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ESI for

Niobium(V) and tantalum(V) halide chalcogenoether complexes – towards single source CVD precursors for ME_2 thin films

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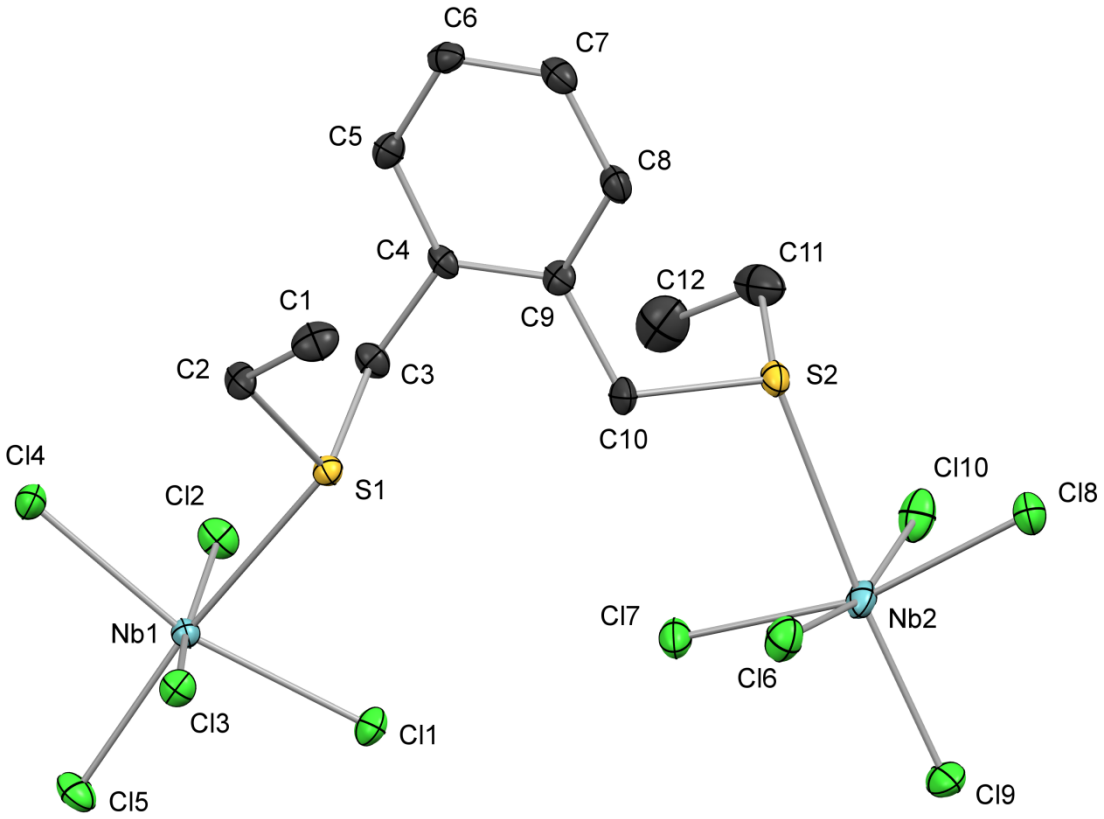

Figure S1. View of the structure of the major (90%) component of $[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ with numbering scheme. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1−Cl1 = 2.3363(8), Nb1−Cl2 = 2.3028(8), Nb1−Cl3 = 2.3517(8), Nb1−Cl4 = 2.3116(8), Nb1−Cl5 = 2.2740(8), Nb1−S1 = 2.6843(8), Nb2−Cl6 = 2.3219(9), Nb2−Cl7 = 2.3169(12), Nb2−Cl8 = 2.3368(13), Nb2−Cl9 = 2.2616(19), Nb2−Cl10 = 2.3242(10), Nb2−S2 = 2.7254(10), S1−Nb1−Cl5 = 170.30(3), S2−Nb2−Cl10 = 175.55(5).

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Table S1: Crystallographic parameters

Compound	$[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$
Formula	$C_{12}H_{18}Cl_{10}Nb_2S_2$
M	766.70
Crystal system	monoclinic
Space group (no.)	P 2_1/c (14)
a /Å	12.4305(10)
b /Å	17.5222(10)
c /Å	11.7030(10)
α/ °	90
β /°	99.150(7)
γ/°	90
U /Å^3	2516.6(3)
Z	4
μ(Mo-K$_\alpha$ /mm^{-1}	2.139
Total number reflns	11656
R_{int}	0.030
Unique reflns	4924
No. of params, restraints	249, 24
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.031, 0.066
R_1, wR_2 (all data)	0.038, 0.068

$[(NbCl_5)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ is isostructural with the Ta analogue. Disorder was identified in some of the atoms bonded to Nb2 (Cl7, Cl8, Cl9 and S2). This was modelled satisfactorily using split atom occupancies, revealing two components in a 90:10 ratio. A second position was expected for C12, with 10% occupancy (C12a), however a Q-peak with a reasonable S2a-C11-C12a angle could not be identified above the background electron density.

