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Synthesis of some dinuclear niobium chloro alkoxy carboxylates $[Nb_2Cl_4(OEt)_4(O_2CR)_2]$, and the X-ray crystal and molecular structure of the compound with R = Ph

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Abstract

The reaction of $NbCl_5$ with aromatic organic acids and ethanol has been found to yield the first examples of trifunctional chloro alkoxy carboxylate niobium(V) complexes $[Nb_2Cl_4(OEt)_4(O_2CR)_2]$ (R = Ph (**1**), p-FC_6H_4, p-ClC_6H_4, p-IC_6H_4, p-MeC_6H_4). Attempts to obtain related compounds by the use of different molar ratios of reactants under a variety of conditions have proved unsuccessful. The structure of **1** has been determined by single crystal X-ray crystallography, the data being as follows: triclinic space group $P\bar{1}$ with unit cell dimensions $a = 10.689(3)$, $b = 9.548(2)$, $c = 9.552(2)$ Å, $V = 753.90$ Å^3, $Z = 2$. The structure was refined to $R = 0.0623$ ($R' = 0.0677$) with 1347 reflections having $I \geqslant 3\sigma(I)$. The dinuclear unit contains unique unsymmetrical bridging carboxylate groups, as well as terminal chlorine atoms and ethoxy groups. The crystal contains chains of dimers which exhibit face-to-face π–π interactions between the aromatic rings of the benzoate ligands.

Keywords: Crystal structures; Niobium complexes; Alkoxo complexes; Carboxylato complexes; Dinuclear complexes

1. Introduction

By far the most studied area of the solvolysis reactions of $NbCl_5$ is that of the alkoxides. A large amount of literature has built up concerning the pentaalkoxides $Nb(OR)_5$ and the chloro alkoxides $NbCl_x(OR)_{5-x}$ ($x = 1$–4) [1,2], as well as other alkoxy compounds such as $[Nb(NCS)(OPr^i)_3(C_6H_5COCH_2COC_6H_5)]$ [3]. In contrast far less is known about niobium(V) carboxylate chemistry especially in the area of mixed alkoxy carboxylate species. Several workers have described the preparations of niobium chlorocarboxylates using the alkyl carboxylic acids, with the products being formulated as $[NbCl_4(O_2CR)]$ (R = H, Me, Et, Pr^n, CH_2Cl, $CHCl_2$, CCl_3) [4] together with the related oxo derivatives $[NbO_2(O_2CR)]$ (R = H, Me, Et, Pr^i, CH_2Cl, $CHCl_2$, CCl_3), $[NbOCl_2(O_2CR)]$ (R = Me, Et, Pr^i, Bu^t, CH_2Cl, CH_2F) [5] and the oxo-oxalato complexes $Cs[NbO(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ [6], $[(NH_4)_3NbO(C_2O_4)_3]\cdot H_2O$, $[(NH_4)_3Nb(O_2)_2(C_2O_4)_2]\cdot H_2O$ [7] and the $[Nb_2Cl_6O_2(C_2O_4)]^{2-}$ ion [8]. More recently we have prepared and structurally characterised the dinuclear species $[\{NbCl_3(O_2CPh)\}_2O]$ and $[Nb_2Cl_8(O_2CC_6F_5)_2]$ [9,10].

Among the few alkoxy carboxylates reported $[Nb(OEt)_{5-x}L_x]$ ($x = 1,2$) derivatives have been isolated from the reaction of $[Nb(OEt)_5]$ with the α-hydroxycarboxylic acids (H_2L), lactic, mandelic and salicylic acids [11], and $[Nb(OEt)_{5-x}L_x]$ ($x = 1$–3; L = *trans*-$C_6H_5CH{:}CHCO_2^-$, $C_6H_5CH_2CH_2CO_2^-$) have also been described [12]. In attempts to isolate reactive precursors which may provide possible structural models for the intermediates found in the sol–gel processing of early transition metal alkoxides [13], we have investigated the reactions between niobium(V) chloride and a mixture of ethanol and a carboxylic acid. The results of these studies, together with an X-ray crystal structure of one of the products, are described below.

