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Synthesis, properties and structures of $NbOF_3$ complexes and comparisons with $NbOCl_3$ analogues†

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The first series of complexes of niobium(v) oxide trifluoride, $[NbOF_3(OPR_3)_2]$ (R = Me or Ph), $[NbOF_3(dppmO_2)]$ ($dppmO_2$ = $Ph_2P(O)CH_2P(O)Ph_2$), $[NbOF_3(dmso)_2]$, $[NbOF_3(tmeda)]$ (tmeda = Me_2N-$(CH_2)_2NMe_2$) and $[NbOF_3(diimine)]$ (diimine = 2,2′-bipy, 1,10-phen) have been prepared, either by reaction of the corresponding complexes of NbF_5 and hexamethyldisiloxane (HMDSO) in CH_2Cl_2–MeCN solution, or directly from NbF_5, ligand and HMDSO. They were characterised by IR, ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy, and X-ray crystal structures are reported for $[NbOF_3(OPR_3)_2]$ (R = Me or Ph) and $[NbOF_3(dppmO_2)]$. Complexes of $NbOCl_3$, $[NbOCl_3(OPPh_3)_2]$, $[NbOCl_3(dppmO_2)]$, $[NbOCl_3(dppeO_2)]$ ($dppeO_2$ = $Ph_2P(O)(CH_2)_2P(O)Ph_2$), $[NbOCl_3(tmeda)]$ and $[NbOCl_3(diimine)]$ were made from $NbCl_5$ and HMDSO in MeCN (which forms $[NbOCl_3(MeCN)_2]$ *in situ*), followed by addition of the neutral ligand. Their properties are compared with the oxide fluoride analogues. X-ray structures are reported for $[NbOCl_3(dppmO_2)]$, $[NbOCl_3(dppeO_2)]$, $[NbOCl_3(tmeda)]$ and $[NbOCl_3(2,2'\text{-bipy})]$. The synthesis and spectroscopic characterisation of $[MF_5L]$ (M = Nb or Ta; L = OPR_3, $OAsPh_3$) and $[MF_4(diimine)_2][MF_6]$ are also described, and the key properties of the four series of complexes compared.

Introduction

The fluorides and oxide fluorides of early transition metals in high oxidation states are strong Lewis acids and form a substantial range of complexes with F^- and with hard N- or O-donor ligands, whilst their more limited chemistry with soft donor ligands (P, S *etc.*) sometimes includes redox chemistry at the metal centre and oxidation/fluorination of the heteroatom donor, in addition to adduct formation.[1] The properties of the metal centre are significantly altered by the small very electronegative fluoride ligands, and the chemistry of these fluorides/oxide fluorides is often very different to that of the chloride analogues.[1]

Within Group V, the coordination chemistry of the oxide fluorides VOF_3,[2] and VO_2F[2,3] has been studied in some detail recently, whilst that of VF_5 is completely unexplored. In contrast, an extensive series of complexes of MF_5 (M = Nb or Ta) with both hard N- and O-donor[1,4] and soft S-donor[5] ligands are known, but the oxide-fluorides, MOF_3, are intractable and very little studied.[6,7] Here we report the synthesis, spectroscopic and structural characterisation of a series of adducts of $NbOF_3$. Complexes of $NbOCl_3$ have long been known, originally obtained by adventitious hydrolysis, or O-abstraction from the solvent or ligand in reactions of $NbCl_5$.[8] More systematic syntheses used the reaction of $NbCl_5$ with siloxanes or occasionally direct reaction with the polymeric $NbOCl_3$,[9] and selected examples have been re-examined in the present work to provide comparisons with the $NbOF_3$ complexes. $NbOF_3$ is obtained by heating NbF_5 with NbO_2F in argon, and has a structure based upon six-coordinate niobium (SnF_4 type), but the O/F disorder is only partially understood.[6] It decomposes on heating above 180 °C, hydrolyses in air in a few hours, and is insoluble in organic solvents, making it completely unsuitable as a synthon to explore the coordination chemistry. $TaOF_3$, which is formed similarly from TaO_2F and TaF_5, is also disordered and unreactive.[6]

We describe here a convenient alternative route to $NbOF_3$ complexes involving F/O exchange from the corresponding NbF_5 adducts, using hexamethyldisiloxane (HMDSO). Similar halogen/oxygen exchange has proved to be a useful route for the preparation of complexes of polymeric oxide halides, including, for example, MO_2X_2 (M = Mo or W; X = Cl or Br),[10] although it has rarely been used for oxide fluoride complexes.[1]

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† Electronic supplementary information (ESI) available: The crystallographic data and selected bond lengths and angles for $[Me_3TACNH]_2[NbOCl_5]$ are also available in the ESI. CCDC 973570–973577. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C3DT53322K

Table 1 Comparison of spectroscopic data

Complex	$^{19}F\{^1H\}$[a]	$^{31}P\{^1H\}$[a]	ν(P/AsO)[b]	ν(Nb/TaX)[b]/cm^{-1}	ν(NbO)[b]/cm^{-1}
$[NbF_5(OPPh_3)]$	161.8(s, [F]), 128.6(s, [4F])	53.9[c]	1061(vs)[c]	624(sh), 608(vs, br)	—
$[NbF_5(OPMe_3)]$	157.6(s, [F]), 134.5(s, [4F])	75.6[d]	1092(vs)[d]	615(vs, br), 582(m)	—
$[NbF_5(OAsPh_3)]$	145.0(s, [F]), 110.5(s, [4F])	—	845(s)	620(sh), 600(vs, br)	—
$[NbF_4(2,2'\text{-bipy})_2][NbF_6]$	139.7(s, [4F]), 103.2 (10 lines, J = 335 Hz)	—	—	615(vs), 603(s), 585(vs)	—
$[NbF_4(1,10\text{-phen})_2][NbF_6]$	138.0(s, [4F]), 103.4 (10 lines, J = 335 Hz)	—	—	608(vs), 586(vs), 565(sh)	—
$[NbOF_3(OPPh_3)_2]$	49.5(s, [F]), 37.8(s, [2F])	45.0(s, [P]), 36.0(s, [P])	1155(m), 1067(s)	602(m), 579(s)	941(s)
$[NbOF_3(OPMe_3)_2]$	41.5(s, [F]), 30.6(s, [2F])	67.1(s, [P]), 53.3(s, [P])	1140(m), 1087(s)	614(s), 582(m), 555(s)	958(s)
$[NbOF_3(dppmO_2)]$	55.7(s, [F]), 36.4(s, [2F])	46.6(d, [P])[e], 36.8(d, [P])[f]	1156(s), 1088(s)[f]	608(vs), 582(s)	944(s)
$[NbOF_3(dmso)_2]$	50.4(s, [F]), 38.0(s, [2F])	—	—	590(s), 564(s)	920(s)
$[NbOF_3(2,2'\text{-bipy})]$	49.0(s, [F]), 42.8(s, [2F])	—	—	612(vs), 579(s)	959(s)
$[NbOF_3(1,10\text{-phen})]$	Insol	—	—	610(sh), 594(s), 583(s)	970(s)
$[NbOF_3(tmeda)]$	Insol	—	—	587(s), 557(s)	920(s)
$[TaF_5(OPPh_3)]$	84.2(s, [F]), 54.7(s, [4F])	53.2(s)	1078(s)	617(sh), 592(vs, br)	—
$[TaF_5(OPMe_3)]$	82.5(s, [F]), 55.9(s, [4F])	76.9(s)	1092(vs)	601(sh), 583(vs, br)	—
$[TaF_5(OAsPh_3)]$	62.5(s, [F]), 48.6(s, [4F])	—	845(s)	617(sh), 592(vs, br)	—
$[TaF_4(2,2'\text{-bipy})_2][TaF_6]$	68.1(s, [4F]), 38.0(s, [6F])	—		605(sh), 581(vs)	—
$[TaF_4(1,10\text{-phen})_2][TaF_6]$	66.1(s, [4F]), 37.9(s, [6F])	—	—	605(sh), 576(s)	—
$[NbOCl_3(OPPh_3)_2]$	—	50.0(s, [P]), 38.8(s, [P])	1159(s), 1074(s)	325(s), 294(m)	936(s)
$[NbOCl_3(dppmO_2)]$	—	48.5(d, [P]), 36.8(d, [P])	1157(s), 1095(s)	327(s), 296(m)	928(s)
$[NbOCl_3(dppeO_2)]$	—	56.7(s, [P]), 44.9(s, [P])	1172(s), 1066(s)	320(s), 293(w)	943(s)
$[NbOCl_3(2,2'\text{-bipy})]$	—	—	—	349(s), 338(s)	943(s)
$[NbOCl_3(1,10\text{-phen})]$	—	—	—	338(br)	944(s)
$[NbOCl_3(tmeda)]$	—	—	—	341(s), 320(sh)	945(s)

[a] CH_2Cl_2–CD_2Cl_2 solution 298 K. [b] Nujol mull. [c] Ligand δ(P) = +28.0, ν(PO) = 1195. [d] Ligand δ(P) = +35.0, ν(PO) = 1160. [e] Ligand δ(P) = +25.0, ν(PO) = 1187. [f] Ligand δ(P) = +35.0, ν(PO) = 1174 cm^{-1} data from ref. 24.

