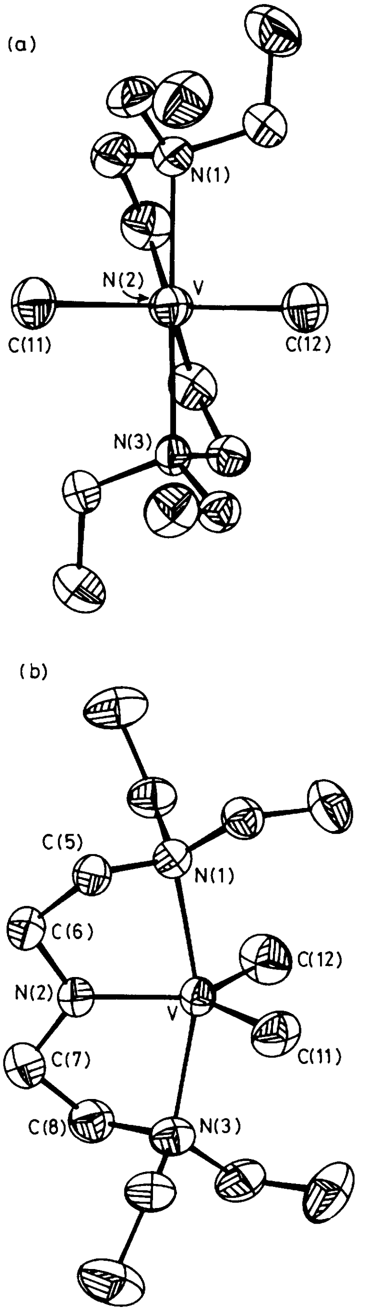
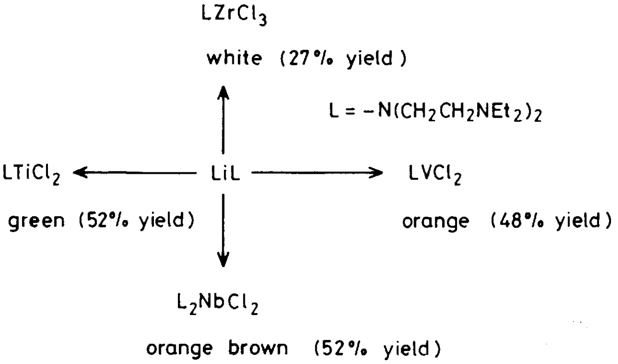


Figure 1. Two views of the structure of $Cl_2VN(CH_2CH_2NEt_2)_2$. Selected bond angles: Cl(2)–V–Cl(1) 123.1, N(1)–V–Cl(2) 94.9(2), N(2)–V–Cl(2) 119.5(2), N(3)–V–Cl(1) 96.1(2), N(1)–V–Cl(1) 94.0(2), N(2)–V–Cl(1) 117.4(2), N(3)–V–Cl(2) 93.6(2), N(3)–V–N(2) 80.3(2), N(3)–V–N(1) 160.5(1), C(6)–N(2)–V 121.2(3), C(7)–N(2)–V 121.7(3), C(5)–N(1)–V 98.1(3), C(8)–N(3)–V 98.6(2)°; Selected bond lengths: V–Cl(1) 2.308(3), V–Cl(2) 2.308(3), V–N(1) 2.244(4), V–N(2) 1.834(4), V–N(3) 2.241(4), N(2)–C(6) 1.461(4), N(2)–C(7) 1.449(4), N(3)–C(8) 1.492(4), N(1)–C(5) 1.491(4) Å.

with a d^1 electronic configuration.[‡] No nitrogen super-hyperfine coupling was observed. The magnetic susceptibility in the solid state is also consistent with a d^1 configuration (μ_{eff} 1.76 μ_B). The mass spectrum[§] displays a molecular ion for the monomeric species and the compound is monomeric in solution (cryoscopy[¶]).



Scheme 1. The new compounds were prepared by addition of toluene solutions of LiL to cooled (−78 °C) suspensions of the corresponding metal halide (Zr in toluene) or metal halide tetrahydrofuranate (Ti, V, Nb in tetrahydrofuran) in stoicheiometric ratios, followed by stirring at ambient temperature (24 h). The yields given are of isolated recrystallised (petroleum, −20 °C), analytically pure materials based on metal halide. For the Zr, V and Nb compounds the crude yields were considerably higher.