2. Experimental

IR spectra (4000–200 cm^{-1}) were recorded from hexachlorobutadiene (HCB) and Nujol mulls using CsI plates and a Perkin-Elmer 580B or a Perkin-Elmer 1720X FT spectrophotometer. ^1H and ^{13}C NMR were

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run on a Bruker Associates ACF 250 at 250 MHz in $CDCl_3$. All the complexes prepared are air sensitive and were handled under dry nitrogen using Schlenk techniques and a dry box. All solvents were dried by distillation from CaH_2 before use. $NbCl_5$ (Aldrich) and the organic acids were used as supplied.

2.1. Preparation of [$Nb_2Cl_4(OEt)_4(O_2CR)_2$]

A typical procedure is given first (R = Ph). Benzoic acid (1.45 g, 16 mmol) was added to a suspension of $NbCl_5$ (4.34 g, 16 mmol) in toluene (100 cm^3). A red suspension resulted, and addition of ethanol (1.9 cm^3, 32 mmol) yielded a clear yellow solution. This was refluxed for 1 h; the volume of the solution was then reduced in vacuo to 50 cm^3. Hexane (100 cm^3) was added and the mixture pumped down by ~60%. A small quantity of precipitate was filtered off and the washings allowed to stand. Colourless crystals of [$Nb_2Cl_4(OEt)_4(O_2CPh)_2$] (**1**) suitable for X-ray diffraction were obtained on cooling the washings at 0 °C overnight. The chosen crystal was sealed in a Lindemann tube. Yield 0.9 g (15%). *Anal.* Found: Nb, 24.90. Calc. for $C_{22}H_{30}Cl_4O_8Nb_2$: Nb, 24.79%. Major IR bands at 1596, 1543, 1312, 1178, 1098, 1050, 927, 850, 719, 665, 583, 415 (Nujol); 1494, 1444, 1413, 1390, 1380, 350 (HCB) cm^{-1}. $^{13}C\{^1H\}$ NMR data ($CDCl_3$) (ppm): 16.30 (CH_3), 79.04–79.85 (CH_2), 128.39–128.69, 130.40–132.60, 134.28–135.35 (Ph), carboxylate C not clearly observed.

Other [$Nb_2Cl_4(OEt)_4(O_2CR)_2$] compounds, R group, solvent, yield, analysis, IR cm^{-1} (Nujol), IR (HCB carboxylate region only) cm^{-1}, $^{13}C\{^1H\}$ NMR, ppm.

p-$CH_3C_6H_4$, toluene, 20%. *Anal.* Found: C, 37.23; H, 4.64; Nb, 24.52. Calc. for $C_{24}H_{34}Cl_4O_8Nb_2$: C, 37.03; H, 4.40; Nb, 23.90%. IR: 1600, 1540, 1410, 1090, 1050, 930, 760, 730, 720, 600, 430, 340 (Nujol); 1593, 1562, 1511, 1455, 1410, 1378, (HCB). $^{13}C\{^1H\}$ 16.25 (CH_3 in CH_3CH_2O): 21.84 (CH_3 on C_6H_4), 79.73, 129.29, 130.53, 131.87, carboxylate not observed.

p-FC_6H_4, toluene, 22%. *Anal.* Found: C, 33.62; H, 3.66; Nb, 23.15. Calc. for $C_{22}H_{28}Cl_4F_2O_8Nb_2$: C, 33.60; H, 3.59; Nb, 23.66%. IR: 1600, 1550, 1410, 1400, 1280, 1200, 1090, 1040, 1020, 930, 850, 780, 720, 690, 600, 410, 300 (Nujol); 1506, 1465, 1410 (HCB). $^{13}C\{^1H\}$: 16.24, 79.18–79.99, 115.84–116.19, 127.18, 133.27–135.09, 168.83 (carboxylate).

