DALTON

Preparation and characterization of dialkylcarbamato derivatives of niobium and tantalum†

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The mononuclear compounds $M(O_2CNR_2)_n$ (M = Nb or Ta, R = Et, $n = 5$; M = Nb, R = Et or Pr^i, $n = 4$) have been prepared by treating the corresponding metal chlorides or their adducts, *i.e.* $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran), with CO_2–NHR_2 in toluene. The molecular structures of $Ta(O_2CNEt_2)_5$ and $Nb(O_2CNEt_2)_4$ have been solved by X-ray diffraction methods. The tantalum atom is eight-co-ordinated, being surrounded by three bi- and two mono-dentate diethylcarbamato groups, in a slightly distorted square-antiprismatic arrangement. The niobium compound consists of mononuclear units, where the niobium atom is dodecahedrally co-ordinated to eight oxygen atoms of four bidentate diethylcarbamate ligands. The reaction of $[NbCl_3(dme)]$ (dme = 1,2-dimethoxyethane) with CO_2–NHR_2 (R = Et or Pr^i) gave the corresponding dialkylcarbamates; on the basis of spectroscopic and magnetic data these niobium(III) derivatives are suggested to be dinuclear with bridging and terminal carbamato groups. Improved yields of $[M_2(\eta^6\text{-}C_6Me_6)_2Cl_4]$ (M = Nb or Ta), which are the precursors to the dialkylcarbamates of niobium(II) and tantalum(II), have been obtained. The $[M_2(\eta^6\text{-}C_6Me_6)_2Cl_4]$–$CO_2$–$NHPr^i_2$ system (M = Nb or Ta) in toluene gave metal(II) dialkylcarbamato complexes of analytical composition $M(\eta^6\text{-}C_6Me_6)(O_2CNPr^i_2)_2$: these substantially diamagnetic compounds are suggested to be dinuclear with bridging carbamato groups, a metal–metal bond and axially co-ordinated hexamethylbenzene.

Earlier work from these Laboratories had shown that in most cases dialkylcarbamato complexes of transition elements of general formula $[\{M(O_2CNR_2)_n\}_m]$ are obtained from the reaction of an anhydrous metal halide with carbon dioxide and the secondary amine in a hydrocarbon solvent,[1] and several complexes of this class, with main group and transition d or f elements have been reported.

Recently we became interested in studying the structural and chemical properties of homoleptic dialkylcarbamato complexes of a given metal as a function of the oxidation state. The purpose is to verify the influence of the oxidation state on: (*a*) the reactivity of the carbamato complexes; (*b*) the nuclearity of the system; (*c*) the co-ordination geometry around the metal; (*d*) the compatibility of the O_2CNR_2 ligand with other co-ordinated groups. Among the transition elements, niobium and tantalum appeared to be appropriate candidates for our purpose because they have stable oxidation states, among the positive ones, ranging from V to II, and the highest oxidation state is not strongly oxidizing. Further stimulus was the observation that, generally speaking, only a limited number of homoleptic compounds of niobium and tantalum with bidentate ligands are known,[2] especially in low oxidation states. A survey of the literature for the more common bidentate ligands shows that, as far as the oxidation state V is concerned, the pentakis(dimethylcarbamato) complexes of niobium and tantalum have been reported by Chisholm and co-workers,[3] being prepared by carbonation of the corresponding dialkylamides: an X-ray diffractometric experiment[3a] has shown the niobium complex $Nb(O_2CNMe_2)_5$ to be mononuclear with two mono- and three bi-dentate carbamato groups. Partial carbonation of the dimethylamido complexes of niobium(V) and tantalum(V) leads[3b,4] to non-homoleptic compounds of formula $[M(NMe_2)_2(O_2CNMe_2)_3]$ (M = Nb or Ta); for the tantalum compound, an X-ray diffractometric experiment[4a] showed the central metal atom to be seven-co-ordinate, with two bi- and one mono-dentate carbamato groups. Moreover, alkylcarbamato derivatives of tantalum(V) have been prepared[4b] by reaction of $[Ta(NMe_2)_4R]$ (R = Bu^t, Pr^i or CH_2SiMe_3) with carbon dioxide. The dialkyldithiocarbamates $Ta(S_2CNR_2)_5$[5] have also been reported, obtained by treating $Ta(NR_2)_5$ with CS_2[5a] or Ta_2Cl_{10} with $Na(S_2CNR_2)$.[5b] In the IV oxidation state, a few eight-co-ordinate chelate complexes of both niobium and tantalum are known, particularly M(β-diketonate)$_4$, normally with the metal having an approximately square-antiprismatic geometry.[6] A serious drawback to the preparation of classical co-ordination compounds of niobium and tantalum in oxidation states lower than IV is the availability of appropriate metal precursors. To the best of our knowledge, the only such homoleptic compound is $[Ta(dbm)_3]$ (dbm = dibenzoylmethanate).[7]

In this paper we describe the preparation and properties of $M(O_2CNR_2)_n$, (M = Nb or Ta, $n = 5$, R = Et; $n = 4$ or 3, R = Et or Pr^i) and of the mixed-ligand arene–carbamato complexes with the metal in the oxidation state II, $[M_2(\eta^6\text{-}C_6Me_6)_2(O_2CNPr^i_2)_4]$ (M = Nb or Ta). The reactivity of some of the complexes is also reported.

Experimental

All operations were carried out on a conventional vacuum line using standard Schlenk-tube techniques, under an atmosphere

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† *Non-SI units employed:* Torr ≈ atm ≈ 133 Pa, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, eV ≈ 1.60×10^{-19} J, cgs units = $4\pi \times 10^{-6}$ m^3 mol^{-1}.

of prepurified argon. The reaction vessels were oven dried prior to use.

Infrared spectra were recorded with a Perkin-Elmer model FT 1725X instrument on solutions or Nujol or poly(chlorotrifluoroethylene) mulls of the compounds prepared under rigorous exclusion of moisture and oxygen. The NMR spectra {^{1}H (200 MHz), ^{13}C (50.3 MHz), reference $SiMe_4$; ^{93}Nb (48.9 MHz), reference $[NEt_4][NbCl_6]$} were recorded with a Varian Gemini 200 BB spectrometer. The X-ray powder diagrams were obtained with a Siemens D5000 instrument equipped with a germanium monochromator and operating with Cu-Kα (λ = 1.5405 Å) radiation. Magnetic susceptibility measurements were performed in the temperature range 290–70 K with a Faraday balance using $CuSO_4 \cdot 5H_2O$ as standard. For the diamagnetic correction, Pascal contributions[8] were used.

The compounds Nb_2Cl_{10} and Ta_2Cl_{10} were commercial products (Fluka), sublimed at 100–110 °C (10^{-2} Torr) before use. Aluminium chloride was sublimed (130 °C, 10^{-2} Torr) prior to use. Finely divided aluminium was a commercial product (C. Erba, Milano) used as received. The compounds $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran),[9] $[NbCl_3(dme)]$ (dme = 1,2-dimethoxyethane)[9] and $[Co(\eta^5\text{-}C_5Me_5)_2]$[10] were prepared according to the literature.

Syntheses

$Nb(O_2CNEt_2)_5$. A solution of $NHEt_2$ (6.35 g, 86.8 mmol) in toluene (25 cm^3) was treated with CO_2. When the absorption of gas had ceased the solution was cooled at *ca.* −10 °C and treated with Nb_2Cl_{10} (2.22 g, 4.1 mmol). A vigorous gas evolution occurred and the solution turned from colourless to yellow-orange. After 15 h of stirring at room temperature the reaction mixture was filtered and the colourless solid ($NHEt_2 \cdot HCl$) washed with toluene (2 × 10 cm^3). The volume of the light yellow solution was reduced to *ca.* 10 cm^3 and the residue treated with heptane (25 cm^3). The resulting solution was cooled to *ca.* −30 °C. The required compound (2.65 g) was filtered off and dried *in vacuo* at room temperature. From the solution, after partial evaporation of the solvent and cooling at *ca.* −30 °C, another crop (1.33 g) of colourless crystals was obtained to give a total yield of 3.98 g, (72%) of $Nb(O_2CNEt_2)_5$ (Found: C, 44.0; H, 7.2; CO_2, 32.6; N, 10.0; Nb, 13.9. $C_{25}H_{50}N_5NbO_{10}$ requires C, 44.5; H, 7.5; CO_2, 32.7; N, 10.4; Nb, 13.8%). $\tilde{\nu}$/cm^{-1} 1652m, 1576m-s (*sym*-$C_2H_2Cl_4$); 2970vs, 2933s, 2874s, 1666vs, 1590vs, 1494s, 1440vs, 1406s, 1380s, 1325vs [poly(chlorotrifluoroethylene)]. NMR(C_6D_6): ^{1}H, δ 0.97 (3 H, t, CH_3) and 3.16 (2 H, q, CH_2); ^{13}C-{^{1}H}, δ 13.80 (CH_3); 40.74 (CH_2), and 162.31 (O_2CN); ^{93}Nb, δ −1049 ($w_{\frac{1}{2}}$ = 7443 Hz).