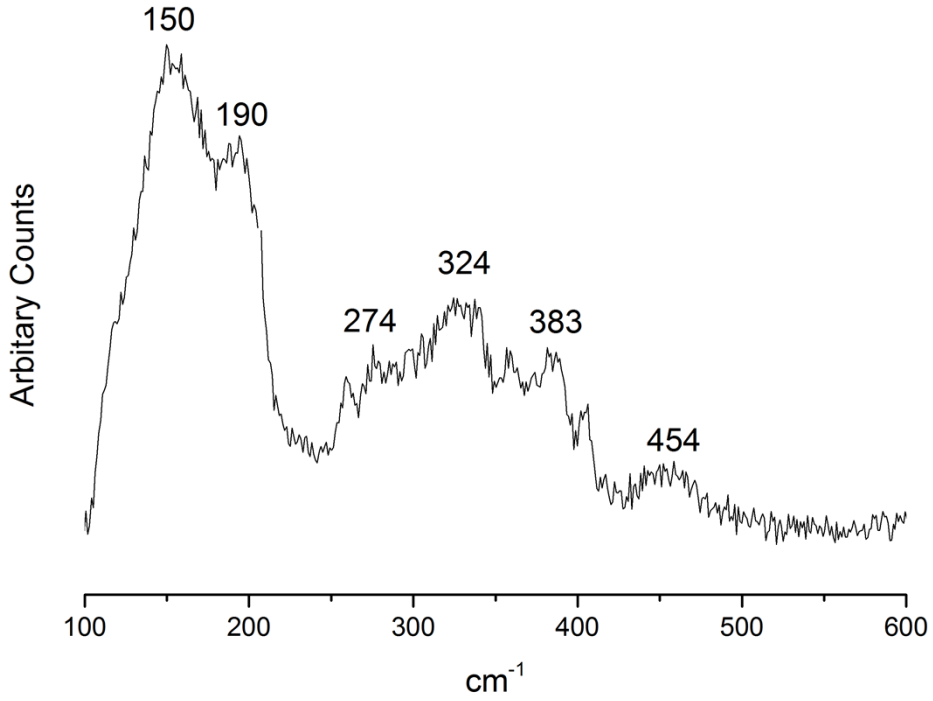

Figure S2. Raman spectrum of NbS_2 film deposited by LPCVD from $[NbCl_5(S^nBu_2)]$ at 750 °C

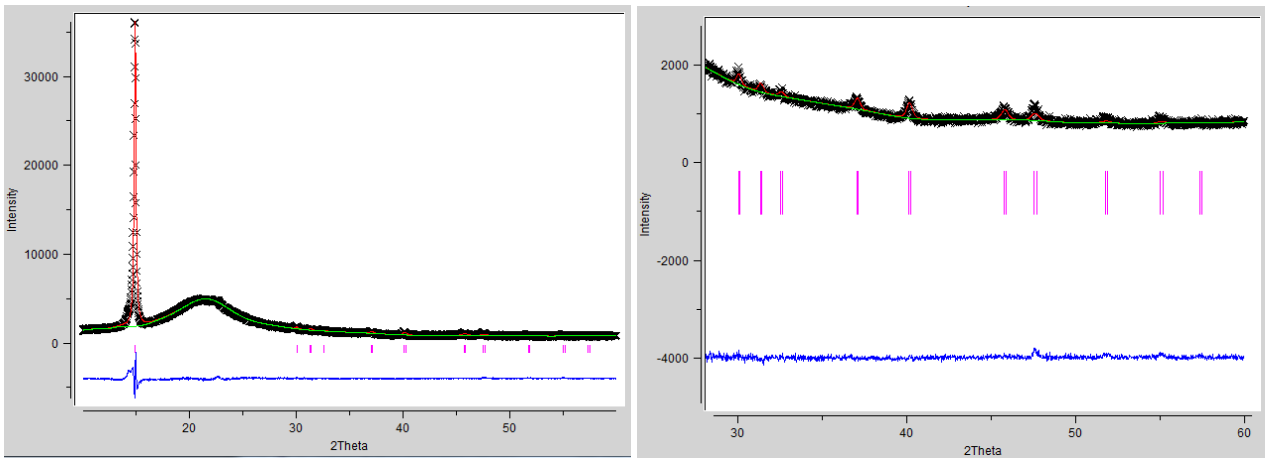

Figure S3: Rietveld refinement of the grazing incidence XRD pattern derived from an NbS_2 film grown by LPCVD using $[NbCl_5(S^nBu_2)]$ at 750 °C; R_{wp} = 5.3%, R_p = 3.5%, R3m, a = 3.3343(14), c = 17.820(11) Å; March-Dollase preferred orientation ratio along [001] = 0.46. The figure on the right is an expansion showing the fit to the weaker reflections.