p-ClC_6H_4, toluene, 10%. *Anal.* Found: Nb, 21.71. Calc. for $C_{22}H_{28}Cl_6O_8Nb_2$: Nb, 22.70%. IR: 1634, 1593, 1308, 1237, 1174, 1094, 1058, 932, 772, 725, 593, 557, 350 (Nujol); 1565, 1531 (HCB). $^{13}C\{^1H\}$: 16.06, 78.33, 125.00, 129.56, 132.37, 143.33, 175.56 (carboxylate).

p-IC_6H_4, toluene, 28%. *Anal.* Found: Nb, 18.43. Calc. for $C_{22}H_{28}Cl_4I_2O_8Nb_2$: Nb, 18.56%. IR: 1623, 1581, 1556, 1307, 1261, 1095, 1058, 1034, 935, 723, 616, 557, 340 (Nujol); 1584, 1533, 1484, 1411, 1353 (HCB). $^{13}C\{^1H\}$: 16.17, 78.20, 105.83, 125.78, 132.04, 138.61, 175.80 (carboxylate).

Table 1
Selected bond lengths (Å) and angles (°) for [$Nb_2Cl_4(OEt)_4(O_2CPh)_2$] (**1**)

Nb(1)–Cl(1)	2.364(4)	Nb(1)–Cl(2)	2.366(4)
Nb(1)–O(1)	2.114(7)	Nb(1)–O(2)	2.037(13)
Nb(1)–O(3)	1.813(7)	Nb(1)–O(4)	1.784(14)
O(1)–C(1)	1.234(13)	O(3)–C(31)	1.394(17)
C(31)–C(32)	1.37(3)	O(4)–C(41)	1.36(3)
C(41)–C(42)	1.29(3)	C(1)–C(2)	1.491(18)
O(2′)–C(1)	1.244(13)		
Cl(2)–Nb(1)–Cl(1)	166.2(1)	O(1)–Nb(1)–Cl(1)	83.5(2)
O(1)–Nb(1)–Cl(2)	85.6(2)	O(2)–Nb(1)–Cl(1)	85.7(3)
O(2)–Nb(1)–Cl(2)	85.6(3)	O(2)–Nb(1)–O(1)	89.1(4)
O(3)–Nb(1)–Cl(1)	93.8(3)	O(3)–Nb(1)–Cl(2)	97.1(3)
O(3)–Nb(1)–O(1)	177.3(4)	O(3)–Nb(1)–O(2)	90.7(5)
O(4)–Nb(1)–Cl(1)	92.8(3)	O(4)–Nb(1)–Cl(2)	94.8(3)
O(4)–Nb(1)–O(1)	85.5(4)	O(4)–Nb(1)–O(2)	174.5(3)
O(4)–Nb(1)–O(3)	94.6(5)	C(1)–O(1)–Nb(1)	145(1)
C(31)–O(3)–Nb(1)	156(1)	C(32)–C(31)–O(3)	114(2)
C(41)–O(4)–Nb(1)	165(1)	C(42)–C(41)–O(4)	121(2)
C(2)–C(1)–O(1)	118(1)	Nb(1)–O(2)–C(1′)	166.3(7)
O(2′)–C(1)–O(1)	125(1)		

Table 2
Atomic coordinates and equivalent isotropic displacement coefficients (Å^2) for **1** with their standard deviations

Atom	x	y	z	U_{iso}/U_{eq}[a]
Nb(1)	0.19647(12)	0.14771(14)	0.16871(13)	0.0664(7)
Cl(1)	−0.0228(4)	0.3390(4)	0.1977(5)	0.100(2)
Cl(2)	0.3764(4)	−0.0802(5)	0.0882(5)	0.097(3)
O(1)	0.0674(8)	0.1062(10)	−0.0860(9)	0.074(5)
O(2)	0.1201(10)	−0.0088(10)	0.1809(9)	0.087(6)
O(3)	0.2996(10)	0.1907(12)	0.3892(10)	0.095(6)
C(31)	0.3813(20)	0.2750(24)	0.5422(20)	0.128(14)
C(32)	0.3125(19)	0.3477(19)	0.6544(21)	0.106(11)
O(4)	0.2506(10)	0.2836(11)	0.1385(12)	0.104(7)
C(41)	0.2590(23)	0.3853(26)	0.0789(24)	0.164(17)
C(42)	0.3524(22)	0.4701(23)	0.1665(28)	0.158(18)
C(1)	−0.0488(12)	0.0758(12)	−0.1929(13)	0.056(6)
C(2)	−0.1111(11)	0.1287(11)	−0.3448(12)	0.053(6)
C(3)	−0.2381(12)	0.0913(13)	−0.4726(13)	0.066(7)
C(4)	−0.2889(13)	0.1371(14)	−0.6126(14)	0.065(7)
C(5)	−0.2179(14)	0.2183(15)	−0.6269(14)	0.071(8)
C(6)	−0.0959(14)	0.2586(16)	−0.5038(14)	0.083(8)
C(7)	−0.0415(12)	0.2116(14)	−0.3588(14)	0.069(7)

