Electronic Supporting Information

Can $[TcF(CO)_5]$ does Exist? Crystal and Molecular Structure of $[Tc(CO)_3(OH)_{0.49}F_{0.51}]_4$*$[Tc(CO)_5(BF_4)]$

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Table of Contents

Page #

Table S1. Selected bond lengths (*d*, Å) for **1**.

Bond		Bond	
Complex $[Tc(CO)_3(OH)_{0.49}F_{0.51}]_4$			
Tc1-F1	2.189(3)	Tc4-F4	2.184(2)
Tc1-F2	2.224(2)	Tc4-C41	1.861(5)
Tc1-F3	2.181(3)	Tc4-C42	1.886(5)
Tc1-C11	1.897(4)	Tc4-C43	1.892(5)
Tc1-C12	1.898(4)	O11-C11	1.134(5)
Tc1-C13	1.866(5)	O12-C12	1.137(5)
Tc2-F1	2.196(3)	O13-C13	1.157(5)
Tc2-F3	2.192(3)	O21-C21	1.138(5)
Tc2-F4	2.193(3)	O22-C22	1.135(5)
Tc2-C21	1.903(4)	O23-C23	1.152(5)
Tc2-C22	1.901(4)	O31-C31	1.143(5)
Tc2-C23	1.875(5)	O32-C32	1.144(5)
Tc3-F2	2.195(2)	O33-C33	1.150(6)
Tc3-F3	2.178(3)	O41-C41	1.151(5)
Tc3-F4	2.188(2)	O42-C42	1.139(5)
Tc3-C31	1.888(5)	O43-C43	1.148(5)
Tc3-C32	1.874(4)	O1-H1	0.85(10)
Tc3-C33	1.883(5)	O2-H2	0.90(2)
Tc4-F1	2.187(3)	O3-H3	0.87(9)
Tc4-F2	2.180(2)	O4-H4	0.90(2)
Complex $[Tc(CO)_5(BF_4)]$			
Tc5-F56	2.178(3)	F58-B1	1.392(6)
Tc5-C51	1.895(6)	F59-B1	1.380(6)
Tc5-C52	2.002(6)	O51-C51	1.144(7)
Tc5-C53	2.006(5)	O52-C52	1.120(6)
Tc5-C54	2.027(5)	O53-C53	1.121(5)
Tc5-C55	2.024(5)	O54-C54	1.115(5)
F56-B1	1.451(6)	O55-C55	1.104(6)
F57-B1	1.405(6)		

Table S2. Selected bond angles (ω, °) for $[Tc(CO)_3(OH)_{0.49}F_{0.51}]_4$ in the structure of **1**.