Results and discussion

MF_5 complexes

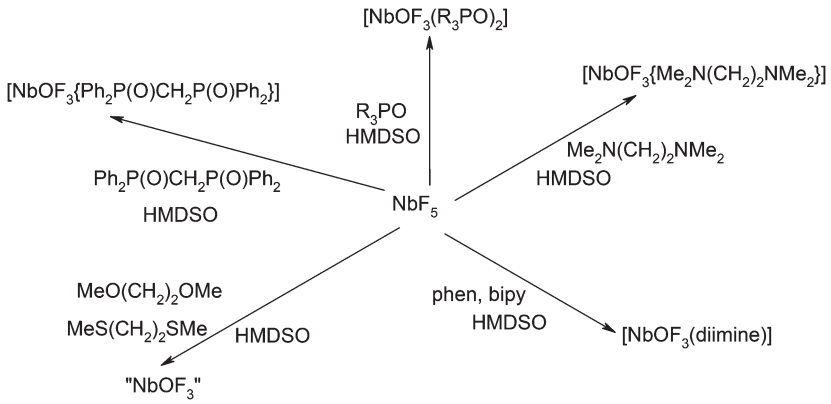
The reaction of NbF_5 with OPR_3 (R = Me or Ph) in rigorously anhydrous CH_2Cl_2 solution gave $[NbF_5(OPR_3)]$ as white powders, easily soluble in halocarbon solvents. The complexes have been mentioned before, but with limited characterisation data.[4d,11] The $^{19}F\{^1H\}$ NMR spectra show two singlets with relative intensities 1 : 4 and the $^{31}P\{^1H\}$ NMR spectra are singlets with large, high frequency coordination shifts (Table 1), consistent with their formulation as octahedral monomers. They also show broad singlet ^{93}Nb NMR resonances‡ $\delta \sim -1530$. The IR spectra show strong terminal Nb–F vibrations in the range 630–570 cm^{-1}, and ν(PO) are markedly lower than the "free" ligand values (Table 1). The $[NbF_5(OAsPh_3)]$ was made similarly from cold (0 °C) CH_2Cl_2 solution, but must be isolated rapidly, otherwise significant decomposition occurs, forming Ph_3AsF_2 ($\delta(^{19}F)$ = −89.4),[3a] $[NbF_6]^-$ (identified by *in situ* ^{19}F NMR spectroscopy)[5a] and other unidentified products. The tantalum complexes $[TaF_5(OPR_3)]$ and $[TaF_5(OAsPh_3)]$ were prepared similarly, and show corresponding trends in their spectroscopic properties (Table 1). However, the large quadrupole moment of ^{181}Ta (I = 7/2, Q = 3 × 10^{-28} m^2) results in fast quadrupolar relaxation and hence ^{181}Ta NMR resonances are not observable.

‡ ^{93}Nb 100% abundance, I = 9/2, Ξ = 24.44 MHz, Q = −0.2 × 10^{-28} m^2, D_c = 2740 is one of the more sensitive nuclei and, despite the medium size quadrupole moment, is readily observed in many systems. The zero reference is $[NbCl_6]^-$ in MeCN.

The reaction of NbF_5 with 2,2′-bipyridyl or 1,10-phenanthroline in CH_2Cl_2 solution gave very poorly soluble complexes with a 1 : 1 NbF_5 : diimine composition, originally assumed[12] to be seven-coordinate monomers. We found them to be sufficiently soluble in CD_2Cl_2 solution to obtain ^{1}H and ^{19}F $\{^1H\}$ NMR spectra after long accumulations, which show equivalent pyridyl rings and two ^{19}F resonances with intensity ratio of 2 : 3. The more intense resonance is the characteristic 10 line multiplet of $[NbF_6]^-$,[5a] leading to the revised formulation, $[NbF_4(diimine)_2][NbF_6]$, with an eight-coordinate cation, as found in other adducts with chelating bidentate ligands.[1] The $[TaF_4(diimine)_2][TaF_6]$ were made similarly and were even less soluble. Eight-coordination is also found in the diimine complexes of Zr and Hf (M′), $[M'F_4(diimine)_2]$.[13] The very poor solubility of the isolated $[MF_4(diimine)_2][MF_6]$ complexes made them unsuitable as synthons for the O/F exchange reactions, and hence studies were switched to using *in situ* syntheses, although the data on the isolated MF_5 adducts are useful for comparison purposes (Table 1).

$NbOF_3$ complexes

Treatment of an anhydrous CH_2Cl_2 solution of $[NbF_5(OPPh_3)]$ with one mol. equivalent of $OPPh_3$, followed by one mol. equivalent of HMDSO, resulted in slow formation of a white precipitate, identified as $[NbOF_3(OPPh_3)_2]$. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF_5 and two mol. equivalents of $OPPh_3$ to anhydrous CH_2Cl_2 yields a colourless solution,



Scheme 1 Synthesis of $NbOF_3$ adducts.

which was stirred for 20 min. and then one mol. equivalent of HMDSO and a small amount of MeCN were added. After 24 h the mixture, now containing much white precipitate, was concentrated *in vacuo*, and the $[NbOF_3(OPPh_3)_2]$ isolated. If the HMDSO was added before, or simultaneously with, the $OPPh_3$, very impure products resulted, and several hours seem necessary to complete the O/F exchange. The role of the MeCN is not entirely clear, but its presence seems necessary to obtain pure samples from the *in situ* preparations. In the syntheses of $[WO_2Cl_2\{RS(CH_2)_2SR\}]$ from WCl_6 or $WOCl_4$, $RS(CH_2)_2SR$ and HMDSO, use of MeCN–CH_2Cl_2 as solvent prevents the precipitation of polymeric WO_2Cl_2, by forming the nitrile adduct *in situ*.[10c] While a similar role may be present in the niobium systems, we note that attempts to isolate nitrile complexes failed (see below). The complexes $[NbOF_3(OPMe_3)_2]$ and $[NbOF_3(dppmO_2)]$ were prepared similarly to $[NbOF_3(OPPh_3)_2]$, but all attempts to obtain $[NbOF_3(OAsPh_3)_2]$ gave mixtures containing $[NbF_5(OAsPh_3)]$, $[NbF_6]^-$ and Ph_3AsF_2 (identified based upon *in situ* ^{19}F and ^{93}Nb NMR spectra). $[NbOF_3(OAsPh_3)]$ was originally reported to be formed from adding $OAsPh_3$ to a solution of Nb_2O_5 in conc. aqueous HF, although identified only by an IR spectrum.[7b] Using a 4 : 2 : 1 molar ratio of $OPPh_3$: HMDSO : NbF_5 in CH_2Cl_2–MeCN resulted only in isolation of $[NbOF_3(OPPh_3)_2]$, further O/F exchange did not occur. The complex $[NbOF_3(dmso)_2]$ was also isolated in high yield from reaction of NbF_5, dmso and HMDSO. As noted above, the very poor solubility of $[NbF_4(diimine)_2][NbF_6]$ made it impossible to redissolve them in CH_2Cl_2 for conversion to oxide-fluoride complexes. However, combination of the diimine and NbF_5 in a large volume of CH_2Cl_2 (which gave a opalescent solution), followed by addition of HMDSO, did give $[NbOF_3(diimine)]$. The $[NbOF_3(tmeda)]$ was made in high yield as an air-stable white powder by sequential reaction of NbF_5, tmeda and HMDSO.

In contrast, reaction of NbF_5 with ethers, including thf and $MeO(CH_2)_2OMe$ or with MeCN in CH_2Cl_2 followed by addition of HMDSO, gave white insoluble powders, which showed only traces of organic ligand in the IR spectra, and had very broad, ill-defined bands in the IR spectra, similar to those reported for $NbOF_3$.[6,7a] The attempted reaction of NbF_5, $MeS(CH_2)_2SMe$ and HMDSO also failed. Ether, nitrile and thioether adducts of NbF_5 are well characterised,[1,4,5] but it seems that these ligands are too weakly bound to the "$NbOF_3$" to prevent polymerisation and precipitation of ligand-free $NbOF_3$. Similar behaviour was observed with VO_2F,[3] and the niobium system seems to be a further example of the metal centre preferring to form oxide/fluoride bridges rather than coordinate to weak, neutral donor groups.[1] Thus far, attempts to isolate $TaOF_3$ complexes from TaF_5, ligand (ligand = OPR_3, dmso or 2,2′-bipy) and HMDSO under similar reaction conditions, have been unsuccessful.

