Electronic Supplementary Information

A series of compounds containing various (oxalato)tantalate(V) complex anions – synthesis, properties and the mixed-metal oxide formation *via* thermal decomposition

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X-ray crystallographic study

Hydrogen atoms and water molecules treatment

Hydrogen atoms attached to the C atoms of the phenanthroline ligands and the phenanthrolinium cation were treated as riding in idealized positions, with the C–H distances of 0.93 Å and displacement parameters assigned as U_{iso}(H) = 1.2U_{eq}(C). Hydrogen atoms from the CH_3 fragment of the ethoxyl group in **3** and methoxyl group in **4** were treated as riding and were positioned according to the idealized tetrahedral geometry around C atoms, with the C–H distances of 0.96 Å and displacement parameters assigned as U_{iso}(H) = 1.5U_{eq}(C). Hydrogen atoms from the CH_2 fragment of the ethoxyl group were also placed in idealized positions of 0.97 Å from the C atom and with displacement parameters assigned as U_{iso}(H) = 1.2U_{eq}(C). There are four and a half disordered water molecules in **1**. For the following water molecules two positions were found and they were refined isotropically together with an occupancy factor (in brackets): O20a [0.51(1)], O20b [0.49(1)]; O22a [0.44(1)], O22b [0.56(1)]. One water molecule (O19) is disordered over a centre of symmetry with an occupancy of 0.25 in the centre and 0.25 near the centre. Water O21 is disordered over three positions: O21a [0.46(1)], O21b [0.42(1)], O21c [0.12(1)]. It has to be noted that this is the best model of the disordered water molecules. There is still unmodelled small electron density in the void near the disordered water molecules. In compound **2**, water

molecule O21 is near the inversion centre and forms a hydrogen bond with its centrosymmetrical pair. Obviously, the hydrogen atoms have to be disordered and they were not modelled. All hydrogen atoms of water molecules that are not in disordered positions could be recognized in the difference Fourier maps. The geometry of these water molecules was restrained to the target values (O–H distance of 0.90 Å, using the DIFX command, and H–O–H angles of 104°, using the DANG command). Displacement parameters of hydrogen atoms from these water molecules were assigned as $U_{iso}(H) = 1.5U_{eq}(O)$. The hydrogen atom attached to the N atom of the phenanthrolinium cation in **1** and the hydrogen atom of the hydroxyl group in **2** were located in the difference Fourier maps and their positions and isotropic displacement parameters were refined freely.

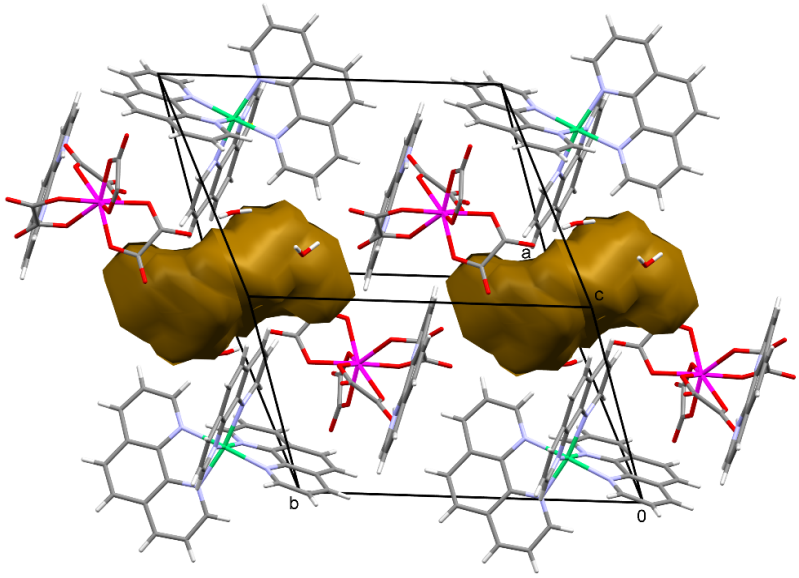

Fig. S1. The void (8.1% of the unit cell volume) inside the hydrophilic layer in compound **1**.