Angle		Angle	
F1-Tc1-F2	75.05(11)	C33-Tc3-F3	170.10(17)
F3-Tc1-F1	75.46(12)	C33-Tc3-F4	95.31(16)
F3-Tc1-F2	73.21(10)	C33-Tc3-C31	87.9(2)
C11-Tc1-F1	173.26(16)	F2-Tc4-F1	75.99(10)
C11-Tc1-F2	99.21(15)	F2-Tc4-F4	75.02(9)
C11-Tc1-F3	99.66(15)	F4-Tc4-F1	73.49(10)
C11-Tc1-C12	88.16(17)	C41-Tc4-F1	98.38(18)
C12-Tc1-F1	96.24(14)	C41-Tc4-F2	173.07(17)
C12-Tc1-F2	99.90(15)	C41-Tc4-F4	99.65(16)
C12-Tc1-F3	170.23(16)	C41-Tc4-C42	86.7(2)
C13-Tc1-F1	98.69(14)	C41-Tc4-C43	89.1(2)
C13-Tc1-F2	170.96(12)	C42-Tc4-F1	171.35(17)
C13-Tc1-F3	99.08(14)	C42-Tc4-F2	98.41(17)
C13-Tc1-C11	86.59(18)	C42-Tc4-F4	98.83(16)
C13-Tc1-C12	87.15(18)	C42-Tc4-C43	85.0(2)
F3-Tc2-F1	75.10(11)	C43-Tc4-F1	101.98(16)
F3-Tc2-F4	75.14(10)	C43-Tc4-F2	95.98(15)
F4-Tc2-F1	73.15(10)	C43-Tc4-F4	170.59(16)
C21-Tc2-F1	98.95(14)	Tc1-F1-Tc2	102.13(12)
C21-Tc2-F3	170.72(17)	Tc4-F1-Tc1	102.63(12)
C21-Tc2-F4	96.44(16)	Tc4-F1-Tc2	105.42(13)
C22-Tc2-F1	170.80(16)	Tc3-F2-Tc1	104.27(10)
C22-Tc2-F3	98.13(16)	Tc4-F2-Tc1	101.71(9)
C22-Tc2-F4	99.29(15)	Tc4-F2-Tc3	103.12(9)
C22-Tc2-C21	86.95(18)	Tc1-F3-Tc2	102.55(13)
C23-Tc2-F1	99.92(15)	Tc3-F3-Tc1	106.34(13)
C23-Tc2-F3	100.00(15)	Tc3-F3-Tc2	102.29(12)
C23-Tc2-F4	172.26(13)	Tc3-F4-Tc2	101.91(10)
C23-Tc2-C21	87.9(2)	Tc4-F4-Tc2	105.61(10)
C23-Tc2-C22	87.28(19)	Tc4-F4-Tc3	103.22(9)
F3-Tc3-F2	73.83(10)	O11-C11-Tc1	178.2(4)
F3-Tc3-F4	75.51(11)	O12-C12-Tc1	179.1(4)
F4-Tc3-F2	74.64(9)	O13-C13-Tc1	179.1(4)
C31-Tc3-F2	99.44(15)	O21-C21-Tc2	179.1(4)
C31-Tc3-F3	100.93(17)	O22-C22-Tc2	179.0(5)
C31-Tc3-F4	173.69(15)	O23-C23-Tc2	178.8(4)
C32-Tc3-F2	169.52(16)	O31-C31-Tc3	176.2(4)
C32-Tc3-F3	96.28(17)	O32-C32-Tc3	176.6(5)
C32-Tc3-F4	99.81(16)	O33-C33-Tc3	177.8(5)
C32-Tc3-C31	85.7(2)	O41-C41-Tc4	178.9(5)
C32-Tc3-C33	88.8(2)	O42-C42-Tc4	177.7(5)
C33-Tc3-F2	100.42(15)	O43-C43-Tc4	176.7(4)

Table S3. Selected bond angles (ω, °) for complex $[Tc(CO)_5(BF_4)]$ in the structure of **1**.

Angle		Angle	
C51-Tc5-F56	179.2(3)	C55-Tc5-C54	90.77(18)
C51-Tc5-C52	89.7(3)	B1-F56-Tc5	127.2(3)
C51-Tc5-C53	90.5(2)	O51-C51-Tc5	177.0(8)
C51-Tc5-C54	89.9(3)	O52-C52-Tc5	177.8(4)
C51-Tc5-C55	90.2(3)	O53-C53-Tc5	177.0(4)
C52-Tc5-F56	90.99(18)	O54-C54-Tc5	176.6(4)
C52-Tc5-C53	90.0(2)	O55-C55-Tc5	176.8(5)
C52-Tc5-C54	178.64(19)	F57-B1-F56	110.3(4)
C52-Tc5-C55	87.9(2)	F58-B1-F56	109.8(4)
C53-Tc5-F56	89.26(15)	F58-B1-F57	106.7(4)
C53-Tc5-C54	91.31(18)	F59-B1-F56	109.6(4)
C53-Tc5-C55	177.80(19)	F59-B1-F57	109.4(4)
C54-Tc5-F56	89.42(15)	F59-B1-F58	111.0(4)
C55-Tc5-F56	90.04(17)		

Figure S1. IR-spectrum [$TcI(CO)_5$] in CH_2Cl_2.