The solid $[NbOF_3(OPR_3)_2]$, $[NbOF_3(dmso)_2]$ and $[NbOF_3(dppmO_2)]$ complexes are white powders, relatively air-stable in the solid state (some appear hygroscopic on prolonged exposure), although hydrolysed by wet solvents. They are easily soluble in CH_2Cl_2, whereas the $[NbOF_3(diimine)]$ are very poorly soluble, and $[NbOF_3(tmeda)]$ is insoluble. The ^1H and $^{31}P\{^1H\}$ NMR spectra (Table 1) of $[NbOF_3(OPMe_3)_2]$ show two phosphine oxide environments, and the $^{19}F\{^1H\}$ NMR spectrum contains two singlets with integrals in the ratio 1 : 2, which is consistent with *mer*-fluorines and one $OPMe_3$ *trans* to O and one *trans* to F. Attempts to record a ^{93}Nb NMR spectrum were unsuccessful (an effect observed for all the $NbOF_3$ adducts), contrasting with the ready observation of resonances from the NbF_5 adducts described above. The low symmetry at the niobium centre will result in a large electric field gradient, and unobservably broad lines due to fast quadrupolar relaxation. The different *trans*-influences of Nb–F and Nb=O groups in these complexes are also shown by the difference in ^{31}P chemical shifts for the *trans* disposed $OPMe_3$ ligands (~14 ppm), and similar differences are seen in the ν(PO) frequencies in the IR spectra which differ by >50 cm^{-1}. A strong band in the range 970–920 cm^{-1} is assignable to the terminal Nb=O vibrations.

Confirmation of the geometry of $[NbOF_3(OPMe_3)_2]$ comes from the X-ray crystal structure (Fig. 1).

There is no evidence in this molecule for O/F disorder in plane, which is a common problem in this area of chemistry (*cf.* $[VOF_3(OPPh_3)_2]$[2b]). The niobium is in a distorted octahedral environment with the axial F–Nb–F unit bent away from the

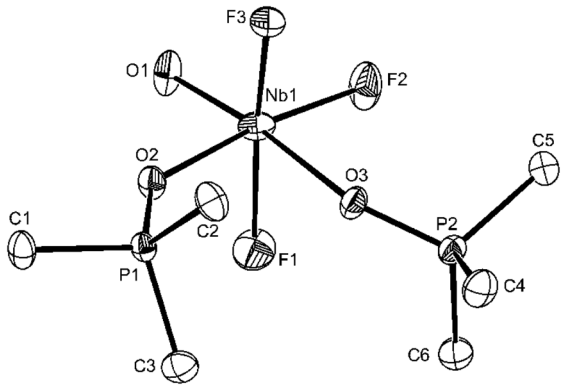


Fig. 1 The structure of the Nb1 centred molecule in $[NbOF_3(OPMe_3)_2]\cdot 1/3CH_2Cl_2$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms and the solvate molecule are omitted for clarity. The second Nb2 centred molecule is similar with the third (Nb3) being disordered. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.773(2), Nb1–F2 = 1.868(2), Nb1–F3 = 1.9184(19), Nb1–F1 = 1.935(2), Nb1–O2 = 2.104(2), Nb1–O3 = 2.205(2), P1–O2 = 1.526(2), P2–O3 = 1.521(2), O1–Nb1–F2 = 98.58(10), O1–Nb1–F3 = 97.00(11), F2–Nb1–F3 = 92.20(10), O1–Nb1–F1 = 95.09 (11), F2–Nb1–F1 = 92.72(10), F3–Nb1–F1 = 166.12(9), O1–Nb1–O2 = 91.75(9), F3–Nb1–O2 = 86.21(9), F1–Nb1–O2 = 86.63(9), F2–Nb1–O3 = 87.90(8), F3–Nb1–O3 = 84.76(9), F1–Nb1–O3 = 82.46(9), O2–Nb1–O3 = 81.80(8).

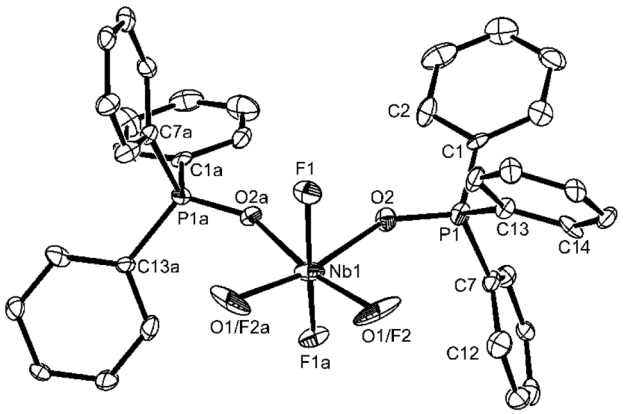


Fig. 2 The structure of $[NbOF_3(OPPh_3)_2]$ showing the atom numbering scheme. The phenyl rings are numbered cyclically starting at the *ipso* C atom. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The molecule has two-fold symmetry. Notice the disorder at the atom site O1/F2. Symmetry operation: $a = 1 - x, -y, z$. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.850(4), Nb1–F2 = 1.850(4), Nb1–F1 = 1.932(4), Nb1–O2 = 2.189(4), P1–O2 = 1.532(4), O1–Nb1–F2 = 108.2(4), O1–Nb1–F1 = 92.06(19), F2–Nb1–F1 = 95.36(18), F1–Nb1–F1a = 167.3(2), O1–Nb1–O2 = 86.8(2), F1–Nb1–O2 = 84.23(16), O2–Nb1–O2 = 78.3(2).

oxido-ligand. The Nb–$F_{trans\ F}$ are longer than Nb–$F_{trans\ O}$ by ~0.06 Å and the Nb=O of 1.773(2) Å is consistent with the expected multiple bond character. The Nb–$O(P)_{trans\ F}$ distances of 2.104(2) Å and Nb–$O(P)_{trans\ O}$ = 2.205(2) Å show the disparate effects of the *trans* donor and parallel the spectroscopic evidence. Curiously, *d*(P–O) in the two phosphine oxide ligands are only slightly different. The spectroscopic data on $[NbOF_3(OPPh_3)_2]$ (Table 1) are very similar to those of the $OPMe_3$ complex discussed, but in this case the X-ray structure (Fig. 2) shows F/O disorder *trans* to $OPPh_3$, and the bond length and angle data are correspondingly unreliable, although the identity of the complex is confirmed.

The structural parameters of $[NbOF_3(dppmO_2)]$ are generally similar to those already discussed above, and this complex seems free of O/F disorder (Fig. 3).

The $[NbOF_3(tmeda)]$ is insoluble in non-coordinating solvents and MeCN, and is partially decomposed by dmf or dmso which prevented solution measurements. However, the $[NbOF_3(diimine)]$, although very poorly soluble in chlorocarbons or MeCN (a property shared with the NbF_5 analogues above, and also the ZrF_4, HfF_4, VOF_3 and VO_2F diimine complexes),[2,3,13] gave ^1H NMR spectra showing inequivalent pyridyl rings, and hence that the diimine was *trans* to O/F. The $^{19}F\{^1H\}$ NMR spectrum of $[NbOF_3(2,2'\text{-bipy})]$ (Table 1) shows two resonances in the ratio 1 : 2 consistent with a *mer* arrangement of the fluorines, and the chemical shifts are ~100 ppm to low frequency of those observed for the $[NbF_4(diimine)_2]^+$. The $[NbOF_3(1,10\text{-phen})]$ was very poorly soluble in weakly coordinating solvents and a convincing $^{19}F\{^1H\}$ NMR spectrum was not obtained. The diimine complexes are readily hydrolysed in solution in CH_2Cl_2 or MeCN forming $[NbF_6]^-$ ions, based upon ^{19}F NMR evidence and also shown by attempts to obtain crystals of $[NbOF_3(2,2'\text{-bipy})]$ for an X-ray study which produced a few poor quality crystals of $[2,2'\text{-bipyH}][NbF_6]$. The solids also hydrolyse slowly on exposure to the atmosphere.