Table S1. Thermoanalytical data for compounds **1**–**4**

Compound	Mass loss/%						Residue/%	
	w(H_2O)		w(phen)		w($CO+CO_2$)		w(oxide)	
	exp.	*calc.*	*exp.*	*calc.*	*exp.*	*calc.*	*exp.*	*calc.*
1	8.88	8.19	50.43	50.42	20.03	20.71	20.66	20.68
2	11.43	11.95	44.43	44.85	19.68	18.68	24.46	24.52
3	1.60	1.63	50.06	48.82	18.14	18.79	26.18	26.70
4	1.70	1.65	49.11	49.44	19.45	19.03	26.93	27.04

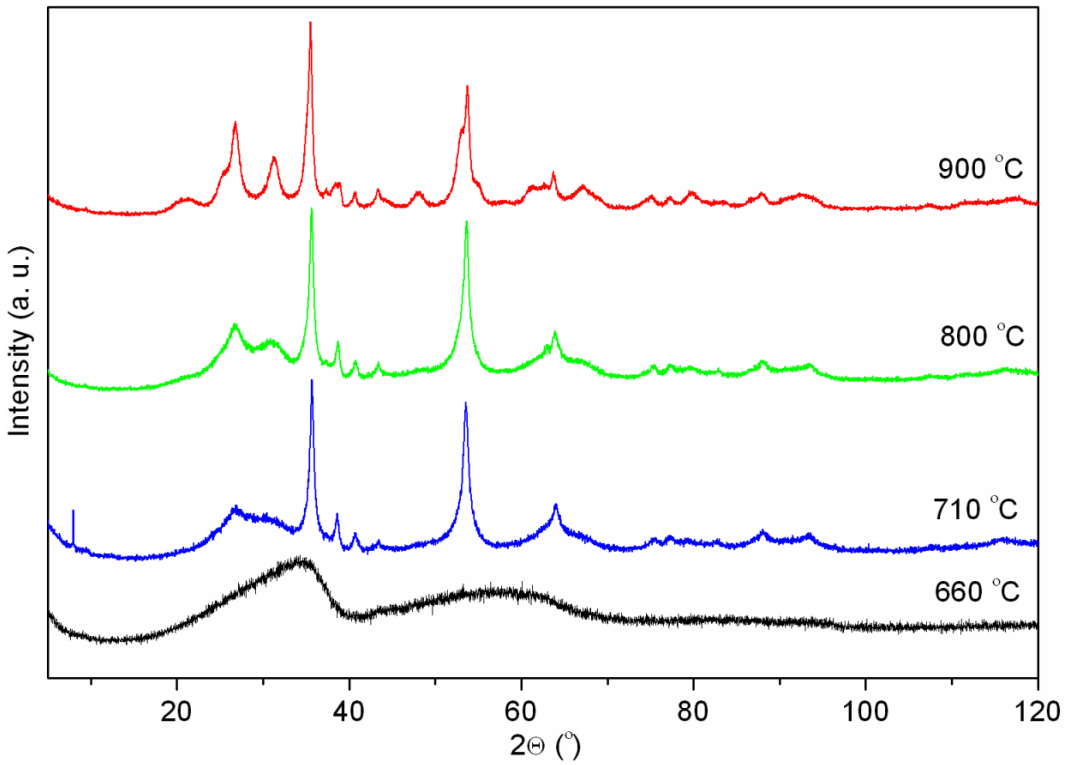

Fig. S2. Powder X-ray diffraction patterns of the samples residues of compound **3** heated on a thermobalance at different temperatures.