$[TaCl_2(O_2CNEt_2)_3]$. A solution of $NHEt_2$ (6.64 g, 90.8 mmol) in toluene (50 cm^3) was treated with CO_2. When the absorption of gas had ceased the solution was treated with Ta_2Cl_{10} (4.98 g, 6.95 mmol) at *ca.* 20 °C. Two liquid layers were observed. After 15 h of stirring at room temperature the reaction mixture was filtered and the colourless solid ($NHEt_2 \cdot HCl$) washed with toluene (2 × 10 cm^3). Toluene (*ca.* 50 cm^3) was evaporated under reduced pressure at room temperature and the resulting biphasic liquid was added to heptane (25 cm^3). The solid which formed after 72 h of vigorous stirring at room temperature was filtered off and dried *in vacuo* at room temperature affording 5.62 g (67% yield) of $[TaCl_2(O_2CNEt_2)_3]$ as a colourless microcrystalline solid sensitive to moisture (Found:[*] Cl, 12.2; CO_2, 20.4; Ta, 31.0. $C_{15}H_{30}Cl_2N_3O_6Ta$ requires Cl, 11.8; CO_2, 22.0; Ta, 30.1%). $\tilde{\nu}$/cm^{-1} 1636m-s, 1592m, 1475s, 1424s (*sym*-$C_2H_2Cl_4$); 2971m, 2935m, 2873m, 2748w, 1631m, 1597s, 1476m, 1440s, 1381m, 1349m, 1321m, 1269m-s, 1193m-s [poly(chlorotrifluoroethylene)]. NMR(C_6D_6): ^{1}H, δ 0.90 (3 H, br, CH_3) and 3.04 (2 H, br, CH_2); ^{13}C-{^{1}H}, δ 13.62 (CH_3), 40.69 (CH_2) and 167.90 (O_2CN).

$Ta(O_2CNEt_2)_5$. A solution of $NHEt_2$ (17.65 g, 241 mmol) in toluene (150 cm^3) was placed in a glass autoclave (Büchi, Uster) and treated with CO_2. When the absorption of gas had ceased, the solution was treated with Ta_2Cl_{10} (8.1 g, 11.3 mmol). The autoclave was charged with CO_2 at a pressure of 5 atm at room temperature. In addition to the colourless precipitate of $NHEt_2 \cdot HCl$, a biphasic liquid system readily formed at room temperature. The liquid portion was converted into a homogeneous solution after stirring at 50 °C for 20 h. The maximum CO_2 pressure at 50 °C was *ca.* 6 atm. After this period the autoclave contents were filtered and the solid on the filter ($NHEt_2 \cdot HCl$) was washed with toluene (3 × 10 cm^3). The volume of the yellow solution was reduced to *ca.* 10 cm^3; after addition of heptane (50 cm^3) the resulting solution was cooled to *ca.* −30 °C. Filtration of the cold suspension afforded a colourless crystalline solid which was dried *in vacuo* and identified as $Ta(O_2CNEt_2)_5$ (12.03 g, 70% yield), a crystalline compound very sensitive to moisture (Found: C, 39.1; H, 6.6; CO_2, 28.6; N, 9.0; Ta, 23.6. $C_{25}H_{50}N_5O_{10}Ta$ requires C, 39.4; H, 6.6; CO_2, 28.9; N, 9.2; Ta, 23.8%). $\tilde{\nu}$/cm^{-1} 1662s, 1605vs (*sym*-$C_2H_2Cl_4$); 2976m, 2934m, 2876w, 2728m-w, 1651s, 1587vs, 1494vs, 1473vs, 1461vs, 1440vs, 1412s, 1380m, 1349w, 1324m, 1278vs [poly(chlorotrifluoroethylene)]. NMR(C_6D_6): ^{1}H, δ 0.98 (3 H, t, CH_3) and 3.18 (2 H, q, CH_2); ^{13}C-{^{1}H}, δ 13.53 (CH_3), 40.47 (CH_2) and 161.75 (O_2CN).

$Nb(O_2CNR_2)_4$ (R = Et or Pr^i). A solution of $NHEt_2$ (6.6 g, 90.2 mmol) in toluene (50 cm^3) was treated with CO_2. When the absorption of gas had ceased the solution was treated with $[NbCl_4(thf)_2]$ (4.01 g, 11.0 mmol). A rapid change from colourless to deep blue was observed. After 15 h of stirring at room temperature the reaction mixture was filtered and the colourless solid washed with toluene (2 × 10 cm^3). The volume of the blue solution was reduced to *ca.* 2 cm^3 and heptane (10 cm^3) was added. The solid which formed was filtered off and dried *in vacuo* at room temperature to give $Nb(O_2CNEt_2)_4$ (4.23 g, 69% yield) in the form of a deep blue microcrystalline compound very sensitive to oxygen and moisture (Found:[†] CO_2, 30.2; Nb, 17.0. $C_{20}H_{40}N_4NbO_8$ requires CO_2, 31.6; Nb, 16.7%). $\tilde{\nu}$/cm^{-1} 1567m-s, 1495m-s, 1460s (*sym*-$C_2H_2Cl_4$); 2972s, 2932s, 2873m, 1558m-s, 1505m-s, 1483m-s, 1441m-s, 1377m-s, 1348m [poly(chlorotrifluoroethylene)]. NMR (C_6D_6): ^{1}H, δ 1.00 (br, CH_3) and 2.97 (br, CH_2); ^{13}C-{^{1}H}, δ 13.20 (CH_3), 39.64 (CH_2), and 169.28 (O_2CN); ^{93}Nb, δ 1070 ($w_{\frac{1}{2}}$ = 6936 Hz). χ_m^{corr} = 10.20 × 10^{-4} cgs units (diamagnetic correction: −302 × 10^{-6} cgs units), μ_{eff} = (293 K), 1.55 μ_B. The molar susceptibility and magnetic moments in the temperature range 90–293 K are reported in Table 1.

Tetrakis(diisopropylcarbamato)niobium(IV), $Nb(O_2CNPr^i_2)_4$, was obtained in 88% yield as a blue, oxygen- and moisture-sensitive compound (Found:[†] CO_2, 25.1; Nb, 14.0. $C_{28}H_{56}N_4NbO_8$ requires CO_2, 26.3; Nb, 13.9%). $\tilde{\nu}$/cm^{-1}, 1618m-w, 1549vs, 1490s, 1460m (*sym*-$C_2H_2Cl_4$); 2967m, 2932s, 2874w, 1607w, 1544m-s; 1500m-s, 1471m-s, 1455vs, 1383vs [poly(chlorotrifluoroethylene)].

$Nb(O_2CNR_2)_3$ (R = Et or Pr^i). A solution of $NHPr^i_2$ (2.7 g, 26.7 mmol) in toluene (25 cm^3) was treated with CO_2. When the absorption of gas had ceased the solution was treated with $[NbCl_3(dme)]$ (1.18 g, 4.6 mmol). A rapid colour change to deep violet was observed. After 15 h of stirring at room

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[*] No satisfactory C, H, N analyses were obtained due to the reactivity of the compound towards moisture.