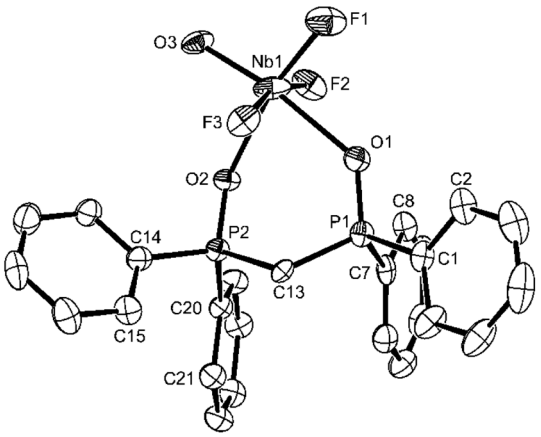
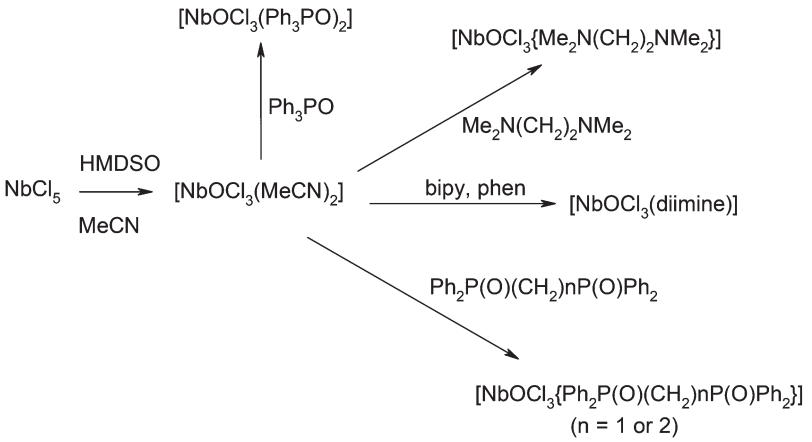


Fig. 3 The structure of $[NbOF_3(dppmO_2)]$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1–O3 = 1.782(4), Nb1–F1 = 1.850(3), Nb1–F2 = 1.912(3), Nb1–F3 = 1.970(3), Nb1–O2 = 2.171(3), Nb1–O1 = 2.257(4), P1–O1 = 1.508(4), P2–O2 = 1.509(3), O3–Nb1–F1 = 100.96(17), O3–Nb1–F2 = 98.04(16), F1–Nb1–F2 = 95.28(15), O3–Nb1–F3 = 95.34(16), F1–Nb1–F3 = 94.41(15), O3–Nb1–O2 = 91.31(15), F2–Nb1–O2 = 83.99(13), F3–Nb1–O2 = 83.24(13), F1–Nb1–O1 = 87.03(15), F2–Nb1–O1 = 84.16(14), F3–Nb1–O1 = 80.84(13), O2–Nb1–O1 = 80.66(13), F2–Nb1–F3 = 161.67 (13).



Scheme 2 Synthesis of $NbOCl_3$ adducts.

$NbOCl_3$ complexes

Solid $NbOCl_3$ contains dimeric $[Cl_2Nb(O)(\mu\text{-}Cl)_2Nb(O)Cl_2]$ units linked into chains *via* unsymmetrical oxide bridges, giving six-coordinate niobium.[14] The syntheses of the $[NbOCl_3(L\text{–}L)]$ (L–L = 2,2′-bipy, 1,10-phen, $dppmO_2$, $dppeO_2$, tmeda and 2 × $OPPh_3$) were carried out in anhydrous MeCN solution, with the reversed order of reagent addition to that used for the oxide-fluoride syntheses, *i.e.* reacting $NbCl_5$ with HMDSO to form '$NbOCl_3$' *in situ*, followed by addition of the neutral ligand (Scheme 2). The initially yellow solution of $NbCl_5$ in MeCN rapidly pales on addition of HMDSO, indicating formation of $[NbOCl_3(MeCN)_2]$ *in situ*,[9b,15] which was converted into near colourless $[NbOCl_3(L\text{–}L)]$ upon addition of the neutral ligand. Once isolated, the $[NbOCl_3(tmeda)]$ is essentially insoluble in non-coordinating solvents, although crystals were grown adventitiously from the reaction filtrate. The other complexes are soluble in CH_2Cl_2 or MeCN. The IR spectra of the complexes (Table 1) show strong ν(Nb═O) in the region 920–950 cm^{-1} and ν(NbCl) 290–350 cm^{-1} with disparate ν(P═O) vibrations for the phosphine oxide groups *trans* to Cl and *trans* to O. In solution, the ^1H and $^{31}P\{^1H\}$ NMR spectra of $[NbOCl_3(L\text{–}L)]$ (L–L = $dppmO_2$, $dppeO_2$, 2 × $OPPh_3$) show the expected inequivalence of the neutral donor groups, but attempts to record ^{93}Nb spectra were unsuccessful; as with the oxide-fluorides this is attributed to fast quadrupolar relaxation in the low symmetry electric fields.

X-Ray crystal structures were obtained for five of the complexes. The structure of $[NbOCl_3(OPPh_3)_2]$ has been reported previously and shows[16] *mer*-chlorines, and *cis* $OPPh_3$ groups, with O/Cl disorder *trans* to $OPPh_3$. The crystal structures of the two diphosphine dioxide complexes (Fig. 4 and 5) show *d*(Nb═O) slightly shorter by ~0.1 Å compared to the oxide fluoride complexes, but with similarly disparate *d*(Nb–O(P)) suggesting the *trans* influence of F and Cl are similar in these complexes. The *d*(Nb═O) and *d*(Nb–Cl) distances in a range of $NbOCl_3$ adducts cover quite a narrow range,[8,9,15,16] suggesting that these are the dominant bonding interactions, with the neutral ligands completing the coordination sphere, but having little influence on the Nb═O and Nb–Cl bonds.

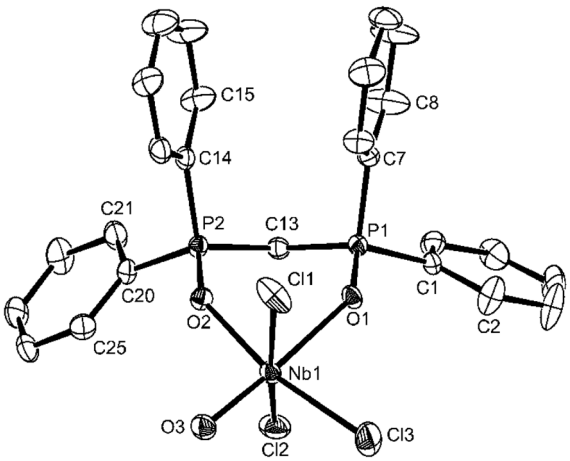


Fig. 4 The structure of $[NbOCl_3(dppmO_2)]\cdot n$MeCN showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are omitted for clarity. The solvate acetonitrile is also omitted. The phenyl rings are numbered cyclically starting at the *ipso*-C atom. Selected bond lengths (Å) and angles (°): Nb1–O3 = 1.706(3), Nb1–O2 = 2.095(3), Nb1–O1 = 2.266(3), Nb1–Cl3 = 2.3463(13), Nb1–Cl1 = 2.3815(13), Nb1–Cl2 = 2.4203(12), O3–Nb1–O2 = 94.47(12), O2–Nb1–O1 = 80.48(10), O3–Nb1–Cl3 = 98.84(10), O1–Nb1–Cl3 = 86.17(7), O3–Nb1–Cl1 = 97.53(10), O2–Nb1–Cl = 86.85(8), O1–Nb1–Cl1 = 84.56(7), Cl3–Nb1–Cl1 = 92.45(6), O3–Nb1–Cl2 = 93.91(10), O2–Nb1–Cl2 = 85.00(8), O1–Nb1–Cl2 = 83.41(7), Cl3–Nb1–Cl2 92.98(5), Cl1–Nb1–Cl2 = 166.43(4).

The structure of $[NbOCl_3(tmeda)]$ (Fig. 6) shows the same features as those of the oxygen donor complexes, although the carbon atoms about N2 show some disorder; there is no evidence for O/Cl disorder. The dimensions in the structure of $[NbOCl_3(2,2'\text{-bipy})]$ (Fig. 7) are also unexceptional, although the octahedron about the niobium is more distorted due to the small chelate bite of the 2,2′-bipyridyl (<N1–Nb1–N2 = 69.52(21)°).

Attempts to obtain a complex of $NbOCl_3$ with 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3-tacn) gave a mixture of products. Recrystallisation of the mixture from MeCN gave a few crystals identified as $[(Me_3\text{-tacn})H]_2[NbOCl_5]$. The anion

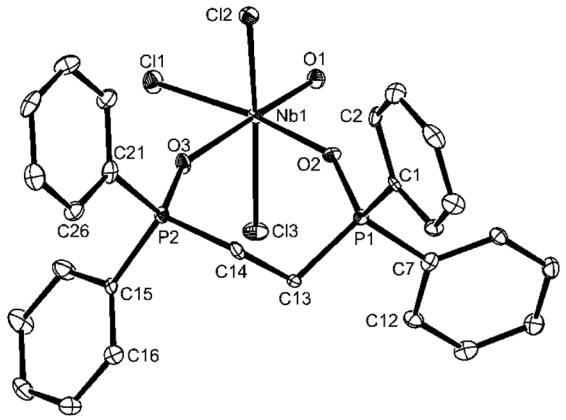


Fig. 5 The structure of $[NbOCl_3(dppeO_2)]\cdot n$MeCN showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are omitted for clarity. The phenyl rings are numbered cyclically starting at the *ipso*-C atom. The solvate acetonitrile is also omitted. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.702(3), Nb1–O2 = 2.077(3), Nb1–O3 = 2.219(3), Nb1–Cl1 = 2.3602(12), Nb1–Cl3 = 2.4136(12), Nb1–Cl2 = 2.4210(13), O1–Nb1–O2 = 93.09(12), O2–Nb1–O3 = 82.31(10), O1–Nb1–Cl1 = 97.74(10), O3–Nb1–Cl1 = 86.86(8), O1–Nb1–Cl3 = 97.02(10), O2–Nb1–Cl3 = 86.17(8), O3–Nb1–Cl3 = 84.91(8), Cl1–Nb1–Cl3 = 92.43(4), O1–Nb1–Cl2 = 94.82(10), O2–Nb1–Cl2 = 86.11(8), O3–Nb1–Cl2 = 82.73(8), Cl1–Nb1–Cl2 93.00(4), Cl3–Nb1–Cl2 = 166.19(4).