[a] U_{eq} has been defined as $\frac{1}{3}\Sigma U_{ij}$.

2.2. X-ray structure analysis

2.2.1. Crystal data

[$Nb_2Cl_4(OC_2H_5)_2(O_2CC_6H_5)_2$], $C_{11}H_{15}O_4Cl_2Nb$, $M = 375$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.689(3)$, $b = 9.548(2)$, $c = 9.552(2)$ Å, $\alpha = 114.50(2)$, $\beta = 118.11(2)$, $\gamma = 65.78(2)°$, $V = 753.90$ Å^3, $\rho_{calc} = 1.652$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 10.9 cm^{-1}, $F(000) = 376$.

2.2.2. Data collection

Data were collected with a Philips PW1100 four circle diffractometer in the θ range 3–25° with a constant scan speed of 0.05° s^{-1} and an ω scan width of 0.90° using the method described previously [14]. Three reference reflections were measured at 5 h intervals and showed no significant changes in intensities. Data was corrected for Lorentz and polarisation factors and equivalent reflections were merged to give 1347 unique reflections with $I/\sigma(I) \geqslant 3$.

2.2.3. Structure solution and refinement [15]

The niobium atom was located from a Patterson synthesis and the remaining non-hydrogen atoms of the asymmetric unit were located from subsequent difference-Fourier syntheses. A difference-Fourier synthesis using low angle data ($\sin\theta \leqslant 0.35$) revealed positions for onc hydrogen atom in each methyl group of the asymmetric unit and both *ortho*-hydrogens of the phenyl ring. The remaining hydrogen atoms were included in idealised positions (–H 1.08 Å). Absorption corrections [16] were applied after refinement with isotropic thermal parameters for all non-hydrogen atoms. In the final cycles of full-matrix least-squares refinement the niobium, chlorine and oxygen atoms were assigned anisotropic thermal parameters. Neutral scattering factors, corrected for the real and imaginary components of anomalous dispersion, were used throughout [17]. Individual wcights of $1/\sigma^2(I)$ were assigned to each reflection and refinement converged at R 0.0623 and $R' = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o|w^{1/2}$. Selected bond lengths and angles are listed in Table 1, selected final atomic coordinates are given in Table 2.

3. Results and discussion

Initial attempts to obtain niobium(V) intermediates containing halo, alkoxy and carboxylate groups consisted of adding varying amounts of ethanol to a toluene solution of $NbCl_5$ (1 mol) and a carboxylic acid (RCO_2H, R = Ph, p-MeC_6H_4 etc.; 1.5 mol), since it is known that such a mixture yields the well characterised $[\{NbCl_3(O_2CR)\}_2O]$ [9]. Although these experiments yielded only intractable oils, it was noticed that when further acid (R = Ph) was added, giving a mole ratio of $NbCl_5$:acid:EtOH of 1:2:2, and the mixture refluxed in hexane, a small quantity of a colourless crystalline material deposited from the filtrate after filtering off some unreacted acid. Analytical data indicated this material was best formulated as $[NbCl_2(OEt)_2(O_2CPh)]$. Surprisingly a repeat experiment run under similar conditions, but with an excess of ethanol present (mole ratio $NbCl_5$:acid:EtOH now 1:1:4) also yielded small quantities of a similar product containing Nb–Cl bonds indicating that such bonds are apparently inactive towards an excess of either acid or alcohol.