[†] No satisfactory C, H, N analyses were obtained due to the reactivity of the compound towards both oxygen and moisture.

temperature the reaction mixture was filtered and the colourless solid washed with toluene (2 × 10 cm^3). The volume of the red-violet solution was reduced to *ca.* 2 cm^3 and the residue treated with heptane (10 cm^3). The solid which formed was filtered off and dried *in vacuo* at room temperature to give $Nb(O_2CNPr^i_2)_3$ (1.88 g, 67% yield) in the form of a microcrystalline deep violet compound sensitive to oxygen and moisture (Found: C, 47.1; H, 8.1; CO_2, 24.5; N, 7.6; Nb, 18.7. $C_{21}H_{42}N_3NbO_6$ requires C, 48.0; H, 8.0; CO_2, 25.1; N, 8.0; Nb, 17.7%). $\tilde{\nu}$/cm^{-1} 1651m-w, 1548vs, 1525vs, 1495s, 1469m (*sym*-$C_2H_2Cl_4$); 2967s, 2932s, 2874m, 2718w, 1703m, 1634m-w, 1526vs, 1505vs, 1471vs, 1388s, 1358s [poly(chlorotrifluoroethylene)]. NMR: $^1H(C_6D_5CD_3)$ δ 1.29 (br, CH_3) and 3.79 (br, CH_2); ^{13}C-$\{^1H\}(C_6D_5CD_3)$, δ 20.89 (CH_3), 44.53 (CH_2) and 164.62 (O_2CN); $^{93}Nb(C_6D_6)$, δ −1032 ($w_{\frac{1}{2}}$ = 7324 Hz). $\chi_m^{corr} = 3.43 \times 10^{-4}$ cgs units (diamagnetic correction: -297.6×10^{-6} cgs units), μ_{eff}(298 K) 0.91 μ_B. The molar susceptibility and magnetic moment values in the temperature range 70–298 K are reported in Table 1.

Tris(diethylcarbamato)niobium(III), $Nb(O_2CNEt_2)_3$, was similarly obtained in 81% yield as a violet, moisture- and air-sensitive compound (Found: CO_2, 30.0; Nb, 20.8. $C_{15}H_{30}N_3NbO_6$ requires CO_2, 29.9; Nb, 21.0%). $\tilde{\nu}$/cm^{-1} 1603m-w, 1543vs, 1538vs, 1495s (*sym*-$C_2H_2Cl_4$); 2988vs, 2875m, 1603m-w, 1543vs, 1538vs, 1495vs, 1459s, 1440s [poly(chlorotrifluoroethylene)].

$[M_2(\eta^6\text{-}C_6Me_6)_2Cl_4]$ (M = Nb or Ta). A suspension in benzene (60 cm^3) of finely divided Al (2.74 g, 102 mmol), C_6Me_6 (4.14 g, 25.5 mmol) and $AlCl_3$ (2.26 g, 17 mmol) was stirred for 2 h. Solid Nb_2Cl_{10} (4.72 g, 8.73 mmol) was added and the mixture refluxed for 20 h. After cooling to room temperature, the brown suspension was treated with thf (100 cm^3) with vigorous stirring; an exothermic reaction took place with formation of a deep brown solution in the presence of unreacted aluminium. The suspension was filtered; the resulting brown solution was evaporated to dryness *in vacuo* at room temperature. The solid residue was treated with mesitylene (100 cm^3). After 15 h of stirring at room temperature the niobium(II) complex was filtered off, washed with mesitylene (5 cm^3) and heptane (2 × 10 cm^3) and dried *in vacuo* at room temperature; $[Nb_2(\eta^6\text{-}C_6Me_6)_2Cl_4]$ (3.61 g, 63% yield) was isolated as a brown microcrystalline solid sensitive to oxygen and moisture (Found: Cl, 21.5; Nb, 29.4. $C_{24}H_{36}Cl_4Nb_2$ requires Cl, 21.7; Nb, 28.5%; NMR (C_6D_6): ^1H, δ 1.64 (C_6Me_6); ^{93}Nb, δ 604 ($w_{\frac{1}{2}}$ = 820 Hz).

The brown microcrystalline tantalum analogue, $[Ta_2(\eta^6\text{-}C_6Me_6)_2Cl_4]$, was prepared similarly in 92% yield. It is moderately sensitive to oxygen and moisture (Found: C, 34.8; H, 4.5; Cl, 17.8; Ta, 43.4. $C_{24}H_{36}Cl_4Ta_2$ requires C, 34.8; H, 4.3; Cl, 17.1; Ta, 43.7%).

$[M_2(\eta^6\text{-}C_6Me_6)_2(O_2CNPr^i_2)_4]$ (M = Nb or Ta). A solution of $NHPr^i_2$ (1.3 g, 12.8 mmol) in toluene (25 cm^3) was treated with CO_2. When the absorption of gas had ceased the solution was treated with $[Nb_2(\eta^6\text{-}C_6Me_6)_2Cl_4]$ (0.98 g, 1.5 mmol). The solution became deep brown. No dihydrogen was detected in the gas phase by gas chromatography. After 12 h of stirring at room temperature the reaction mixture was filtered and the colourless solid ($NHPr^i_2$·HCl) was washed with toluene (2 × 5 cm^3). The volume of the brown solution was reduced to *ca.* 10 cm^3 and the residue treated with heptane (10 cm^3). The solid $[Nb_2(\eta^6\text{-}C_6Me_6)_2(O_2CNPr^i_2)_4]$ which separated was filtered off and dried *in vacuo* at room temperature (1.4 g, 85.7% yield) as a microcrystalline deep brown compound sensitive to oxygen and moisture (Found: CO_2, 15.6; Nb, 17.3. $C_{52}H_{92}N_4Nb_2O_8$ requires CO_2, 16.2; Nb, 17.1%). $\tilde{\nu}$/cm^{-1} 1543vs, 1538vs, 1510vs, 1470m, 1453m (*sym*-$C_2H_2Cl_4$); 2965s, 2931s, 2874m 2718w, 1544vs, 1510vs, 1505vs, 1452s, 1391s, 1361vs, 1262s [poly(chlorotrifluoroethylene)]. NMR (C_6D_6): ^1H, δ 1.20 (CH_3), 2.11 (C_6Me_6), and 3.89 (CH); ^{13}C-$\{^1H\}$, δ 16.90 $[C_6(CH_3)_6]$, 21.40 (CH_3), 46.30 (CH), 112.00 $[C_6(CH_3)_6]$ and 160.20 (O_2CN); ^{93}Nb, δ 756 ($w_{\frac{1}{2}}$ = 4347 Hz).

The tantalum analogue, $[Ta_2(\eta^6\text{-}C_6Me_6)_2(O_2CNPr^i_2)_4]$, was prepared similarly and isolated in 86% yield as a brown microcrystalline solid sensitive to oxygen and moisture (Found: CO_2, 14.6; Ta, 28.4. $C_{52}H_{92}N_4O_8Ta_2$ requires CO_2, 13.9; Ta, 28.6%). $\tilde{\nu}$/cm^{-1} 1558vs, 1549vs, 1544vs, 1538vs, 1468s (*sym*-$C_2H_2Cl_4$); 2964s, 2927s, 2873s, 1505vs (br), 1391vs, 1359vs, 1279vs [poly(chlorotrifluoroethylene)]. NMR (C_6D_6): ^1H, δ 1.26 (CH_3), 2.09 (C_6Me_6), and 3.89 (CH); ^{13}C-$\{^1H\}$, δ 17.3 $[C_6(CH_3)_6]$, 21.11 (CH_3), 45.93 (CH), 112.02 $[C_6(CH_3)_6]$ and 160.03 (O_2CN).

At 80 K both compounds have negative magnetic susceptibilities.

Reaction of $Nb(O_2CNEt_2)_5$ with $[Co(\eta^5\text{-}C_5Me_5]$. A solution of $[Co(\eta^5\text{-}C_5Me_5)_2]$ (0.39 g, 1.2 mmol) in toluene (25 cm^3) was treated with $Nb(O_2CNEt_2)_5$ (0.739 g, 1.1 mmol) at room temperature. A yellow solid in a blue-green solution formed as soon as the reagents were mixed. The reaction mixture was stirred at room temperature overnight and filtered. The solid thus obtained was washed with toluene (2 × 5 cm^3) and dried *in vacuo* at room temperature affording $[Co(\eta^5\text{-}C_5Me_5)_2][O_2CNEt_2]$·$C_6H_5Me$ (0.26 g, 53% yield) as a moisture-sensitive yellow microcrystalline solid (Found: CO_2, 8.5. $C_{32}H_{48}CoNO_2$ requires CO_2, 8.2%). $\tilde{\nu}$/cm^{-1} 1702s, 1650w, 1607s, 1542w, 1468s (*sym*-$C_2H_2Cl_4$); 2985s, 2935s, 2873s, 1681w, 1640s, 1619s, 1592m, 1556vs, 1500s, 1479s, 1466s, 1427m, 1387s, 1315s, 1269vs [poly(chlorotrifluoroethylene)]. NMR (CD_3CN): ^1H, δ 1.0 (t, CH_3), 1.65 (C_5Me_5) and 3.2 (q, CH_2); ^{13}C-$\{^1H\}$, δ 8.3 $[C_5(CH_3)_5]$, 14.3 (CH_3), 40.36 (CH_2), 95.1 $[C_5(CH_3)_5]$ and 169.29 (O_2CN).