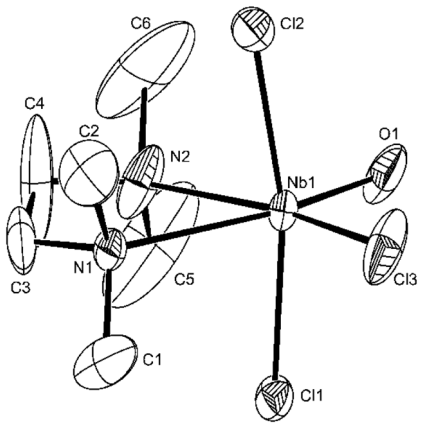


Fig. 6 The structure of $[NbOCl_3(tmeda)]$ showing the atom labelling scheme. The carbon atoms associated with N2 show some disorder. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.798(5), Nb1–N2 = 2.331(8), Nb1–N1 = 2.518(5), Nb1–Cl3 = 2.328(3), Nb1–Cl2 = 2.348(3), Nb1–Cl1 = 2.358(2), O1–Nb1–N2 = 92.5(3), O1–Nb1–Cl3 = 103.5(2), O1–Nb1–Cl2 = 94.3(3), N2–Nb1–Cl2 = 86.1(3), Cl3–Nb1–Cl2 = 91.21(16), O1–Nb1–Cl1 = 96.5(3), N2–Nb1–Cl1 = 87.6(3), Cl3–Nb1–Cl1 = 91.87(10), N2–Nb1–N1 = 74.1(2), Cl3–Nb1–N1 = 89.86(16), Cl2–Nb1–N1 = 84.00(15), Cl1–Nb1–N1 = 84.09(15), Cl2–Nb1–Cl1 = 167.70(10).

has been structurally characterised with a variety of cations, but often the niobium is on a high symmetry site which results in O/Cl disorder.[17] In the present case the structure appears to free of such disorder and the data are presented as ESI.†

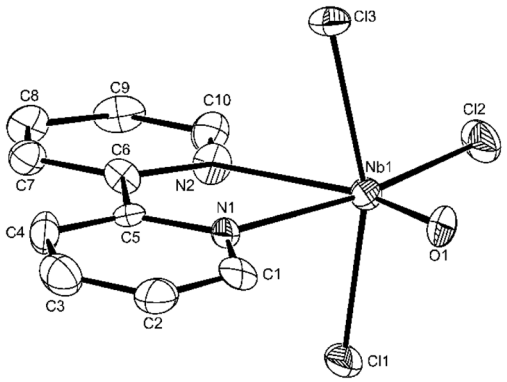


Fig. 7 The structure of the Nb1 centred molecule in $[NbOCl_3(2,2'\text{-bipy})]$ showing the atom labelling scheme. This molecule has no crystallographic symmetry whereas the Nb2 centred molecule has 2-fold symmetry. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.694(6), Nb1–Cl1 = 2.363(2), Nb1–Cl2 = 2.356(2), Nb1–Cl3 = 2.372(2), Nb–N1 = 2.262(6), Nb1–N2 = 2.385(6), O1–Nb1–N1 = 89.3(3), O1–Nb1–Cl2 = 104.8(2), O1–Nb1–Cl1 = 98.0(2), O1–Nb1–Cl3 = 97.7(2), Cl2–Nb1–N2 = 96.41(15), N1–Nb1–N2 = 69.5(2), Cl1–Nb1–N1 = 84.50(16), Cl2–Nb1–Cl1 = 94.18(7), Cl3–Nb1–Cl2 = 92.76(7), Cl3–Nb1–N1 = 84.37(16), N2–Nb1–Cl1 = 81.08(15), Cl3–Nb1–N2 = 80.13 (15).

Comparisons of NbF_5, $NbOF_3$ and $NbOCl_3$ complexes

Comparison of the spectroscopic data in Table 1 for $[NbF_5(OPR_3)]$ and $[NbOF_3(OPR_3)_2]$ shows very significant differences due to replacement of two fluoride ligands by the oxo-group. The ^{19}F and ^{31}P chemical shifts are very different, with those of $[NbF_5(OPR_3)]$ at much higher frequency for each nucleus. Similar differences are apparent in the ^{19}F chemical shifts for the two series of N-donor complexes. The data demonstrate that the presence of the strong π-donating oxo-group significantly changes the electron density at the Nb(v) centre, making it much less electron poor, and hence a weaker Lewis acid. Within the $NbOF_3$ complexes there is also a large *trans* influence of the oxo-group which results in significantly longer bonds to the *trans* ligand than for those groups *trans* to fluorine. The *d*(P═O) show very small differences, although the relative *trans* influence is clear in the *ν*(P═O) vibrations in the IR spectra. Comparing the structural and spectroscopic data on corresponding $NbOF_3$ and $NbOCl_3$ complexes reveals rather small differences. The *d*(Nb═O) in these and in literature examples of the oxide chloride complexes[8,9,15,16] show they occur in a narrow range, ~1.7–1.8 Å, irrespective of the halide or neutral co-ligands present. Similarly, $d(\text{Nb–Cl})_{trans\ L}$ are relatively insensitive to the nature of L (the ligand types are too restricted to make a similar comparison for the fluoride).

The bond angles about the niobium centres also show significant deviations from those expected for a regular octahedral geometry. The factors determining the geometry adopted by ML_6 complexes of transition metals as a function of ligand types (σ-donor only, or σ and π donor), d^n count and ligand architecture have been discussed in several articles,[18] and the fact that $[MF_6]^{n-}$ species are O_h and $[M(CH_3)_6]^{n-}$ (n =

0, 1, 2 *etc*.) are trigonal prisms has been rationalised in terms of electronic factors by MO calculations.[19] The niobium oxide halide structures discussed in the present work (12e, d^0 complexes) are based upon distorted octahedral geometries, as would be expected, given the presence of dominant σ and π donor ligands. As observed in many early transition metal complexes containing M═O bonds, the angles involving the latter, O═M–L and O═M–X are larger than X–M–X, X–M–L, or L–M–L, in effect the electron rich multiply bonded M═O unit occupies more space about the metal centre. Superimposed upon this are smaller effects arising from the steric demands of the X and L groups and constraints of neutral ligand geometries, such as chelate bites in the bidentates. In the *cis*-MOX_3L_2 unit the axial X–M–X group bends away from the M═O and towards the neutral co-ligands.[2,3,5,8–10]

Comparing the IR data within the two series of $NbOX_3$ complexes shows ν(Nb═O) lying in a range ~920–970 cm^{-1}, and the ν(P═O) in corresponding phosphine oxide adducts also show little difference. Hence we conclude that the $NbOX_3$ core has the dominant structural and spectroscopic effects in these complexes.

The differences between $NbOF_3$ and $NbOCl_3$ as acceptors towards weaker donor ligands such as ethers or nitriles, where the latter forms complexes with thf, $MeO(CH_2)_2OMe$, MeCN, *etc*.,[4,9,15] but attempts to isolate analogues with $NbOF_3$ result in intractable, ligand-free products ($NbOF_3$ polymer). This can be ascribed to the preference of the niobium centre to form fluoride bridges over weak Nb–L bonds, and is seen in other fluoride and oxide fluoride systems.[1]

Finally, these niobium complexes can be compared with those of the 3d analogue, vanadium. VOF_3 forms similar phosphine oxide, diimine and diamine complexes to $NbOF_3$, but also complexes with ethers, thioethers and nitriles.[2] The differences are again readily rationalised by the niobium's preference for fluorine bridges; $NbOF_3$ is an inert, very strongly bridged polymer (above), whereas VOF_3 although (weakly) F-bridged in the solid,[20] easily vapourises as a monomer on heating and dissolves in most organic solvents. The complexes of $VOCl_3$ with neutral ligands are thermally and often photochemically unstable, and extremely readily hydrolysed and reduced (often spontaneously) to V(IV) or V(III) compounds,[21] whereas the $NbOCl_3$ adducts remain pentavalent, unless specifically treated with reducing agents.

Conclusions

The O/F exchange reaction between complexes of the binary fluoride NbF_5 and a siloxane have been shown to produce complexes of the otherwise intractable oxide-fluoride, $NbOF_3$, in good yield. However, further O/F exchange to form derivatives of NbO_2F did not occur under similar conditions. Comparison of the spectroscopic properties of the NbF_5 and $NbOF_3$ complexes demonstrates the substantial effect on the metal centre of replacing two fluoride by the stronger π-donor oxido-group.

The $HMDSO/MF_n$ route may well offer a synthetic pathway to oxide fluoride complexes of other high valent early metal complexes, *e.g.* those of Mo, W, Ti or Zr. $TaOF_3$ complexes are not formed under analogous reaction conditions; further studies are required to develop a suitable route to these.