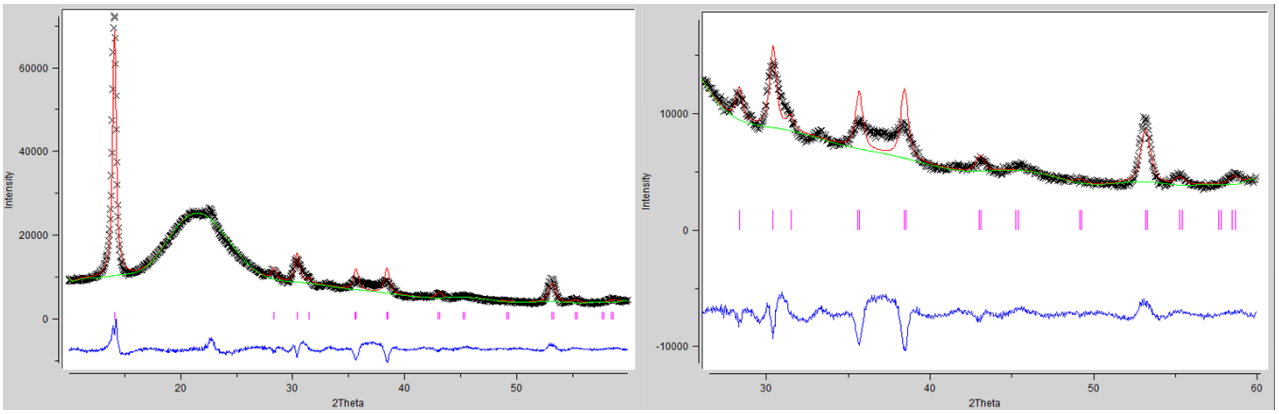

Figure S4: Rietveld refinement of the grazing incidence XRD pattern derived from an $NbSe_2$ film grown by LPCVD using $[NbCl_5(Se^nBu_2)]$ at 650 °C; R_{wp} = 6.4%, R_p = 4.5%, R3m, a = 3.4469(9), c = 18.940(14) Å. The figure on the right is an expansion showing the weaker reflections.

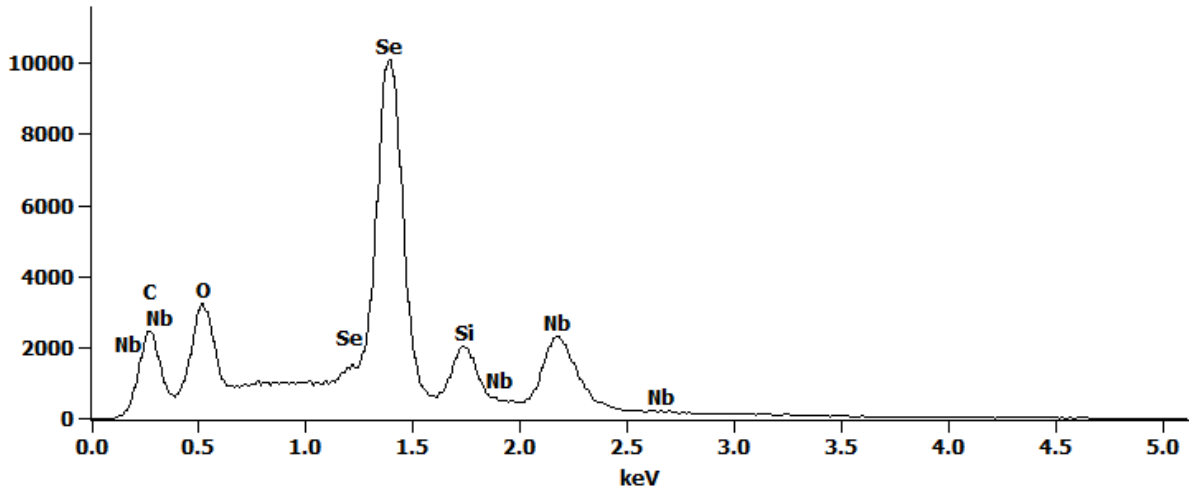

Figure S5. EDX spectrum of a $NbSe_2$ thin film deposited on SiO_2 by LPCVD from $[NbCl_5(Se^nBu_2)]$ at 650 °C