The volume of the solution was reduced to 10 cm^3, heptane (25 cm^3) was added and the solution cooled to *ca.* −30 °C. After some days blue and yellow crystals were present which were filtered off and dried *in vacuo* at room temperature affording 0.796 g of a mixture of $Nb(O_2CNEt_2)_4$ and $[Co(\eta^5\text{-}C_5Me_5)_2][O_2CNEt_2]$ (IR spectra) which it was not possible to separate.

Crystallography

Crystals were obtained by slowly cooling solutions of $Ta(O_2CNEt_2)_5$ or $Nb(O_2CNEt_2)_4$ in heptane to *ca.* −30 °C. For both compounds the X-ray data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Crystal data and collection parameters are reported in Table 4.

$Ta(O_2CNEt_2)_5$. The data were corrected for non-linear decay. An empirical absorption correction (PSI-SCAN[11a]) was applied. The structure was solved by conventional heavy-atom methods followed by Fourier-difference syntheses. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were calculated in idealized positions with isotropic thermal parameters $B(H) = 1.3B(C)$ and included in structure-factor calculations. Refinement on F[11b] converged with 370 parameters using a statistical weighting scheme $w = 1/\sigma^2|F_o|$ to $R = 0.047$ and $R' = 0.048$ with a goodness of fit of 1.304. The atomic coordinates are given in Table 5.

$Nb(O_2CNEt_2)_4$. The structure was solved by the Patterson method (positions of the niobium and oxygen atoms) followed by Fourier-difference syntheses (positions of the carbon, nitrogen and hydrogen atoms). The atomic coordinates are given in Table 6. Full-matrix least-squares refinement was carried out first with isotropic thermal parameters for all atoms and then with anisotropic thermal parameters for all non-hydrogen atoms. An empirical absorption correction (DIFABS[12]) was applied. Refinement on F^2[11b] converged to $R = 0.0264$ with a goodness of fit of 0.999 for 230 parameters.

Table 1 Molar susceptibilities and magnetic moments of $Nb(O_2CNEt_2)_4$ and $Nb(O_2CNPr^i_2)_3$ as a function of temperature

Compound	$Nb(O_2CNEt_2)_4$		$Nb(O_2CNPr^i_2)_3$	
T/K	$10^3\chi_m^{corr}$/cgs	μ_{eff}/μ_B	$10^4\chi_m^{corr}$/cgs	μ_{eff}/μ_B
70			*	—
80			*	—
90	3.54	1.60	*	—
100	3.06	1.57		
110			1.48	0.36
115	2.83	1.62		
120				
125			3.50	0.59
130	2.61	1.66		
140			3.94	0.67
150	2.25	1.65		
160			4.78	0.78
170	1.98	1.65		
180			4.44	0.80
200	1.63	1.62	3.89	0.79
220	1.42	1.59		
230			3.65	0.82
240	1.27	1.57		
260	1.09	1.61	4.04	0.92
290				
293	1.02	1.55		
298			3.43	0.91

* Negative value.

The X-ray powder spectrum recorded on a microcrystalline sample of $Nb(O_2CNEt_2)_4$ gave a monoclinic cell having a = 14.057(1), b = 12.329(4), c = 16.799(4) Å and β = 108.98(1)°, in good agreement with the single-crystal structure.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Dialkylcarbamates of niobium(V) and tantalum(V)

The diethylcarbamato derivatives of niobium(V) were prepared by treating Nb_2Cl_{10} with a CO_2-saturated solution of a secondary amine in toluene at −8 °C [equation (1)]. The

$$Nb_2Cl_{10} + 10CO_2 + 20NHEt_2 \xrightarrow{-8\,^{\circ}C} 2Nb(O_2CNEt_2)_5 + 10[NH_2Et_2]Cl \quad (1)$$

exothermic reaction has to be carried out at low temperature in order to suppress the reduction of niobium(V) by the secondary amine. It has been observed[13] that Nb_2Cl_{10} reacts with secondary amines to give HCl and amido derivatives of niobium(IV). In the reaction between Nb_2Cl_{10} and $LiNR_2$ the extent of reduction was found to depend on the length of the linear alkyl chain, longer chains increasing the amount of reduction products.[14] In our system the product recovered from reaction (1) carried out at room temperature is coloured, suggesting the presence of some reduced niobium species.

Pure $Nb(O_2CNEt_2)_5$ is colourless, rapidly hydrolysed by moisture, and stable indefinitely under an inert atmosphere; it is soluble in aromatic hydrocarbons and slightly soluble in aliphatic ones. It is characterized by intense IR absorptions between 1666 and 1576 cm^{-1}, associated with carbamato groups,[1] similar to those reported for the methyl derivative $Nb(O_2CNMe_2)_5$.[3] The ^1H and ^{13}C NMR spectra at 20 °C are well resolved (see Experimental section) and agree with those reported for the methyl complex.[3] Furthermore, the ^{93}Nb NMR spectrum shows a broad band at δ −1049 ($w_{\frac{1}{2}}$ = 7.4 kHz), as expected for the low symmetry of the system.

The reaction of Ta_2Cl_{10} with a CO_2-saturated solution of diethylamine in toluene at room temperature is different. After filtration of the insoluble diethylammonium chloride, a biphasic liquid system, consisting of a dark orange lower layer and a yellow one, was obtained. Evaporation of the solvent and addition of heptane yielded the colourless $[TaCl_2(O_2CNEt_2)_3]$ in 67% yield [equation (2)]. The moisture-sensitive tantalum

$$Ta_2Cl_{10} + 6CO_2 + 12NHEt_2 \longrightarrow 2[TaCl_2(O_2CNEt_2)_3] + 6[NH_2Et_2]Cl \quad (2)$$

complex is well soluble in CH_2Cl_2, acetone or thf and slightly soluble in aliphatic hydrocarbons and in p-xylene or mesitylene. Two liquid layers are promptly obtained upon addition of benzene or toluene to the solid compound. The physical and spectroscopic properties of the product obtained by reaction (2) confirm $[TaCl_2(O_2CNEt_2)_3]$ to be a well defined compound rather than a mixture of chlorocarbamato complexes of tantalum(V) in the molar ratio consistent with the observed analytical composition.

The compound $[TaCl_2(O_2CNEt_2)_3]$ is characterized by two intense IR absorption bands at 1631 and 1597 cm^{-1}, assigned to mono- and bi-dentate carbamate ligands, respectively.[1] The ^1H NMR spectrum in C_6D_6 of the biphasic liquid system shows two broad signals at δ 0.90 and 3.04 due to the methyl and methylene groups of the carbamate ligand respectively. On the other hand, in CD_3CN or CD_2Cl_2 solution, well resolved ^1H and ^{13}C NMR spectra were observed with two sets of bands of approximate intensity 2:1, associated with different types of carbamate ligands, presumably bi- and mono-dentate. The ^{13}C NMR resonance for the $O_2\mathit{C}NEt_2$ carbon atom at δ 167.90 is particularly diagnostic of the dichloro derivative, and it is distinctly different from that at δ 161.75 of the corresponding group in $Ta(O_2CNEt_2)_5$, see below.