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. ^1H, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and ^{93}Nb NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to the protio resonance of the solvent, external $CFCl_3$, 85% H_3PO_4, and $[NEt_4][NbCl_6]$ in CD_3CN, respectively. Microanalyses were undertaken by Medac Ltd or London Metropolitan University. Solvents were dried prior to use: THF, Et_2O and $MeOCH_2CH_2OMe$ by distillation from sodium benzophenone ketyl, MeCN and CH_2Cl_2 from CaH_2. $OPMe_3$ was sublimed *in vacuo*, $OPPh_3$, $OAsPh_3$, 2,2′-bipy, 1,10-phen were heated *in vacuo*, and tmeda distilled from BaO. All preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere.

$[NbF_5(OPPh_3)]$: A solution of $OPPh_3$ (0.262 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added to finely powdered NbF_5 (0.188 g, 1.0 mmol), and vigorously stirred to give a clear solution. This was filtered to remove any residual solid and concentrated *in vacuo* to ~5 mL. On standing a white powdered separated, which was filtered off and dried *in vacuo*. Yield 0.40 g, 85%. Anal: required for $C_{18}H_{15}F_5NbOP$ (466.2): C, 46.4; H, 3.2. Found: C, 46.9; H, 3.6%. ^1H NMR (CD_2Cl_2, 293 K): 7.1–7.6 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): +161.8 (s, [F]), +128.6 (s, [4F]); (210 K): +157.0 (s, [F]), +125.7 (s, [4F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 53.9 (s). ^{93}Nb NMR (CD_2Cl_2, 293 K): −1530 (br s). IR (Nujol/cm^{-1}): 1061 (vs) PO, 624 (sh), 608 (vs, br) NbF.

$[NbF_5(OPMe_3)]$: Made similarly to the $OPPh_3$ adduct. Yield 75%. Anal: required for $C_3H_9F_5NbOP$ (280.0): C, 12.9; H, 3.2. Found: C, 13.2; H, 3.5%. ^1H NMR (CD_2Cl_2, 293 K): 1.9 (d, $^2J_{PH}$ = 15 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 157.6 (s, [F]), 134.5 (s, [4F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): +75.6 ^{93}Nb NMR (CD_2Cl_2, 293 K): −1530 (br, s). IR (Nujol/cm^{-1}): 1092 (vs) PO, 615 (vs, br), 582 (m) NbF.

$[NbF_5(OAsPh_3)]$: Prepared as for the $OPPh_3$ analogue except that the complex was prepared in ice-bath and solution stirred for 5 min. It was then concentrated *in vacuo* and the precipitated solid isolated immediately. If the solid is left in solution a yellow and then brown colour develops and *in situ* NMR data shows formation of Ph_3AsF_2, $[NbF_6]^-$ and other unidentified impurities. The pure solid seems stable for some weeks in a freezer. Yield 55%. Anal: required for $C_{18}H_{15}AsF_5NbO$ (510.1): C, 42.4; H, 3.0. Found: C, 42.4; H, 3.0%. ^1H NMR (CD_2Cl_2, 293 K): 7.2–7.6 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): +145.0 (s, [F]), +110.5 (s, [4F]). ^{93}Nb NMR (CD_2Cl_2, 293 K): −1511 (br, s). IR (Nujol/cm^{-1}): 845 (m) AsO, 620 (sh), 600 (vs, br) NbF.

$[NbF_4(2,2'\text{-bipy})_2][NbF_6]$: NbF_5 (0.188 g, 1.0 mmol) was added to CH_2Cl_2 (20 mL) and vigorously stirred, whilst a solution of 2,2′-bipy (0.16 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added, resulting in rapid precipitation of a fine white powder. After 2 h the solid was isolated by filtration, rinsed with diethyl ether (5 mL) and dried *in vacuo.* Yield 0.30 g, 86%. Anal: required for $C_{20}H_{16}F_{10}N_4Nb_2$ (688.2): C, 34.9; H, 2.3; N, 8.1. Found: C, 34.7; H, 2.2, N, 8.1%. ^{1}H NMR (CD_2Cl_2, 293 K): 9.34 (d, [2H], J = 9 Hz), 8.63 (d, [2H], J = 9 Hz), 8.40 (m, [2H]), 7.78 (m, [2H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): +139.7 (s, [4F]), +103.2 (10 lines, J = 335 Hz). IR (Nujol/cm^{-1}): 615 (vs), 603 (s), 585 (vs) NbF.

$[NbF_4(1,10\text{-phen})_2][NbF_6]$: was made similarly in 89% yield. Anal: required for $C_{24}H_{16}F_{10}N_4Nb_2$ (736.2): C, 39.2; H, 2.2; N, 7.6. Found: C, 39.2; H, 2.3, N, 7.4%. ^{1}H NMR (CD_3CN, 293 K): 9.20 (d, [2H], J = 9 Hz), 8.96 (d, [2H], J = 9 Hz), 8.27 (m, [2H]), 8.17 (m, [2H]). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): +138.0 (s, [4F]), +103.4 (10 lines, J = 335 Hz). IR (Nujol/cm^{-1}): 608 (vs), 586 (vs), 565 (sh) NbF.

$[NbOF_3(OPPh_3)_2]$: NbF_5 (0.19 g, 1 mmol) and $OPPh_3$ (0.56 g, 2 mmol) were added to dry CH_2Cl_2 (25 mL) and the mixture stirred for 20 min. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred overnight at room temperature. The solvents were removed *in vacuo* leaving a slightly sticky white powder which was stirred with dry diethyl ether (40 mL) when it became a fine white powder. This was filtered off, rinsed with diethyl ether (10 mL) and dried *in vacuo*. Yield 0.41 g, 57%. Refrigeration of the filtrate gave small crystals used for the X-ray data collection. Anal: required for $C_{36}H_{30}F_3NbO_3P_2$ (722.5): C, 59.9; H, 4.2. Found: C, 59.6; H, 4.3%. ^{1}H NMR (CD_2Cl_2, 293 K): 7.1–7.7 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 49.5 (s, [F]), 37.8 (s, [2F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 45.0 (s, [P]), 36.0 (s, [P]). ^{93}Nb NMR (CD_2Cl_2, 293 K): not observed. IR (Nujol/cm^{-1}): 1155 (m), 1067 (s) PO, 941 (s) NbO, 602 (m), 579 (s) NbF.

$[NbOF_3(OPMe_3)_2]$: was made similarly Yield 50.5%. Crystals were obtained by refrigeration overnight of the filtrate from the synthesis solution. Anal: required for $C_6H_{18}F_3NbO_3P_2{\cdot}CH_2Cl_2$ (435.0): C, 19.3; H, 4.6. Found: C, 18.7; H, 4.3%. ^{1}H NMR (CD_2Cl_2, 293 K): 1.60 (d, [H] $^2J_{PH}$ = 13 Hz), 1.86 (d, [H] $^2J_{PH}$ = 13 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 41.5 (s, [F]), 30.6 (s, [2F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 67.1 (s, [P]), 53.3 (s, [P]). ^{93}Nb NMR (CD_2Cl_2, 293 K): not observed. IR (Nujol/cm^{-1}): 1140 (m), 1087 (s) (PO), 958 (s), NbO, 614 (s), 555 (s) NbF.

$[NbOF_3(2,2'\text{bipy})]$: NbF_5 (0.19 g, 1 mmol) was dissolved in CH_2Cl_2 (200 mL) and dry 2,2′-bipy (0.16 g, 1 mmol) in CH_2Cl_2 (10 mL) was added with stirring. After 15 min. hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred overnight at room temperature, producing a white precipitate. The mixture was concentrated to ~5 mL *in vacuo*, the white solid filtered off, rinsed with diethyl ether and dried *in vacuo*. Yield 0.27 g, 83%. Anal: required for $C_{10}H_8F_3N_2NbO$ (322.1): C, 37.3; H, 2.5; N, 8.7. Found: C, 37.5; H, 2.4; N, 8.6%. ^{1}H NMR (CD_2Cl_2, 293 K): 9.28 (s, [H]), 9.17 (s, [H]), 8.54 (m, [H]), 8.36 (m, [H]), 8.32 (s, [2H]), 7.85 (s, [H]), 7.72 (s, [H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 49.0 (s, [F]), 42.8 (s, [2F]). IR (Nujol/cm^{-1}): 959 (s) NbO, 612 (vs), 579 (s) NbF.

$[NbOF_3(1,10\text{-phen})]$: NbF_5 (0.19 g, 1 mmol) was dissolved in CH_2Cl_2 (200 mL) and dry 1,10-phen (0.18 g, 1 mmol) in CH_2Cl_2 (10 mL) added with stirring, producing some fine white precipitate. After 5 min hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred for 48 h. at room temperature, producing a dense white precipitate. The precipitate was filtered off, rinsed with diethyl ether (10 mL) and dried *in vacuo*. Yield 0.30 g, 86%. Anal: required for $C_{12}H_8F_3N_2NbO$ (346.1): C, 41.6; H, 2.3; N, 8.1. Found: C, 41.4; H, 2.3; N, 7.9%. ^{1}H NMR (CD_2Cl_2, 293 K): 9.36 (s, [H]), 9.28 (s, [H]), 8.77 (m, [H]), 8.56 (m, [H]), 8.19 (s, [H]), 8.13 (s, [H]), 8.02 (s, [H]), 7.90 (s, [H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): insufficiently soluble. IR (Nujol/cm^{-1}): 970 (s) NbO, 610 (sh), 594 (s), 583 (s) NbF.