The reaction conditions are clearly important, and a series of experiments for a range of aryl acids (RCO_2H, R = Ph, p-XC_6H_4 where X = F, Cl, I, Me) established that optimum yields of the products were obtained by the use of a 1:1:2 molar ratio of reactants (Eq. (1)) in toluene at 70 °C. All the products are colourless, slightly air-sensitive solids. Their general high solubility in organic solvents (aromatics, halocarbons) and even a slight solubility in petroleum ethers, renders the workup of the reactions somewhat tricky. Indeed when R = $CH_3CH{:}CH$ or o-MeC_6H_4 only intractable oils were again obtained. The best general procedure for isolating the solids was found to be a reduction of the mother liquor under vacuum, followed by the addition of a ~two-fold excess of hexane with cooling overnight to produce a crystalline precipitate. Although the species isolated are present in the mother liquor, as indicated from thc IR spcctra of the reaction solutions, the isolation procedure undoubtedly leads to rather low yields, but the advantage is that crystalline materials of high purity are obtained by this method.

$$NbCl_5 + RCO_2H + 2EtOH \longrightarrow [NbCl_2(OEt)_2(O_2CR)] + 3HCl \quad (1)$$

These are several points of particular interest in the above series of reactions. Firstly, an X-ray structure of the benzoate derivative, as discussed below, reveals a dinuclear structure $[Nb_2Cl_4(OEt)_4(O_2CPh)_2]$ with bridging carboxylate groups. We believe the products reported here are unique in providing the first structural example of a species containing the three functional groups halide, alkoxy and carboxylate. Since all the three groups are well known bridging entities between metal centres it is noteworthy that it is the carboxylate group which is favoured here. This is not always the case, for example in other structures where alkoxy and carboxylate groups are present either one can occupy the bridging sites as in $[W_2O(OBu^t)_3(O_2CCF_3)_2(\mu\text{-}OBu^t)(\mu\text{-}CMe_2)(C_5H_5N)]$ [18] and $[Mo_2(OBu^t)_4(\mu\text{-}O_2CPh)_2$ [19], respectively.

Secondly, it is surprising that no products containing the μ-oxo group are observed in these reactions, since we have shown previously that the oxo abstraction process occurs even at room temperature in mixtures of $NbCl_5$ with a carboxylic acid. Presumably in the present reactions the π-donation from the terminal ethoxy groups is sufficient to satisfy the electronic requirement of the metal centres without the need to introduce a μ-oxo ligand. As mentioned above this behaviour is still observed even when an excess of acid is used. Significantly in the absence of ethanol, with a 1:2 ($NbCl_5$:acid) molar ratio, the products are insoluble oxo-carboxylates possibly containing $[Nb–O–Nb–O]_n$ chains, as indicated by the IR spectra, which contain

Table 3
IR bands (cm^{-1}) in the spectra of $[Nb_2Cl_4(OEt)_4(O_2CR)_2]$ (Nujol mulls unless stated otherwise)

R	$\nu_{asym}(CO_2^-)$	$\nu_{sym}(CO_2^-)$	$\Delta[\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)]$	ν(Nb–Cl)	ν(C–O)	ν(Nb–O)
Ph	1444[a]	1390[a]	54	350	1050 1100	590
p-FC_6H_4	1465[a]	1410	55	300	1090 1040	600
p-ClC_6H_4	1531[b]			350	1094 1058	593
p-IC_6H_4	1484[a]	1411[a]	73	340	1095 1058	557
p-MeC_6H_4	1455[a]	1410	45	340	1090 1050	600

[a] Positions of bands in HCB mull.

[b] Tentative only, no $\nu_{sym}(CO_2^-)$ could be assigned at all due to overlapping peaks.