Our data suggest that, at room temperature, partial chloride substitution by $O_2CNEt_2^-$ in $TaCl_5$ occurs, thus leading to the mixed halogenocarbamato complex. A similar case of incomplete chloride substitution has been found in the reaction of anhydrous $CrCl_3$ with CO_2–$NHPr^i_2$ which led to the chlorocarbamato complex $[Cr_2Cl(O_2CNPr^i_2)_5]$.[15]

Thus, our studies qualitatively show that Nb_2Cl_{10} undergoes chloride substitution much more readily than the corresponding

Table 2 Bond distances (Å) and angles (°) in $Ta(O_2CNEt_2)_5$. Estimated standard deviations (e.s.d.s) in parentheses refer to the least significant digit

Ta–O(10)	2.102(5)	Ta–O(11)	2.141(5)
Ta–O(20)	1.968(5)	Ta–O(30)	2.147(5)
Ta–O(31)	2.093(5)	Ta–O(40)	2.143(5)
Ta–O(41)	2.126(5)	Ta–O(50)	1.968(6)
O(10)–Ta–O(11)	61.3(2)	O(31)–Ta–O(50)	93.3(2)
O(10)–Ta–O(20)	92.0(2)	O(40)–Ta–O(41)	59.8(2)
O(10)–Ta–O(30)	141.1(2)	O(40)–Ta–O(50)	134.8(2)
O(10)–Ta–O(31)	157.8(2)	O(41)–Ta–O(50)	74.9(2)
O(10)–Ta–O(40)	79.8(2)	O(10)–Ta–O(41)	81.6(2)
O(10)–Ta–O(50)	93.2(2)	O(11)–Ta–O(20)	80.8(2)
O(11)–Ta–O(30)	79.9(2)	O(11)–Ta–O(31)	141.0(2)
O(11)–Ta–O(40)	132.2(2)	O(11)–Ta–O(41)	131.7(2)
O(11)–Ta–O(50)	77.3(2)	O(20)–Ta–O(30)	79.6(2)
O(20)–Ta–O(31)	92.4(2)	O(20)–Ta–O(40)	73.6(2)
O(20)–Ta–O(41)	133.4(2)	O(20)–Ta–O(50)	151.7(2)
O(30)–Ta–O(31)	61.1(2)	O(30)–Ta–O(40)	131.8(2)
O(30)–Ta–O(41)	130.9(2)	O(30)–Ta–O(50)	79.0(2)
O(31)–Ta–O(40)	80.6(2)	O(31)–Ta–O(41)	79.6(2)

tantalum analogue. On the other hand, the reductive processes by the amine on the metal appeared to be completely suppressed: higher temperatures could therefore be explored in an attempt to obtain complete chloride substitution in Ta_2Cl_{10}.

The colourless, moisture-sensitive pentakis(diethylcarbamato)tantalum(V) was obtained in high yields by treating Ta_2Cl_{10} with a solution of diethylamine in toluene [equation (3)] at 50 °C with CO_2 under pressure (5

$$Ta_2Cl_{10} + 10CO_2 + 20NHEt_2 \xrightarrow{P_{CO_2},\ 50\ ^\circ C} 2Ta(O_2CNEt_2)_5 + 10[NH_2Et_2]Cl \quad (3)$$

atm). The NMR spectra of $Ta(O_2CNEt_2)_5$ are similar to those of the niobium(V) compound and the IR data suggest the presence of bi- (1587 cm^{-1}) and mono-dentate ligands (1651 cm^{-1}),[1] as in the case of $Nb(O_2CNEt_2)_5$ and $Nb(O_2CNMe_2)_5$.[3]

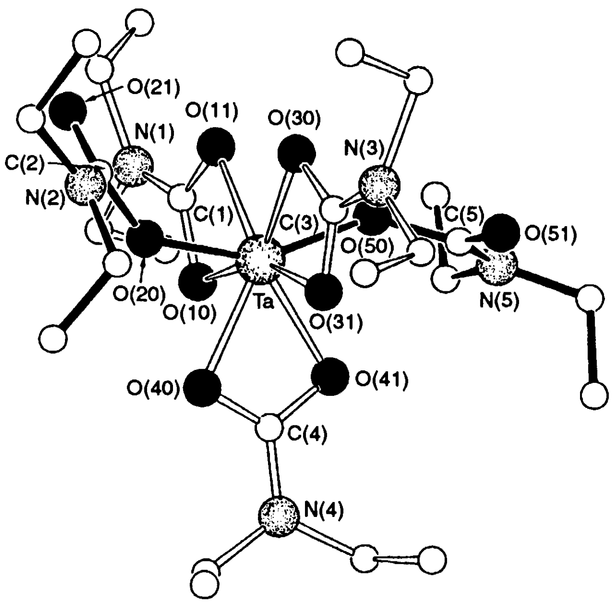


Fig. 1 A SCHAKAL view of the $Ta(O_2CNEt_2)_5$ molecule showing the atom labelling. Monodentate ligands are evidenced by solid lines connecting the bonded atoms

The ligand arrangement around the metal was established by an X-ray diffraction study on single crystals obtained from heptane solution by slow cooling. Fig. 1 shows a SCHAKAL[16] drawing of the molecule while selected bond distances and angles are reported in Table 2. The tantalum atom is eight-co-ordinate, surrounded by eight oxygen atoms of two mono- and three bi-dentate carbamate ligands in a slightly distorted square-antiprismatic geometry. The square antiprism can be visualized by dividing the eight donor atoms into two sets of four, the ligand sites being called A and B; these sites form two tetrahedra describing a dodecahedron, the distortions of which generate the square antiprism.[17] In $Ta(O_2CNEt_2)_5$ the A-type oxygen atoms are O(20), O(31), O(11) and O(41), and the B-type ones are O(30), O(40), O(10) and O(50). Two sets of 'trapezoidal atoms' can be visualized, namely O(30), O(31), O(41), O(10) and O(11), O(50), O(40), O(20). Within each set of atoms the dihedral angle φ between the two triangles is 21.7°, which is close to the value of 24.5° for an ideal square antiprism.[17] The rotation angle between the two square bases, O(20), O(30), O(31), O(40) and O(11), O(10), O(41), O(50) is 43.5°, to be compared with the ideal value of 45°.[17] The O_2CN moiety is strictly planar (mean distance of atoms from the plane: 0.004 Å). The two monodentate ligands are characterized by the atoms O(20), O(21) and O(50), O(51), the three bidentate ones by O(10), O(11); O(30), O(31) and O(40), O(41). The C–O distances within the monodentate carbamate are quite different [C(2)–O(20) 1.318(9), C(2)–O(21) 1.207(9) Å]. There is also a difference in the Ta–O distances between the mono- [1.968(6) Å] and the bi-dentate carbamate ligands, asymmetrically bonded to the metal [average Ta–O 2.107(5) and 2.144(5) Å]. A similar situation has been reported for $Nb(O_2CNMe_2)_5$,[3a] $[Ta(NMe_2)_2(O_2CNMe_2)_3]$[4a] and $[Ta(CH_2SiMe_3)_2(O_2CNMe_2)_3]$.[4b] Even though the bond lengths and angles are similar in $Ta(O_2CNEt_2)_5$ and $Nb(O_2CNMe_2)_5$, the co-ordination geometries are quite different: the latter belongs to the $P\bar{1}$ space group [$P2_1/n$ for $Ta(O_2CNEt_2)_5$] and the geometry at the metal 'does not correspond to any idealized MX_8 polyhedron'.[3a] In the tantalum derivative the angle O(20)–Ta–O(50) between the two monodentate carbamate ligands is 151.7(2)°, while in the niobium complex the angle O–Nb–O is 90.5(7)°.[3a]

Synthesis of $Nb(O_2CNR_2)_n$ (R = Et or Pr^i, n = 4 or 3)

Tetrakis(diethylcarbamato)- and tetrakis(diisopropylcarbamato)-niobium(IV) have been prepared by reaction of $[NbCl_4(thf)_2]$ with a solution of the secondary amine in toluene saturated with CO_2 at room temperature [equation (4),

$$[NbCl_4(thf)_2] + 4CO_2 + 8NHR_2 \longrightarrow Nb(O_2CNR_2)_4 + 4[NH_2R_2]Cl + 2thf \quad (4)$$

R = Et or Pr^i]. The niobium(IV) derivatives are blue, rapidly hydrolysed by moisture, sensitive to oxygen, soluble in aromatic hydrocarbons and slightly soluble in aliphatic hydrocarbons. They are characterized by intense IR bands between 1570 and 1460 cm^{-1}, associated with bidentate carbamato groups.[1] The spectra agree with those reported for corresponding compounds of Group 4 metals, namely $M(O_2CNR_2)_4$ (M = Ti, Zr or Hf; R = Et or Pr^i),[18] thus suggesting a similar mononuclear structure with bidentate carbamato groups.