$[NbOF_3(dppmO_2)]$: NbF_5 (0.19 g, 1 mmol) and $dppmO_2$ (0.41 g, 1 mmol) were added to dry CH_2Cl_2 (25 mL) and the mixture stirred for 20 min. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred overnight at room temperature. The solvents were removed *in vacuo* leaving a slightly sticky cream powder which was extracted with CH_2Cl_2 (20 mL), filtered to remove some undissolved solid, and concentrated to ~5 mL. Dry diethyl ether (20 mL) was added slowly and the cream precipitate filtered off and dried *in vacuo*. Yield 0.34 g, 45%. Refrigeration of the filtrate for 5 d. gave crystals suitable for the X-ray data collection. Anal: required for $C_{25}H_{22}F_3NbO_3P_2$ (582.3): C, 51.6; H, 3.8. Found: C, 51.5; H, 3.9%. ^{1}H NMR (CD_2Cl_2, 293 K): 7.82–7.15 (m, [10H]), 3.70 (m, [H], J = 13 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 55.7 (s, [F]), 36.4 (s, [2F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 46.4(d, [P], $^2J_{pp}$ = 17 Hz), 36.8 (s, [P], $^2J_{pp}$ = 17 Hz). IR (Nujol/cm^{-1}): 1156 (s), 1088 (s) PO, 944 (s) NbO, 608 (vs), 582 (s) NbF.

$[NbOF_3(dmso)_2]$: NbF_5 (0.19 g, 1 mmol) was added to dry CH_2Cl_2 (25 mL), followed by dry dmso (0.5 mL) and the mixture stirred for 20 min. producing a clear colourless solution. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred for 6 h at room temperature, during which a fine microcrystalline solid was deposited. The solid was filtered off, rinsed by diethyl ether (5 mL) and dried *in vacuo.* Yield 0.25 g, 78%. Anal: required for $C_4H_{12}F_3NbO_3S_2$ (322.2): C, 14.9; H, 3.8. Found: C, 15.1; H, 3.9%. ^{1}H NMR (CD_2Cl_2, 293 K): 2.65 (br); (253 K): 2.59 ([6H]), 2.55 ([6H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 50.4 (s, [F]), 38.0 (s, [2F]). IR (Nujol/cm^{-1}): 1039 (s), 1005 (s) Me_2SO, 920 (s) NbO, 590 (s), 564 (s) NbF.

$[NbOF_3(tmeda)]$: NbF_5 (0.19 g, 1 mmol) was added to dry CH_2Cl_2 (200 mL), followed by dry tmeda (0.12 g, 1 mmol) and the mixture stirred for 20 min. producing a cloudy suspension. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred overnight at room temperature, during which a fine white powder was deposited. The solid was filtered off, rinsed by diethyl ether (5 mL) and dried *in vacuo.* Yield 0.24 g, 85%. Anal: required for $C_6H_{16}F_3N_2NbO{\cdot}CH_2Cl_2$ (367.0): C, 21.9; H, 4.9; N, 7.6. Found:

C, 21.4; H, 5.5; N, 7.9%. Insoluble in non-donor solvents. IR (Nujol/cm^{-1}): 920 (s) NbO, 587 (s) 557 (s) NbF.

[$NbOCl_3$(2,2′-bipy)]: $NbCl_5$ (0.067 g, 0.25 mmol) was dissolved into acetonitrile (4 mL) to give a bright yellow-green solution. Hexamethyldisiloxane (0.040 g, 0.25 mmol) was added and the mixture was stirred for 10 min. during which time the solution turned very pale. 2,2′-Bipy (0.039 g, 0.25 mmol) in acetonitrile (4 mL) was added slowly with stirring. After 30 min. the solution was concentrated *in vacuo* and the white precipitate filtered off, and dried *in vacuo*. Yield 0.048 g, 52%. Crystals of [$NbOCl_3$(2,2′-bipy)] were grown from acetonitrile solution in the freezer. Anal: required for $C_{10}H_8Cl_3N_2NbO$ (371.4): C, 32.3; H, 2.2; N, 7.5. Found: C, 32.3; H, 2.1; N, 7.7%. ^{1}H NMR (CD_2Cl_2, 295 K): 8.98 (s, [H]), 8.91 (s, [H]), 8.31 (br m, [4H]), 7.79 (s, [H]), 7.73 (s, [H]). IR (Nujol/cm^{-1}): 943 (s) NbO, 349 (s), 338 (s) NbCl.

[$NbOCl_3$(1,10-phen)]: The white compound was made in an analogous way to [$NbOCl_3$(2,2′-bipy)]. Yield 61%. Anal: required for $C_{12}H_8Cl_3N_2NbO$ (395.4): C, 36.4; H, 2.0; N, 7.1. Found: C, 36.3; H, 2.0; N, 7.1%. ^{1}H NMR (CD_2Cl_2, 295 K): 9.86 (s, [H]), 9.75 (s, [H]), 8.88 (m, [H]), 8.74 (m, [H]), 8.17 (s, [2H]), 8.08 (s, [2H]). IR (Nujol/cm^{-1}): 944 (s) NbO, 338 (vbr, s) NbCl.

[$NbOCl_3$(tmeda)]: $NbCl_5$ (0.270 g, 1.0 mmol) was dissolved into acetonitrile (10 mL) and hexamethyldisiloxane (0.244 g, 1.5 mmol) was added. After 10 min. tmeda (0.14 g, 1.2 mmol) in dichloromethane (4 mL) was added slowly to the reaction mixture with stirring. After 2 h the mixture was concentrated *in vacuo* and the resulting precipitate was filtered off and dried *in vacuo*. Yield 0.055 g, 17%. Single crystals of [$NbOCl_3$(tmeda)] were grown from the filtrate in the freezer. Anal: required for $C_6H_{16}Cl_3N_2NbO$ (331.4): C, 21.7; H, 4.9; N, 8.5. Found: C, 21.6; H, 4.8; N, 8.4%. ^{1}H NMR (CD_2Cl_2, 295 K): insoluble. IR (Nujol/cm^{-1}): 945 (s) NbO, 341 (s) 320 (sh) NbCl.

[$NbOCl_3(OPPh_3)_2$]: $NbCl_5$ (0.270 g, 1.0 mmol) was dissolved in acetonitrile (5 mL) whilst stirring and hexamethyldisiloxane (0.162 g, 1.0 mmol) was added. After 10 min. $OPPh_3$ (0.556 g, 2 mmol) was added producing a milky white mixture. The reaction was left to stir for 2 h and the white solid filtered off and dried *in vacuo*. Yield: 0.450 g, 58%. Anal: required for $C_{36}H_{30}O_3Cl_3NbP_2$ (771.8): C, 56.0; H, 3.9. Found: C, 55.7; H, 3.6%. ^{1}H NMR (CD_2Cl_2, 295 K): 7.7–7.2 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 50.0 (s, [P]), 38.8 (s, [P]). IR (Nujol/cm^{-1}): 1159 (s), 1074(s) PO, 936 (s) NbO, 325(s), 294(m) NbCl.

[$NbOCl_3(dppeO_2)$]: $NbCl_5$ (0.068 g, 0.25 mmol) was dissolved in acetonitrile (5 mL) and hexamethyldisiloxane (0.062 g, 0.38 mmol) was added. The mixture was left to stir for 15 min. and then $dppeO_2$ (0.108 g, 0.25 mmol) was added and the reaction was left to stir overnight. The precipitate was filtered off, rinsed with small amount of CH_2Cl_2 and dried *in vacuo*. Yield 0.102 g, 63%. Crystals of [$NbOCl_3$($dppeO_2$)] were grown from CH_2Cl_2 solution in the freezer. Anal: required for $C_{26}H_{24}Cl_3NbO_3P_2$ (645.6): C, 48.4; H, 3.8. Found: C, 48.6; H, 4.0%. ^{1}H NMR (CD_2Cl_2, 295 K): 7.89–7.48 (m [10H]), 2.84 (m, [H]), 2.62 (m, [H]). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 56.7 (s), 44.9 (s). IR (Nujol/cm^{-1}): 1172 (s), 1066 (s) PO, 943 (s) NbO, 320 (s), 293 (w) NbCl.

