ESI:

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

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$[(Me_3\text{-tacn})H]_2[NbOCl_5]$:

The reaction of Me_3-tacn with $NbOCl_3$ in MeCN gave an undentified dark brown solid, which on recystallisation from MeCN produced a small number of colourless crystals. The X-ray structure of the crystals showed them to be $[(Me_3\text{-tacn})H]_2[NbOCl_5]$. The crystals exhibited υ(NbO) at 926 cm^{-1} and υ(NbCl) at 306 cm^{-1}, in excellent agreement with data on salts containing different cations.[17] As indicated in the main manuscript, although crystal structures of this anion have been reported on several occaisions,[17] the anions often exhibit O/Cl disorder. The present complex appears to be free from such problems. The structure is shown in Fig. S1 and the X-ray data in Table S1.

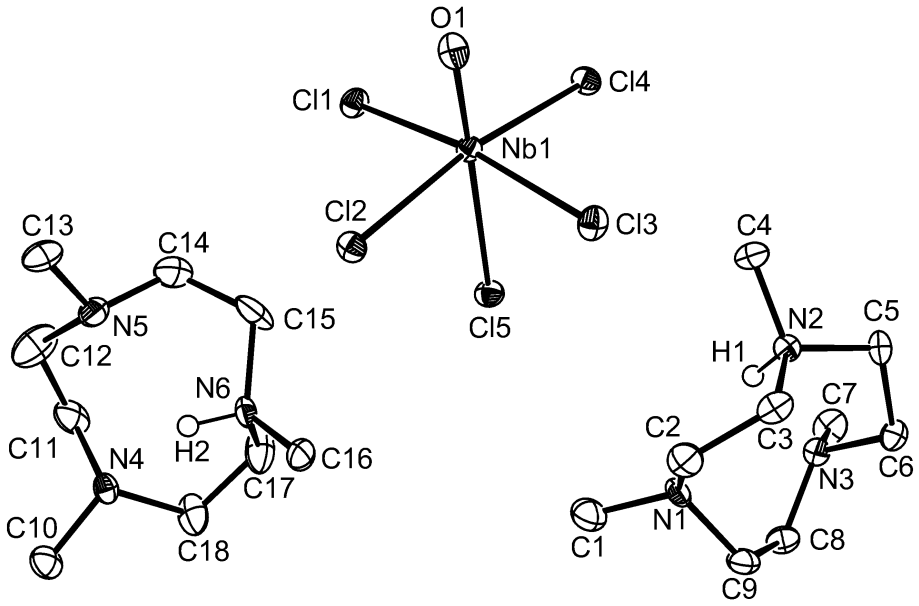

Fig. S1. The structure of $[Me_3\text{-tacnH}]_2[NbOCl_5]$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms bonded to C are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1−O1 = 1.7385(18). Nb1−Cl4 = 2.4036(7), Nb1−Cl3 = 2.4194(8), Nb1−Cl1 = 2.4267(7), Nb1−Cl2 = 2.4364(7), Nb1−Cl5 = 2.6596(8), O1−Nb1−Cl4 = 95.75(6), O1−Nb1−Cl3 = 94.94(6), Cl4−Nb1−Cl3 = 88.79(3), O1−Nb1−Cl1 = 94.94(6), Cl4−Nb1−Cl1 = 91.18(3), O1−Nb1−Cl2 = 93.79(6), Cl3−Nb1−Cl2 = 88.70(3), Cl1−Nb1−Cl2 = 89.69(3), Cl4−Nb1−Cl5 = 86.13(2), Cl3−Nb1−Cl5 = 84.35(2), Cl1−Nb1−Cl5 = 85.75(2), Cl2−Nb1−Cl5 = 84.31(2).

Table S1.

Compound	$[Me_3\text{-tacnH}]_2[NbOCl_5]$
Formula	$C_{18}H_{44}Cl_5N_6NbO$
M	630.75
Crystal system	monoclinic
Space group (no.)	$P2_1/c$ (no. 14)
a /Å	9.9479(15)
b /Å	16.788(2)
c /Å	16.968(3)
α /°	90
β /°	95.576(3)
γ /°	90
U /Å^3	2820.3(7)
Z	4
μ(Mo-K$_\alpha$) /mm^{-1}	0.923
F(000)	1312
Total number reflns	11185
R_{int}	0.0295
Unique reflns	5494
No. of params, restraints	293, 2
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.0370, 0.0701
R_1, wR_2 (all data)	0.0489, 0.0739

The structure of $[Ph_4As]_2[NbOCl_5]\cdot 2CH_2Cl_2$ [17(c)] also reports the anion as free from disorder, but the reported parameters are puzzling, with Nb=O = 1.967(6) and Nb−Cl_{transO} = 2.555(4) Å, which seem anomalously long and short respectively. It would seem likely either that there is unrecognised disorder present here or possibly the anion is co-crystallised with $[NbCl_6]^-$. [17(b)]