The diamagnetic zirconium complex is monomeric in solution (cryoscopy) but no molecular ion is observed in the mass spectrum unlike in the spectra of the titanium and vanadium compounds presented here. The structure of the compound is uncertain and is under investigation.

The niobium compound is a monomeric (cryoscopy), paramagnetic material (μ_{eff} 1.56 μ_B). The e.s.r. spectrum is consistent with a d^1 species with a ten line hyperfine coupling to ^{93}Nb ($I = 9/2$). No super-hyperfine coupling to nitrogen was observed. The bis-ligand complex is formed even when a deficiency of LiL is added to the metal halide, although varying amounts of green crystals are sometimes isolated irrespective of reaction conditions. Attempts are being made to identify this material.

The highly crystalline vanadium complex is also monomeric (cryoscopy, mass spectroscopy). The d^2 paramagnetic species (μ_{eff} 2.55 μ_B) exhibits no e.s.r. spectrum at room temperature or at −110 °C (in solution, glass, or the solid state). Suitable crystals for *X*-ray crystallography were obtained from light petroleum and sealed in glass capillaries. The structure is of a distorted trigonal bipyramidal vanadium atom with the amido nitrogen and two chlorine atoms in the equatorial plane.[††] The amido nitrogen atom is trigonal planar indicating π-bonding to the vanadium(III) atom. The vanadium atom has, then, 14 electrons in its valence shell. The planarity of the central

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[‡] Magnetic resonance spectroscopy for the compounds discussed here will be discussed in detail in a full paper. For Cl_2TiL, $g = 1.96$ and for Cl_2NbL_2, $g = 1.92$.

[§] Molecular ions were observed for Cl_2TiL and Cl_2VL at 334 and 336 a.m.u., respectively.

[¶] Cryoscopic molecular weights were measured in benzene.

[††] *Crystal Data:* $C_{12}H_{28}Cl_2N_3V$, $M = 336.22$ orthorhombic space group *Pbca*, $a = 13.747(4)$, $b = 18.850(4)$, $c = 13.145(2)$ Å, $U = 3406.3$ Å^3, $Z = 8$, $D_c = 1.310$ g cm^{-3}, μ(Mo-K_α) 8.24 cm^{-1}, $F(000) = 1424$. 3396 reflections measured on a CAD4 diffractometer with graphite-monochromated Mo-K_α radiation, ω/2θ scan mode, 3001 unique, 2263 observed data, $[I > 1.5\sigma(I)]$; $R = 0.033$, $R_w = 0.034$, $w = [\sigma^2(F) + 0.00005F_o^2]$, non-hydrogen atoms anisotropic, hydrogens free but with group U_{iso} values; 249 parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

nitrogen atom [N(2)] can be seen clearly in Figure 1(a) where N(2) eclipses the vanadium atom.

The alternative view of the structure in Figure 1(b) displays more appropriately the co-ordination geometry around vanadium. The distortion from trigonal bipyramidal geometry may be viewed as a result of the steric requirements of the two chloride ligands and the bite angle at vanadium of the five-membered N–N chelate rings being less than 90° as expected. Trigonal bipyramidal vanadium(III) amino complexes with the anionic ligands in the equatorial plane and amino ligands in axial positions are precedented in the structure of $Cl_3V(NMe_3)_2$.[4] Indeed this example compares favourably with our own, having an average V–Cl bond length of 2.238 Å and an average V–N bond length of 2.213 Å. The only previously reported vanadium(III) dialkylamido V–N bond length is 1.910(5) Å in $V[N(SiMe_3)_2]_3$.[5] This is significantly longer than the amido V–N bond length in our compound [1.834(4) Å] again indicating M–N multiple bonding. In both cases the amido nitrogen atoms are planar within experimental error.

We are presently investigating substitutions and other reactions of these compounds and the indications are that they are a rich source of reactive organometallic and other products. Details of these studies will be published separately, along with more complete spectroscopic characterisation of the zirconium and other complexes.

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