In accordance with the d^1 configuration of niobium(IV), the diethylcarbamato derivative shows a magnetic moment of 1.55 μ_B at 293 K. A plot of $1/\chi_m^{corr}$ *vs.* *T*, obtained from the data of Table 1, shows that $Nb(O_2CNEt_2)_4$ obeys the Curie–Weiss law in the range 90–293 K with a Weiss constant $\theta = -17.4$ K. The magnetic moment is substantially constant in this temperature range. This again is consistent with the presence of magnetically dilute 4d^1 centres. The paramagnetism of the compound does not greatly affect the ^{1}H NMR spectrum which shows broad signals at δ *ca.* 1 and *ca.* 3 due to the methyl and methylene protons, respectively, in agreement with other dialkylcarbamato complexes.[1] Furthermore, the ^{93}Nb NMR spectrum shows a single broad band at δ −1070 ($w_{\frac{1}{2}}$ = 6.9 kHz).

An X-ray powder diagram of a microcrystalline sample of the compound before single crystals had been grown showed $Nb(O_2CNEt_2)_4$ to be isostructural with $Zr(O_2CNEt_2)_4$.[19] This observation was confirmed by X-ray diffraction analysis of single crystals of $Nb(O_2CNEt_2)_4$. Fig. 2 shows a SCHAKAL[16] plot of the molecule and Table 3 selected bond distances and angles. The central niobium atom is eight-co-ordinate surrounded by eight oxygen atoms from four diethylcarbamato groups in a slightly distorted dodecahedral arrangement. The cell contains four molecules, with the metal atom situated on the crystallographic two-fold axis of the *C*2/*c* space group. The dodecahedral co-ordination can be visualized by dividing the eight donor atoms into two sets of four A- and four B-type atoms:[17] O(1), O(1′), O(3) and O(3′) and O(2), O(2′), O(4) and O(4′). The dihedral angle φ is 7.6°, compared with that of an ideal dodecahedron (0°).[17] Another parameter which characterizes the MX_8 polyhedra is the angle δ between the normals of contiguous faces.[17] This angle is 29.5° for an ideal dodecahedron and 28.4° in the case of $Nb(O_2CNEt_2)_4$. The O_2CN groups are strictly planar and the angle between each is 84.5°. The two oxygen atoms of the bidentate carbamate ligands are asymmetrically bonded to the metal atom, average Nb–O bond distances 2.128(1) and 2.192(1) Å, values similar to those reported for the bidentate ligands of $Nb(O_2CNMe_2)_5$.[3a]

To the best of our knowledge, the only other mononuclear niobium(IV) compound with bidentate ligands characterized by X-ray diffraction methods is [Nb(dpm)$_4$] (dpm = dipivaloylmethanate = 2,2,6,6-tetramethylheptane-3,5-dionate),[6] the co-ordination geometry of which is a square antiprism. The difference in geometry between $Nb(O_2CNEt_2)_4$ and [Nb(dpm)$_4$] may be related to the bite of the bidentate ligand. Blight and Kepert[20] have investigated the dependence of the geometry of complexes on the type of ligands, and have

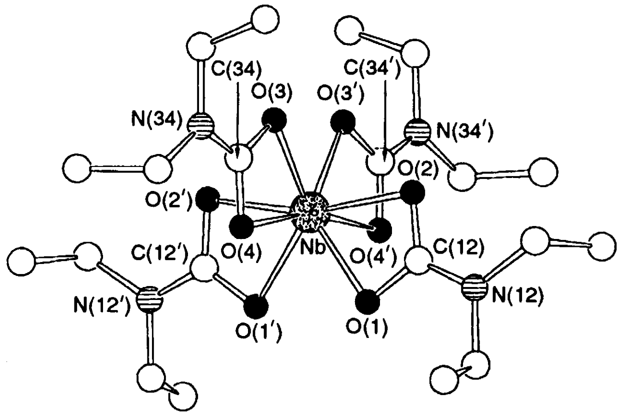


Fig. 2 A SCHAKAL plot of the $Nb(O_2CNEt_2)_4$ molecule showing the atom labelling

Table 3 Bond distances (Å) and angles (°) in $Nb(O_2CNEt_2)_4$ with e.s.d.s in parentheses

Nb–O(1)	2.135(1)	O(1)–C(12)	1.293(2)
Nb–O(2)	2.192(1)	O(2)–C(12)	1.275(2)
Nb–O(3)	2.124(1)	O(3)–C(34)	1.285(2)
Nb–O(4)	2.196(2)	O(4)–C(34)	1.281(2)
O(3′)–Nb–O(3)	74.69(7)	O(3′)–Nb–O(4)	134.76(5)
O(3)–Nb–O(1)	125.21(5)	O(3)–Nb–O(4)	60.60(5)
O(3)–Nb–O(1′)	132.88(5)	O(1)–Nb–O(4)	82.85(5)
O(1)–Nb–O(1′)	75.52(7)	O(1′)–Nb–O(4)	84.97(5)
O(3′)–Nb–O(2)	83.24(5)	O(2)–Nb–O(4)	97.98(5)
O(3)–Nb–O(2)	84.15(5)	O(2′)–Nb–O(4)	84.16(5)
O(1)–Nb–O(2)	60.65(5)	O(4)–Nb–O(4′)	164.58(7)
O(1)–Nb–O(4′)	84.97(5)	O(1′)–Nb–O(2)	135.12(5)
O(2)–Nb–O(2′)	164.12(7)		

Table 4 Crystal data and parameters of the structure determinations of $Ta(O_2CNEt_2)_5$ and $Nb(O_2CNEt_2)_4$

	$Ta(O_2CNEt_2)_5$	$Nb(O_2CNEt_2)_4$
Formula	$C_{25}H_{50}N_5O_{10}Ta$	$C_{20}H_{40}N_4NbO_8$
M	761.65	557.47
Crystal dimensions/mm	0.3 × 0.5 × 0.5	0.1 × 0.1 × 0.2
Space group	*P*2$_1$/*n* (no. 14)	*C*2/*c* (no. 15)
a/Å	13.540(2)	14.021(5)
b/Å	17.181(3)	12.157(2)
c/Å	14.973(4)	16.694(4)
β/°	101.79(2)	109.36(1)
U/Å^3	3409(1)	2684.6(1)
D_c/g cm^{-3}	1.483	1.379
T/K	255	203
μ/cm^{-1}	32.37	4.95
F(000)	1552	1172
Measured reflections	6758	3616
Absorption correction (empirical)	PSI-SCAN[11a]	DIFABS[12]
Independent reflections	4107 [$I > 1.5\sigma(I)$]	2952 [$I > 2\sigma(I)$]
Refined parameters	370	230
R	0.047	0.0264
R′ or *wR*2	0.048[a]	0.066[b]
Goodness of fit	1.304	0.999

[a] $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2|F_o|$. [b] $wR2 = [\Sigma w(\Delta F^2)^2/\Sigma w|F_o^2|^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 1.6927P]$ where $P = (F_o^2 + 2F_c^2)/3$. Details in common: $Z = 4$; λ(Mo-Kα) 0.7107 Å; 2θ 3–28°; ω scans; $R = \Sigma|\Delta F|/\Sigma|F_o|$ where $\Delta F = F_o(hkl) - F_c(hkl)$.