[$NbOCl_3(dppmO_2)$]: was made similarly to [$NbOCl_3$($dppeO_2$)]. Yield 67%. Crystals of [$NbOCl_3$($dppmO_2$)] were grown from a saturated dichloromethane solution in the freezer. Anal: required for $C_{25}H_{22}Cl_3NbO_3P_2$ (631.6): C, 46.7; H, 3.5. Found: C, 46.8; H, 3.9%. ^{1}H NMR (CD_2Cl_2, 295 K): 7.75–7.35 (m, [10H]), 3.80 (t, [H], $^2J_{PH}$ = 15 Hz). $^{31}P\{^1H\}$ NMR (CH_2Cl_2–$CDCl_3$, 298 K): 48.5 (d, $^2J_{PP}$ = 19 Hz) 36.8 (d, $^2J_{PP}$ = 19 Hz). IR (Nujol/cm^{-1}): 1157 (s), 1095 (s) PO, 928 (s) NbO, 327 (s), 294 (m) NbCl.

[$TaF_5(OPPh_3)$]: A solution of $OPPh_3$ (0.26 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added to finely powdered TaF_5 (0.28 g, 1.0 mmol), and vigorously stirred to give a clear solution. This was filtered to remove any residual solid and concentrated *in vacuo* to ~2 mL. On standing a white powder separated, which was filtered off and dried *in vacuo*. Yield 0.45 g, 81%. Anal: required for $C_{18}H_{15}F_5OPTa$ (554.2): C, 39.0; H, 2.7. Found: C, 38.5; H, 2.9%. ^{1}H NMR (CD_2Cl_2, 293 K): 7.2–7.6 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 84.2 (s, [F)], 54.7 (s, [4F]; (210 K): 81.8 (s, [F]), 56.3 (s, [4F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 53.2(s). IR (Nujol/cm^{-1}): 1078 (vs) PO, 617 (sh), 592 (vs, br) TaF.

[$TaF_5(OAsPh_3)$]: was made similarly, from $OAsPh_3$ (0.32 g, 1.0 mmol) and TaF_5 (0.28 g, 1.0 mmol), except that the reaction was worked up and the solid isolated after 20 min. Yield 0.50 g, 85%. Anal: required for $C_{18}H_{15}AsF_5OTa$ (598.2): C, 36.2; H, 2.5. Found: C, 37.3; H 2.6%. ^{1}H NMR (CD_2Cl_2, 293 K): 7.2–7.6 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 62.5 (s, [F]), 48.6 (s, [4F]), weak resonances at 38.6 ($[TaF_6]^-$) and −89.4 (Ph_3AsF_2). IR (Nujol/cm^{-1}): 845 (s) AsO, 620 (sh), 581 (vs, br) TaF.

[$TaF_5(OPMe_3)$]: A solution of $OPMe_3$ (0.092 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added to finely powdered TaF_5 (0.276 g, 1.0 mmol), and vigorously stirred to give a clear solution. This was filtered to remove any residual solid and concentrated *in vacuo* to ~5 mL. A white powder separated, which was filtered off and dried *in vacuo*. Yield 0.25 g, 65%. Anal: required for $C_3H_9F_5OPTa$ (368.0): C, 9.8; H, 2.5. Found: C, 10.2; H, 2.3%. ^{1}H NMR (CD_2Cl_2, 293 K): 1.9 (d, $^2J_{PH}$ = 15 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 82.5 (s, [F]), 55.9 (s, [4F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 76.9 (s). IR (Nujol/cm^{-1}): 1092 (vs) PO, 601 (sh), 583 (vs, br) TaF.

[TaF_4(2,2′-bipy)$_2$][TaF_6]: TaF_5 (0.28 g, 1.0 mmol) was added to CH_2Cl_2 (50 mL) and vigorously stirred, whilst a solution of 2,2′-bipy (0.16 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added, resulting in rapid precipitation of a fine white powder. After 24 h the solid was isolated by filtration, rinsed with diethyl ether (5 mL) and dried *in vacuo.* Yield 0.35 g, 86%. Anal: required for $C_{20}H_{16}F_{10}N_4Ta_2$ (864.2): C, 27.8; H, 1.9; N, 6.5. Found: C, 27.9; H,1.9; N, 6.4%. ^{1}H NMR (CD_2Cl_2, 293 K): 9.34 (d, [2H], J = 9 Hz), 8.50 (d, [2H], J = 8 Hz), 8.37 (m, [2H]), 7.81 (m, [2H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 68.1 (s, [4F]), 38.0 (s, [6F]). IR (Nujol/cm^{-1}): 605 (sh), 581 (vs) TaF.

[TaF_4(1,10-phen)$_2$][TaF_6]: was made similarly. Yield 83%. Anal: required for $C_{24}H_{16}F_{10}N_4Ta_2$ (912.3): C, 31.6; H, 1.8; N, 6.1. Found: C, 31.5; H, 1.8; N, 6.0%. ^{1}H NMR (CD_2Cl_2, 293 K): 9.15 (s, [2H]), 8.63 (d, [2H], J = 10 Hz), 8.09 (s, [2H]), 7.92 (m, [2H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): 66.1 (s, [4F]), 37.9 (s, [6F]). IR (Nujol/cm^{-1}): 605 (sh), 576 (vs) TaF.

Table 2 X-ray data[a]

Compound	$[NbOF_3(OPPh_3)_2]$	$[NbOF_3(OPMe_3)_2]\cdot 0.33CH_2Cl_2$	$[NbOF_3(dppmO_2)]$	$[NbOCl_3(dppmO_2)]\cdot 0.3MeCN$
Formula	$C_{36}H_{30}F_3NbO_3P_2$	$C_6H_{18}F_3NbO_3P_2\cdot 0.33CH_2Cl_2$	$C_{25}H_{22}F_3NbO_3P_2$	$C_{25}H_{22}Cl_3NbO_3P_2\cdot 0.3CH_3CN$
M	722.45	378.36	582.28	643.94
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group (no.)	$Fdd2$ (no. 43)	$P\bar{1}$ (no 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	18.762(9)	7.8890(15)	13.154(8)	10.694(2)
b/Å	33.289(14)	14.584(3)	10.967(6)	15.640(4)
c/Å	10.152(5)	20.046(4)	17.248(10)	17.181(4)
α/°	90	102.497(4)	90	90
β/°	90	99.803(4)	97.173(19)	105.721(6)
γ/°	90	97.324(2)	90	90
U/Å^3	6340(5)	2186.3(7)	2469(3)	2766.0(13)
Z	8	6	4	4
μ(Mo-K$_\alpha$)/mm^{-1}	0.534	1.191	0.665	0.867
F(000)	2944	1140	1176	1298
Total number reflns	7136	22 109	15 969	11 311
R_{int}	0.0849	0.0250	0.0915	0.0386
Unique reflns	3000	9978	4794	5288
No. of params, restraints	204, 20	556, 15	307, 0	320, 2
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.0719, 0.1062	0.0359, 0.0847	0.0770, 0.1725	0.0514, 0.0946
R_1, wR_2 (all data)	0.0888, 0.1148	0.0430, 0.0880	0.0982, 0.1854	0.0742, 0.1045

Compound	$[NbOCl_3(dppeO_2)]\cdot 0.5MeCN$	$[NbOCl_3(2,2'\text{-bipy})]$	$[NbOCl_3(tmeda)]$
Formula	$C_{26}H_{24}Cl_3NbO_3P_2\cdot 0.5CH_3CN$	$C_{10}H_8Cl_3N_2NbO$	$C_6H_{16}Cl_3N_2NbO$
M	666.18	371.44	331.47
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group (no.)	$P2_1/n$ (no. 14)	$Fdd2$ (no. 43)	$Pna2_1$ (no. 33)
a/Å	10.752(2)	12.4975(4)	14.352(7)
b/Å	14.367(3)	21.6322(8)	7.368(4)
c/Å	18.048(4)	29.090(2)	11.781(6)
α/°	90	90	90
β/°	92.519(10)	90	90
γ/°	90	90	90
U/Å^3	2785.1(10)	7864.3(6)	1245.8(11)
Z	4	24	4
μ(Mo-K$_\alpha$)/mm^{-1}	0.864	1.512	1.578
F(000)	1348	4368	664
Total number reflns	14 141	5418	3500
R_{int}	0.0555	0.0243	0.0196
Unique reflns	5451	2991	2135
No. of params, restraints	338, 2	240, 16	119, 2
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.0591, 0.0921	0.0469, 0.1169	0.0449, 0.1102
R_1, wR_2 (all data)	0.0721, 0.0968	0.0506, 0.1204	0.0521, 0.1162

[a] Common items: T = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

X-Ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 2. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (100 μm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinement were straightforward,[22,23] except as detailed below, with H atoms bonded to C being placed in calculated positions using the default C–H distance. Several cases of O/X disorder have been discussed in the text. Three of the carbon atoms in $[NbOCl_3(tmeda)]$, C4, C5 and C6 were elongated, suggesting some disorder, but attempts to split these over two positions were unsuccessful. For $[NbOCl_3(2,2'\text{-bipy})]$ Nb2 was initially placed on the two-fold axis but showed a very elongated ellipsoid with two large Q peaks close to Nb2. A subsequent model displaced Nb2 by a few tenths of an Å from the axis and this gave a better fit to the data, R1 reduced from ~0.08 to ~0.05.

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