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Electronic supplementary information

for

First crystal structures of oxo-bridged [$Cr^{III}Ta^{V}$] dinuclear complexes: spectroscopic, magnetic and theoretical investigations of Cr–O–Ta core

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Table S1. Bond lengths (Å) involved in the first coordination sphere of Ta and Cr atoms in $[Cr(bpy)_2(H_2O)(\mu\text{-}O)Ta(C_2O_4)_3]_2 \cdot 3.5H_2O$ (**1**). Experimental data are compared to the theoretical ones deduced from the geometry optimization using PBE+U functional.

	Exp.	Opt.	Diff. (%)
Ta1–O2	1.805(3)	1.819	0.8
Ta1–O10	2.077(4)	2.098	1.0
Ta1–O5	2.078(3)	2.115	1.8
Ta1–O11	2.091(3)	2.115	1.1
Ta1–O3	2.097(3)	2.105	0.4
Ta1–O14	2.111(3)	2.119	0.4
Ta1–O7	2.130(3)	2.143	0.6
Ta2–O16	1.809(3)	1.818	0.5
Ta2–O20	2.072(4)	2.096	1.2
Ta2–O24	2.072(3)	2.084	0.6
Ta2–O25	2.087(3)	2.109	1.1
Ta2–O17	2.101(3)	2.115	0.7
Ta2–O21	2.121(3)	2.129	0.4
Ta2–O28	2.136(3)	2.154	0.8
Cr1–O2	1.902(3)	1.944	2.2
Cr1–O1	1.964(3)	1.979	0.8
Cr1–N1	2.035(4)	2.066	1.5
Cr1–N2	2.049(4)	2.077	1.3
Cr1–N3	2.061(4)	2.084	1.1
Cr1–N4	2.061(4)	2.090	1.4
Cr2–O16	1.893(3)	1.930	2.0
Cr2–O15	1.960(4)	1.980	1.0
Cr2–N5	2.042(6)	2.083	2.0
Cr2–N8	2.048(4)	2.090	2.1
Cr2–N6	2.055(5)	2.086	1.5
Cr2–N7	2.056(4)	2.076	0.9

Table S2. Selected angles (°) in the coordination spheres of metal centres in $[Cr(bpy)_2(H_2O)(\mu\text{-}O)Ta(C_2O_4)_3]_2 \cdot 3.5H_2O$ (**1**).

Ta1		Ta2	
O2–Ta1–O10	98.90(14)	O16–Ta2–O20	99.25(13)
O2–Ta1–O5	94.24(13)	O16–Ta2–O24	97.23(13)
O2–Ta1–O11	95.45(12)	O16–Ta2–O25	97.54(12)
O2–Ta1–O3	170.69(13)	O16–Ta2–O17	174.05(13)
O2–Ta1–O14	94.23(13)	O16–Ta2–O21	91.16(13)
O2–Ta1–O7	91.82(13)	O16–Ta2–O28	90.99(12)
O10–Ta1–O5	142.13(13)	O20–Ta2–O24	141.53(12)
O10–Ta1–O11	69.48(12)	O20–Ta2–O25	140.27(13)
O10–Ta1–O3	87.63(13)	O20–Ta2–O17	78.85(13)
O10–Ta1–O14	140.86(12)	O20–Ta2–O21	71.89(14)
O10–Ta1–O7	73.0(13)	O20–Ta2–O28	71.40(12)
O5–Ta1–O11	144.30(13)	O24–Ta2–O25	70.35(12)
O5–Ta1–O3	76.60(13)	O24–Ta2–O17	84.92(13)
O5–Ta1–O14	72.38(13)	O24–Ta2–O21	73.27(13)
O5–Ta1–O7	71.18(14)	O24–Ta2–O28	142.74(12)
O11–Ta1–O3	93.06(12)	O25–Ta2–O17	88.41(12)
O11–Ta1–O14	72.69(12)	O25–Ta2–O21	143.35(13)
O11–Ta1–O7	142.48(13)	O25–Ta2–O28	72.57(12)
O3–Ta1–O14	84.68(13)	O17–Ta2–O21	84.13(12)
O3–Ta1–O7	83.69(13)	O17–Ta2–O28	90.61(12)
O14–Ta1–O7	143.39(13)	O21–Ta2–O28	143.09(14)
Cr1		Cr2	
O2–Cr1–O1	90.80(13)	O16–Cr2–O15	93.95(14)
O2–Cr1–N1	91.13(14)	O16–Cr2–N5	90.38(17)
O2–Cr1–N2	89.04(13)	O16–Cr2–N8	92.76(14)
O2–Cr1–N3	94.85(14)	O16–Cr2–N6	87.41(17)
O2–Cr1–N4	173.94(16)	O16–Cr2–N7	171.97(15)
O1–Cr1–N1	93.79(15)	O15–Cr2–N5	169.3(2)
O1–Cr1–N2	173.65(16)	O15–Cr2–N8	90.05(16)
O1–Cr1–N3	93.16(15)	O15–Cr2–N6	90.99(19)
O1–Cr1–N4	88.38(14)	O15–Cr2–N7	87.51(15)
N1–Cr1–N2	79.87(15)	N5–Cr2–N8	99.6(2)
N1–Cr1–N3	170.77(14)	N5–Cr2–N6	79.4(2)
N1–Cr1–N4	94.92(16)	N5–Cr2–N7	89.56(19)
N2–Cr1–N3	93.18(15)	N8–Cr2–N6	178.94(18)
N2–Cr1–N4	92.44(14)	N8–Cr2–N7	79.34(15)
N3–Cr1–N4	79.20(15)	N6–Cr2–N7	100.47(18)