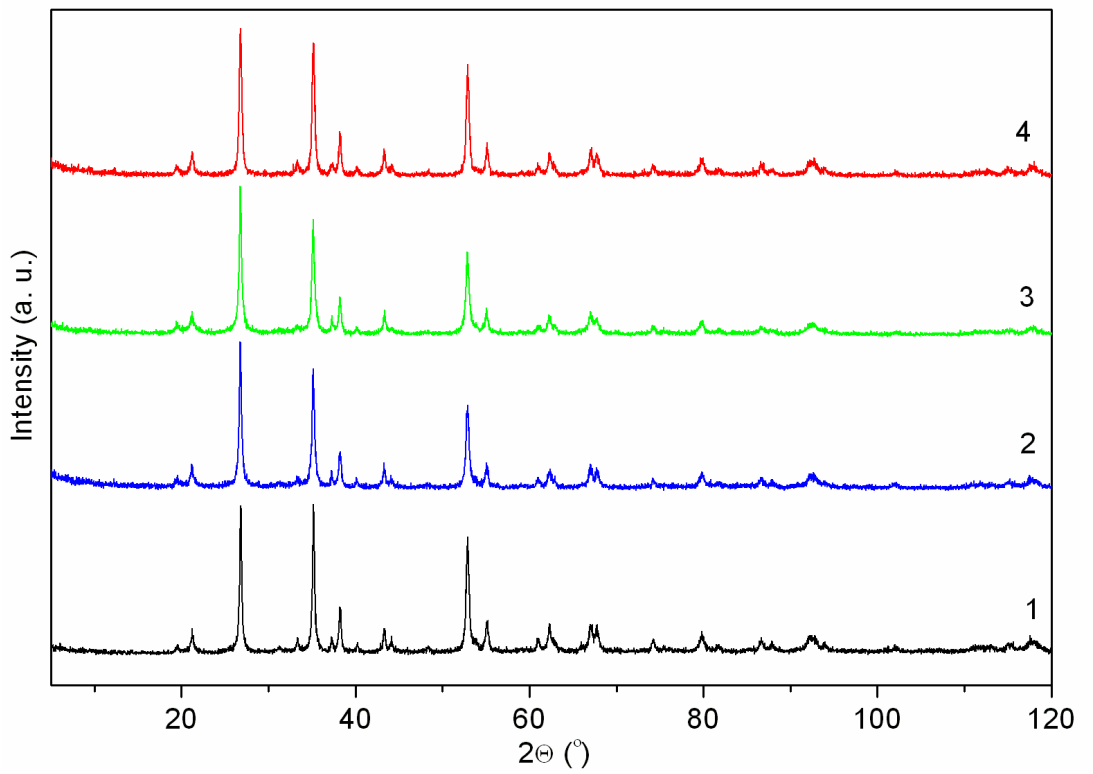

Fig. S3. Powder X-ray diffraction patterns of **1–4** heated on a thermobalance up to 1000 °C.

IR data:

IR (KBr, cm^{-1}) for **1**: 3429 (s, br), 3060 (w), 2921 (w), 1714 (vs), 1681 (s), 1626 (m), 1597 (m), 1542 (m), 1517 (m), 1426 (s), 1383 (s), 1361 (s), 1283 (w), 1223 (m), 1144 (m), 1105 (w), 897 (m), 885 (m), 848 (s), 795 (s), 726 (s), 644 (w), 621 (w), 551 (m), 464 (m), 424 (w).

IR (KBr, cm^{-1}) for **2**: 3439 (s, br), 3081 (w), 2922 (w), 1721 (vs), 1685 (s), 1627 (m), 1586 (m), 1519 (m), 1427 (s), 1367 (vs), 1225 (m), 1210 (m), 1146 (m), 1105 (m), 901 (m), 870 (w), 852 (s), 802 (s), 726 (s), 645 (w), 621 (w), 577 (m), 561 (m), 545 (m), 471 (m), 424 (w).

IR (KBr, cm^{-1}) for **3**: 3561 (w), 3494 (w), 3058 (w), 2936 (w), 1755 (m), 1724 (vs), 1685 (s), 1626 (m), 1586 (w), 1518 (m), 1427 (s), 1359 (s), 1332 (s), 1211 (w), 1195 (m), 1146 (w), 1107 (m), 1073 (m), 898 (m), 869 (w), 851 (s), 800 (s), 726 (s), 644 (w), 561 (m), 545 (m), 459 (m), 444 (m), 425 (w).

IR (KBr, cm^{-1}) for **4**: 3561 (w), 3494 (w), 3062 (w), 2921 (w), 1755 (m), 1724 (vs), 1694 (s), 1626 (m), 1586 (w), 1518 (m), 1426 (s), 1383 (m), 1355 (s), 1332 (s), 1225 (w), 1210 (w), 1188 (m), 1146 (w), 1104 (m), 908 (w), 869 (w), 850 (s), 800 (s), 726 (s), 644 (w), 558 (m), 543 (m), 469 (m), 425 (w).