Table 4
NMR data for the complexes $[Nb_2Cl_4(OEt)_4(O_2CR)_2]$ ($CDCl_3$) ($^{13}C\{^1H\}$ data given in Section 2)

R	δ (ppm)[a]	Multiplicity[b]	Relative intensity
Ph	1.32–1.60	t	6
	4.84–5.09	q	4
	7.46–7.68	multiplets	3
	8.08–8.50		2
p-FC_6H_4	0.89–1.61	t	3
	4.82–5.08	q	2
	7.13–7.26	multiplets	1
	8.08–8.52		1
p-ClC_6H_4	1.38–1.56	t	3
	4.88–5.09	q	2
	7.49–7.53	multiplets	1
	8.10–8.07		1
p-IC_6H_4	1.40–1.53	t	3
	4.87–5.07	q	2
	7.78–7.91	multiplets	2
p-$CH_3C_6H_4$	1.33–1.68	t	6
	2.43–2.50	s	3
	4.83–5.13	q	4
	7.28–7.40	multiplets	2
	7.98–8.23		2

[a] Peaks between 0.89 and 1.68 ppm assigned to $\mathit{CH_3}CH_2O^-$, between 4.82 and 5.13 ppm assigned to $CH_3\mathit{CH_2}O^-$, between 2.50 and 2.43 ppm R = p-MeC_6H_4 assigned to p-Me group; other resonances assigned to phenyl ring protons.

[b] t = triplet, q = quartet, with both showing further splittings, giving an overall complex multiplet, s = singlet.

only bands arising from Nb–O–Nb and Nb–(O_2CR)–Nb groups, but no absorptions from Nb–Cl bonds. It is clear therefore that the addition of ethanol limits the ability of the metal to abstract an oxygen atom from the organic acid.

Thirdly, it is surprising that in spite of the use of a wide range of molar ratios of the reactants, under a variety of conditions, the only product which could be isolated was that with the single composition given above. It is possible that the particular combination of chloro, alkoxy and carboxylate groups provides considerable electronic stability for the six coordinate (12e) metal centres. However, it should be mentioned that in terms of reactivity such stability is limited since, in common with the majority of halide derivatives of the early transition metals, the present compounds are susceptible to hydrolysis, albeit slowly as noted above. We have so far been unable to determine whether it is only the metal–chloro bonds which are affected by such conditions.

3.1. Spectroscopic studies

The relevant IR and ^1H NMR spectroscopic data are given in Tables 3 and 4, respectively; more complete data including the ^{13}C NMR spectra are given in Section 2. IR spectra were recorded in both hexachlorobutadiene (HCB) and Nujol mulls since in some cases one of the two carboxylate bands was obscured by either a Nujol or an HCB band. Correlations between the magnitude of Δ [where $\Delta = \nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)$] in the IR spectrum and the mode of carboxylate bonding have often been made in the past [20,21]. Values of Δ significantly less than the value for ionic species, e.g. $[Na(HCO_2)]$ $\Delta = 164$ cm^{-1}, have been claimed to be consistent with the presence of bridging or chelating groups. The Δ values found in the present work lie between 45 and 73 cm^{-1} consistent with the presence of the two bridging carboxylate groups shown by the X-ray diffraction study. The Nb–Cl bands are present as a single broad peak between 300 and 350 cm^{-1}. Bands present in the Nb–O(alkoxy) and C–O(alkoxy) regions are also listed in Table 3 although assignment of these bands is somewhat tentative [22,23]. The only unusual feature in the ^1H NMR spectra is that a complex multiplet pattern is observed for the alkoxide ethyl groups. This arises from splitting of the expected triplet/

quartet pattern, and we have no convincing explanation for this effect at present.