Table S3. Selected bond lengths (Å) and angles (°) in the first coordination sphere of Ta and Cr atoms in $[H_2(terpy)][Cr(terpy)(C_2O_4)(\mu\text{-}O)Ta(C_2O_4)_3]\cdot 0.5H_2C_2O_4\cdot 2.5H_2O$ (**2**).

Ta1			
Ta1–O1	1.797(3)	O10–Ta1–O5	143.68(13)
Ta1–O10	2.069(3)	O10–Ta1–O2	87.90(13)
Ta1–O9	2.077(3)	O10–Ta1–O13	73.04(13)
Ta1–O5	2.086(3)	O10–Ta1–O6	142.46(13)
Ta1–O2	2.106(3)	O9–Ta1–O5	140.34(13)
Ta1–O13	2.128(3)	O9–Ta1–O2	91.36(13)
Ta1–O6	2.133(3)	O9–Ta1–O13	143.32(13)
O1–Ta1–O10	97.72(14)	O9–Ta1–O6	72.13(13)
O1–Ta1–O9	99.18(14)	O5–Ta1–O2	75.35(13)
O1–Ta1–O5	94.90(14)	O5–Ta1–O13	73.00(13)
O1–Ta1–O2	169.22(14)	O5–Ta1–O6	70.66(13)
O1–Ta1–O13	89.22(14)	O13–Ta1–O6	143.79(13)
O1–Ta1–O6	91.25(14)	O2–Ta1–O13	83.60(13)
O10–Ta1–O9	70.47(13)	O2–Ta1–O6	89.82(13)
Cr1			
Cr1–O1	1.905(3)	O14–Cr1–N2	172.79(18)
Cr1–O14	1.948(4)	O14–Cr1–N1	103.04(17)
Cr1–O17	1.952(4)	O14–Cr1–N3	100.81(17)
Cr1–N2	2.000(4)	O17–Cr1–N2	90.24(17)
Cr1–N1	2.071(4)	O17–Cr1–N1	91.80(18)
Cr1–N2	2.080(4)	O17–Cr1–N3	91.88(18)
O1–Cr1–O14	89.68(16)	N2–Cr1–N1	78.39(17)
O1–Cr1–N17	172.35(15)	N2–Cr1–N3	78.02(17)
O1–Cr1–N2	97.41(16)	O1–Cr1–N4	88.38(14)
O1–Cr1–N1	89.86(16)	N1–Cr1–N2	79.87(15)
O1–Cr1–N3	89.61(16	N1–Cr1–N3	156.14(16)
O14–Cr1–O17	82.67(17)	Cr1–O1–Ta1	153.5(2)

Table S4. Hydrogen–bonding geometry in compounds $[Cr(bpy)_2(H_2O)(\mu\text{-}O)Ta(C_2O_4)_3]_2\cdot 3.5H_2O$ (**1**) and $[H_2(terpy)][Cr(terpy)(C_2O_4)(\mu\text{-}O)Ta(C_2O_4)_3]\cdot 0.5H_2C_2O_4\cdot 2.5H_2O$ (**2**). Interatomic distances involving the water molecules without located hydrogen atoms are given.