Table 5 Atomic coordinates of $Ta(O_2CNEt_2)_5$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ta	0.199 47(3)	0.080 7(2)	0.230 92(2)
O(10)	0.174 4(4)	0.022 2(3)	0.104 8(4)
O(11)	0.158 8(4)	0.147 4(3)	0.108 3(4)
O(20)	0.053 7(4)	0.090 8(3)	0.226 2(4)
O(21)	−0.046 6(5)	0.180 1(4)	0.146 6(4)
O(30)	0.194 4(4)	0.194 9(3)	0.287 6(4)
O(31)	0.234 2(4)	0.093 9(3)	0.372 8(4)
O(40)	0.149 2(4)	−0.030 3(3)	0.270 2(4)
O(41)	0.304 2(4)	−0.012 0(3)	0.267 7(4)
O(50)	0.330 0(4)	0.122 9(3)	0.215 6(4)
O(51)	0.444 4(5)	0.150 7(4)	0.341 7(5)
N(1)	0.112 2(6)	0.087 0(5)	−0.028 7(5)
N(2)	−0.057 7(5)	0.153 3(5)	0.292 4(5)
N(3)	0.248 8(7)	0.212 6(4)	0.440 4(5)
N(4)	0.260 2(6)	−0.127 5(4)	0.321 6(5)
N(5)	0.490 9(6)	0.089 8(5)	0.224 9(6)
C(1)	0.148 5(6)	0.085 7(5)	0.060 0(5)
C(2)	−0.017 0(6)	0.144 6(5)	0.216 5(6)
C(3)	0.226 3(6)	0.168 0(5)	0.368 0(6)
C(4)	0.236 4(6)	−0.057 1(5)	0.287 2(5)
C(5)	0.423 0(7)	0.120 3(6)	0.268 3(7)
C(11)	0.106 6(8)	0.012 5(6)	−0.080 7(6)
C(12)	0.203 4(9)	−0.007 7(7)	−0.108 4(7)
C(13)	0.062(1)	0.160 0(7)	−0.074 4(7)
C(14)	0.120(1)	0.189(1)	−0.135(1)
C(21)	−0.027 2(7)	0.106 2(7)	0.374 1(6)
C(22)	−0.085(1)	0.032 3(8)	0.373 5(9)
C(23)	−0.140 9(8)	0.208 7(7)	0.288 3(8)
C(24)	−0.103(1)	0.288 2(8)	0.315(1)
C(31)	0.283 5(8)	0.179 3(6)	0.532 4(6)
C(32)	0.203(1)	0.170 1(9)	0.583 2(8)
C(33)	0.272(1)	0.306 2(8)	0.426 2(8)
C(34)	0.181(1)	0.328(1)	0.430(1)
C(41)	0.179 4(7)	−0.179 1(5)	0.338 5(6)
C(42)	0.149(1)	−0.166 3(9)	0.425 1(9)
C(43)	0.366 3(7)	−0.152 6(6)	0.349 5(7)
C(44)	0.414(1)	−0.124 3(9)	0.442 6(9)
C(51)	0.595 5(8)	0.079 2(7)	0.275(1)
C(52)	0.608(1)	0.004 8(9)	0.329(1)
C(53)	0.464 9(8)	0.049 8(7)	0.135 7(8)
C(54)	0.459(1)	0.103(1)	0.056 5(9)

Table 6 Atomic coordinates of $Nb(O_2CNEt_2)_4$ with e.s.d.s in parentheses

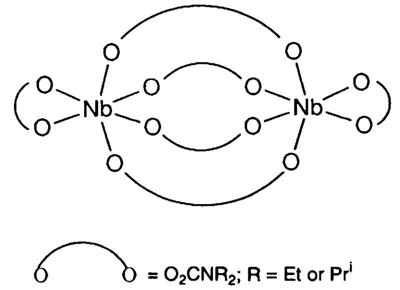
Atom	*x*	*y*	*z*
Nb	0	0.1160(1)	0.2500
O(1)	0.0292(1)	0.2549(1)	0.3329(1)
O(2)	0.0240(1)	0.0911(1)	0.3853(1)
O(3)	0.0962(1)	−0.0229(1)	0.2645(1)
O(4)	0.1585(1)	0.1403(1)	0.2594(1)
C(12)	0.0372(1)	0.1942(1)	0.3985(1)
C(13)	0.0801(2)	0.3567(2)	0.4880(1)
C(14)	0.0625(2)	0.1707(2)	0.5491(1)
C(15)	0.1918(2)	0.3820(2)	0.5148(2)
C(16)	−0.0312(3)	0.1787(3)	0.5724(2)
C(34)	0.1726(1)	0.0360(1)	0.2652(1)
C(35)	0.2738(2)	−0.1298(2)	0.2805(1)
C(36)	0.3463(2)	0.0568(2)	0.2693(2)
C(37)	0.2967(2)	−0.1682(2)	0.3708(2)
C(38)	0.3605(3)	0.0522(4)	0.1836(2)
N(12)	0.0583(1)	0.2390(1)	0.4756(1)
N(34)	0.2613(1)	−0.0102(1)	0.2717(1)

observed that the ratio between the interoxygen distance of the chelating ligand and the average metal–oxygen distance is typical for a given co-ordination geometry. They found that values of *ca.* 1.28:1 are typical of square-antiprismatic co-ordination {as observed in $[Nb(dpm)_4]^6$}, while ratios of *ca.* 1:1 are characteristic of dodecahedral geometry (the value for the homoleptic carbamato compound is *ca.* 1.01:1 in agreement with a smaller bite of the carbamate with respect to β-diketonate ligands).

The oxygen- and moisture-sensitive niobium(III) derivatives, purple tris(diethylcarbamato)- and tris(diisopropylcarbamato)-niobium(III), have been prepared by reaction of $[NbCl_3(dme)]$ with a CO_2-saturated solution of the secondary amine in toluene at room temperature [equation (5), R = Et or Pr^i]. The

$$[NbCl_3(dme)] + 3CO_2 + 6NHR_2 \longrightarrow Nb(O_2CNR_2)_3 + 3[NH_2R_2]Cl + dme \quad (5)$$

compounds are soluble in aromatic hydrocarbons and slightly soluble in aliphatic ones and are characterized by intense IR absorptions between 1600 and 1500 cm^{-1}, associated with bidentate carbamato groups.[1] The ^{93}Nb NMR spectrum for the diisopropyl derivative shows a broad band at δ −1032 ($w_{\frac{1}{2}}$ = 7.3 kHz), with respect to $[NEt_4][NbCl_6]$.



= O_2CNR_2; R = Et or Pr^i

The data in Table 1 for the diisopropyl derivative show a strong decrease in magnetic moment from 298 to 70 K. Even at room temperature the moment (0.91 μ_H) is well below the value expected for two unpaired electrons. At low temperatures the compound is substantially diamagnetic. This suggests a strong spin coupling of the $4d^2$ centres. In view of the moderate solubility of the niobium(III) complexes in hydrocarbons, we suggest a dinuclear structure, with bidentate bridging and bidentate terminal carbamato groups as shown above. A corollary to the proposed structure is the possibility of spin pairing through a metal–metal double bond. Several dinuclear structures containing four bridging dialkylcarbamato groups are known, ranging from the $3d^9$ dialkylcarbamates of copper(II),[21] $[Cu_2(O_2CNEt_2)_4(NHEt_2)_2]$, to the $3d^2$, $3d^4$ and $4d^4$ derivatives of vanadium(III), chromium(II) and molybdenum(II), respectively, $[V_2(\eta\text{-}C_5H_5)_2(O_2CNEt_2)_4]$,[22] $[Cr_2(O_2CNEt_2)_4(NHEt_2)_2]$[23] and $[Mo_2(O_2CNEt_2)_4]$.[23a] The chromium and molybdenum systems are believed to contain multiply bonded metal centres. It is interesting that $[Cr_2(O_2CNEt_2)_4(NHEt_2)_2]$ has been suggested[23b] to be characterized by a small singlet–triplet gap of about 0.1 eV. The metal–metal distance in the chromium system is 2.384(2) Å, compared with 2.658(2) Å in the isostructural copper(II) compound. In the absence of a solid-state structure, a conclusion concerning the presence of a metal–metal bond in our niobium(III) derivatives is impossible, also in consideration of the fact that the vanadium(III) complex, $[V_2(\eta\text{-}C_5H_5)_2(O_2CNEt_2)_4]$, with a vanadium–vanadium distance of 3.553(2) Å, shows a well reduced magnetic moment at 292 K (1.76 μ_B).[22] It is interesting that a similar reduction of the magnetic moment is observed in vanadium(III) carboxylates of similar structure and composition, namely $[V_2(\eta\text{-}C_5H_5)_2(O_2CCR_2)_4]$: spin coupling through the π density of the bridging ligands has been suggested in this case.[24]

Dialkylcarbamates of niobium(II) and tantalum(II)

Our approach to the synthesis of dialkylcarbamato complexes of niobium(II) and tantalum(II) began with the observation that simple dihalides of these elements had not been prepared so far.[2,25] The halides of niobium and tantalum in low oxidation state mostly exist as mixed-valence polynuclear systems or clusters, with metal–metal bonds.[2] Recently, some of us reported[26] the synthesis and the molecular structure of a dinuclear bromo derivative of niobium(II) containing hexamethylbenzene as additional ligand, of formula $[\mathrm{Nb_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Br_4}]$. Owing to the well known affinity of niobium and tantalum for oxygen-containing ligands, we expected the arene ligand to undergo substitution at some stage of the reaction with the $\mathrm{NHR_2}$–$\mathrm{CO_2}$ system. This compound was therefore chosen as starting material.