3.2. X-ray diffraction study

The solid state structure of [$Nb_2Cl_4(OEt)_4(O_2CPh)_2$] (**1**) is dimeric with exact crystallographic C_i symmetry, the two halves of the dimer being related by an inversion centre at the midpoint of the Nb...Nb vector, the origin of the unit cell. The structure of the dimer is shown in Fig. 1 and selected bond lengths (Å) and angles (°) are given in Table 1. Each niobium atom is coordinated in a slightly distorted octahedral environment consisting of *trans*-axial chloride ligands and two terminally-bound *cis*-ethoxides; the coordination spheres are completed by two μ-bridging benzoate ligands producing a bis-μ-carboxylato dimetal core. The relatively large separation of the metal centres in **1** (5.04 Å) is comparable with metal–metal distances of 5.07 and 4.99 Å in independent molecules of the bis-μ-carboxylato diniobium species, [$Nb_2Cl_8(\mu\text{-}O_2CC_6F_5)_2$] [10] and that of 4.84 Å in the bis-μ-carboxylato ditantalum species, [$Ta_2Cl_8(\mu\text{-}O_2CC_6H_4Cl)_2$] [10]. Metal–metal separations of this order contrast that in the μ-oxo(bis-μ-carboxylato) diniobium core of the related carboxylato niobium dimer, [{$NbCl_3(\mu\text{-}O_2CPh)$}$_2(\mu\text{-}O)$] [9] where the metal centres, bridged by a μ-oxo group, are separated by 3.60 Å. The larger metal–metal separations, presumably resulting from the absence of a μ-oxo bridging group to mediate the intermetallic repulsion, result in a unique and interesting feature, namely the opening of the C–O–M [C(1)–O(2)–Nb(1)] angle at one carboxylate oxygen: in **1**, the nearly linear value of 166.3(7)° is substantially larger than the other C(1)–O(1)–Nb(1) angle of 145(1)°. The difference in these angles indicates a distinctly unsymmetrical bridging mode for the carboxylate ligand which appears to be intermediate between the frequently observed *syn–syn* bridging mode and the relatively rare *anti–syn* mode [24].

In the crystal, the aromatic rings of adjacent dimers of **1** are separated by interplanar distances of 3.52 Å and are offset relative to one another by 1.33 Å. Such orientations correspond with favourable π–π interactions [25] and thus the crystal packing features chains of dimers which propagate in the z direction and are stabilised by offset face-to-face π–π interactions between the aromatic rings of the benzoate ligands (Fig. 2). Notably, chains of dimers of this type also feature in the packing of [$Ta_2Cl_8(\mu\text{-}O_2CC_6H_4Cl)_2$] [10].

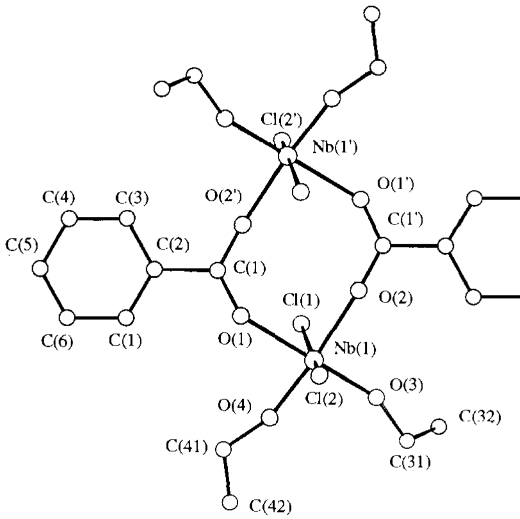

Fig. 1. Perspective view of [$Nb_2Cl_4(OEt)_4(O_2CPh)_2$] (**1**) with the atom numbering. H atoms are omitted for clarity.

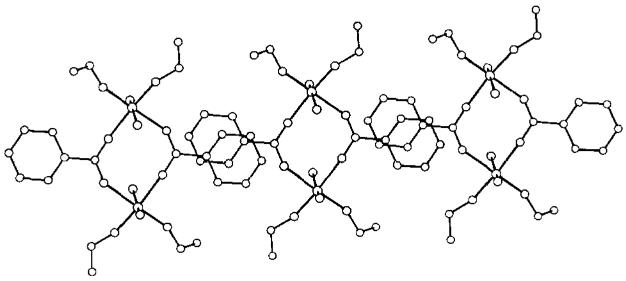

Fig. 2. Stacking arrangement in **1** showing the π–π interaction in the aryl rings.

4. Supplementary material

Additional material consisting of thermal parameters, full bond lengths and angles and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre. The data can be obtained from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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