Compound	*D*–H···*A*	*D*–H/Å	H···*A*/Å	*D*···*A*/Å	*D*–H···*A*/°	Symm. op. on *A*
1	O1–H1A···O12	0.91(7)	1.76(7)	2.665(5)	170(7)	*x*, –1/2 – *y*, 1/2 + *z*
	O1–H1B···O23	0.81(8)	1.85(9)	2.617(5)	160(7)	
	O15–H15A···O8	0.84(6)	1.77(6)	2.608(5)	170(7)	
	O15–H15B···O27	0.85(4)	1.91(4)	2.722(5)	159(6)	*x*, –3/2 – *y*, –1/2 + *z*
	O29–H29A···O31	0.86(6)	1.89(6)	2.744(6)	176(3)	
	O29–H29B···O25	0.87(5)	2.26(5)	3.039(6)	151(6)	
	O30–H30A···O8	0.89(5)	2.21(5)	3.044(6)	156(7)	
	O30–H30B···O29	0.89(5)	1.83(6)	2.715(6)	177(10)	
	O31–H31A···O5	0.87(6)	2.21(5)	2.979(5)	146(7)	2 – *x*, –1 – *y*, 2 – *z*
	O31–H31B···O30	0.87(7)	1.96(6)	2.813(8)	166(6)	2 – *x*, –1 – *y*, 2 – *z*
	O32 ···O3			2.901(12)		*x*, –3/2 – *y*, 1/2 + *z*
	O32 ···O26			3.081(11)		
2	N4–H4N···O7	0.88(15)	1.95(15)	2.823(6)	171(1)	
	N6–H6N···N5	0.87(14)	2.16(17)	2.683(6)	118(15)	
	O18–H18O···O20	0.90(15)	1.73(17)	2.577(7)	157(18)	
	O20–H20A···O4	0.85(11)	1.97(13)	2.811(7)	171(1)	–1 + *x*, *y*, *z*
	O20–H20B···O8	0.85(8)	1.98(8)	2.795(6)	162(1)	
	O21–H21A···O16	0.84(18)	1.91(17)	2.742(19)	167(16)	
	O21–H21B···O22	0.9(2)	1.8(2)	2.47(4)	132(16)	
	O22···O17			3.18(2)		1 – *x*, 2 – *y*, –*z*

Table S5. Geometric parameters of the aromatic interactions in compound $[H_2(terpy)][Cr(terpy)(C_2O_4)(\mu\text{-}O)Ta(C_2O_4)_3]\cdot 0.5H_2C_2O_4\cdot 2.5H_2O$ (**2**).

Cg(*i*)···Cg(*j*)[a]	Cg(*i*)···Cg(*j*)/Å	α/°[b]	β/°[c]	Cg(*i*)···plane [Cg(*j*)]/Å[d]	Symmetry operator
(N2→C10)···(N3→C15)	4.058(4)	3.1(3)	21.3	3.813(2)	1 – *x*, 1 – *y*, –*z*
(N4→C20)···(N5→C25)	3.959(3)	8.2(3)	30.0	3.556(2)	2 – *x*, 2 – *y*, 1 – *z*
(N5→C25)···(N6→C30)	3.815(3)	6.0(3)	25.1	3.454(2)	1 – *x*, 2 – *y*, 1 – *z*

[a] Cg = centre of gravity of the aromatic ring. [b] α = angle between the planes of two aromatic rings. [c] β = angle between the Cg···Cg line and the normal to the plane of the first aromatic ring. [d] γ = angle between Cg(*i*)→Cg(*j*) vector and normal to plane [Cg(*j*)].