The hexamethylbenzene derivatives of niobium(II) and tantalum(II) chlorides were obtained by treating $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{AlCl_4})_2]$, the primary product of the reaction between $\mathrm{M_2Cl_{10}}$ and Al–$\mathrm{AlCl_3}$ and $\mathrm{C_6Me_6}$ in benzene, with thf at room temperature [equations (6) and (7), M = Nb or Ta]. At

$$\mathrm{M_2Cl_{10}} + 2\mathrm{Al} + 2\mathrm{C_6Me_6} + 2\mathrm{AlCl_3} \xrightarrow{\mathrm{C_6H_6},\ \text{reflux, 20 h}} 2[\mathrm{M}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{AlCl_4})_2] \quad (6)$$

$$2[\mathrm{M}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{AlCl_4})_2] + 8\mathrm{thf} \longrightarrow [\mathrm{M_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Cl_4}] + 4[\mathrm{AlCl_3(thf)_2}] \quad (7)$$

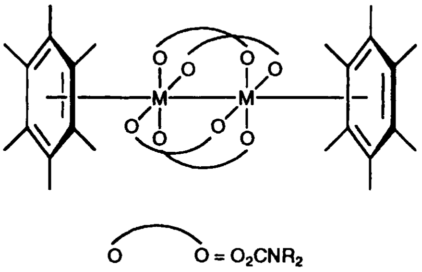
variance with earlier results based on the use of mesitylene as complexed arene,[26] we discovered that, with $\mathrm{C_6Me_6}$, no reduction to niobium(0) or tantalum(0) occurred when the crude reaction mixture, still containing the excess of aluminium, was treated with thf. The latter simply converts $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{AlCl_4})_2]$ into $[\mathrm{M_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Cl_4}]$ and $[\mathrm{AlCl_3(thf)_2}]$.[27] By operating as described in the Experimental section, good or substantially quantitative yields of the niobium(II) and the tantalum(II) derivatives were obtained. The niobium(II) chloride complex had been reported by Fischer and Röhrscheid,[28] who isolated the compound in low yields as a by-product of the reaction of the $\mathrm{Nb_2Cl_{10}}$–Al–$\mathrm{AlCl_3}$–$\mathrm{C_6Me_6}$ mixture with water. The brown compounds of niobium(II) and tantalum(II) are very sensitive to oxygen and moisture and moderately soluble in aromatic hydrocarbons. The ^{1}H NMR resonance for the methyl group is shifted upfield with respect to free $\mathrm{C_6Me_6}$ (δ 2.14), which is in accord with the presence of a metal-co-ordinated arene ($\delta = 1.67$).[29]

The reaction at room temperature of the compounds $[\mathrm{M_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Cl_4}]$ with a $\mathrm{CO_2}$-saturated solution of diisopropylamine in toluene afforded $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{O_2CNPr^i_2})_2]$, (M = Nb or Ta) [equation (8)]. These diamagnetic,

$$4[\mathrm{NH_2Pr^i_2}][\mathrm{O_2CNPr^i_2}] + [\mathrm{M_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Cl_4}] \longrightarrow 2[\mathrm{M}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{O_2CNPr^i_2})_2] + 4[\mathrm{NH_2Pr^i_2}]\mathrm{Cl} \quad (8)$$

dark brown complexes, are rapidly decomposed by oxygen and moisture. That $\mathrm{C_6Me_6}$ is retained in the co-ordination sphere of the metal is confirmed by the ^{1}H and ^{13}C NMR spectra: the ^{1}H resonance of the $\mathrm{C_6Me_6}$ group is at δ *ca.* 2.0 for both complexes; the ^{13}C NMR spectrum shows upfield shifts with respect to the free molecule; greater for the ring carbon atoms (δ 112.0, compared with δ 131.8 for uncomplexed $\mathrm{C_6Me_6}$) than for the methyl carbon atoms (δ 17.3 *vs.* δ 16.9 for free $\mathrm{C_6Me_6}$).[29] The ^{93}Nb NMR spectrum of $[\mathrm{Nb}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{O_2CNPr^i_2})_2]$ shows a band at δ 756 with $w_{\frac{1}{2}} = 4.3$ kHz, compared with the resonance at δ 604 ($w_{\frac{1}{2}} = 820$ Hz) for the starting material, $[\mathrm{Nb_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Cl_4}]$.

The intense IR absorption peaks between 1550 and 1500 $\mathrm{cm^{-1}}$ are attributed to the presence of bidentate carbamate ligands.[1] This fact, together with the diamagnetic behaviour of these compounds of nd^3 configuration, led us to suggest that the complexes may be dinuclear with bridging dialkylcarbamato groups. As schematically shown, the structure would therefore resemble that already established for $[\mathrm{Nb_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Br_4}]$ containing bridging bromides and niobium-bonded $\mathrm{C_6Me_6}$ groups on each side of the $\mathrm{Nb_2Br_4}$ fragment. As already suggested for $[\mathrm{Nb_2}(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Br_4}]$,[26] also in the carbamato complex a metal–metal bond is required to account for the observed diamagnetism.



M = Nb or Ta; R = Et or Pr^i

Treatment of dialkylcarbamates of niobium(V) and tantalum(V) with $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})_2]$

Examples of electron- and/or ligand-transfer reactions involving dialkylcarbamato complexes have been reported previously.[22,30] By this route new carbamato complexes of niobium and tantalum in oxidation states lower than V were anticipated. We therefore studied the behaviour of some reducing agents towards the niobium(V) and tantalum(V) diethylcarbamato complexes. In view of the solubility of $\mathrm{Nb(O_2CNEt_2)_5}$, $\mathrm{Ta(O_2CNEt_2)_5}$ and $[\mathrm{TaCl_2(O_2CNEt_2)_3}]$, in aromatic hydrocarbons, we initially used a hydrocarbon-soluble reducing agent of the cobaltocene series. With bis(cyclopentadienyl)cobalt(II), $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5H_5})_2]$, contrary to our expectations, no reaction with $\mathrm{Nb(O_2CNEt_2)_5}$ occurred. In order to reduce the niobium(V) derivative the more reducing bis(pentamethylcyclopentadienyl)cobalt(II), $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})_2]$,[10] had to be used, see equation (9). The partially

$$[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})_2] + \mathrm{Nb(O_2CNEt_2)_5} \longrightarrow [\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})_2][\mathrm{O_2CNEt_2}] + \mathrm{Nb(O_2CNEt_2)_4} \quad (9)$$

soluble $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})_2][\mathrm{O_2CNEt_2}]$ was recovered in 53% yield and characterized by IR and NMR spectroscopy. The IR spectrum shows strong absorptions between 1650 and 1600 $\mathrm{cm^{-1}}$; the ^{13}C NMR resonance of the $\mathrm{O_2CN}$ carbon atom is at δ 169.29, which may suggest a higher electron density on the oxygen atoms of the carbamate ligand with respect to the homoleptic complexes of niobium and tantalum. Owing to the poor solubility properties of the two products of reaction (9) it was not possible to obtain analytically pure $\mathrm{Nb(O_2CNEt_2)_4}$ by this method.

In the case of $\mathrm{Ta(O_2CNEt_2)_5}$, no reduction occurs either with $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})_2]$ in toluene or thf or with Na in thf. This is in agreement with the general observation that the stability of high oxidation states increases on descending a vertical sequence of transition-metal ions and reduction is correspondingly more difficult.[31]

Conclusion

This paper has shown for the first time that dialkylcarbamate ligands, by virtue of their co-ordination flexibility, can stabilize several oxidation states of the same metal, from V to II. Thus, the pentakis and tetrakis derivatives are mononuclear, as has been established for the tantalum(V) and the niobium(IV) complexes, respectively, by X-ray diffraction methods. The corresponding complexes in oxidation states III and II are presumably dinuclear with bridging carbamato groups. As expected, the nuclearity of the systems increases on decreasing the oxidation state.

Owing to the structural similarity existing between carboxylato and dialkylcarbamato complexes, the present results suggest that similar findings may be expected with the corresponding metal carboxylates $M(O_2CR)_n$ not yet reported or of unknown structure. Work is in progress to ascertain this point.

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