Electronic Supplementary Information

Halogen-bonded *tris*(2,4-*bis*(trichloromethyl)-1,3,5-triazapentadienato)-M(III) [M = Mn, Fe, Co] complexes and their catalytic activity in the peroxidative oxidation of 1-phenylethanol to acetophenone

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X-ray analysis

Table S1. Selected distances (Å) and angles (°) of **1**−**3**

1		**2**		**3**	
Mn(1)-N(5)	1.949(5)	Fe(1)-N(19)	1.912(2)	Co(1)-N(12)	1.892(4)
Mn(1)-N(1)	1.952(6)	Fe(1)-N(1)	1.916(3)	Co(1)-N(1)	1.897(5)
Mn(1)-N(12)	1.956(6)	Fe(1)-N(15)	1.916(3)	Co(1)-N(5)	1.900(4)
Mn(1)-N(15)	1.962(5)	Fe(1)-N(12)	1.936(3)	Co(1)-N(19)	1.907(4)
Mn(1)-N(8)	1.963(5)	Fe(1)-N(5)	1.937(3)	Co(1)-N(8)	1.915(4)
Mn(1)-N(19)	1.966(5)	Fe(1)-N(8)	1.947(3)	Co(1)-N(15)	1.915(5)
N(1)-C(2)	1.288(8)	N(1)-C(2)	1.295(4)	N(1)-C(2)	1.290(7)
C(2)-N(3)	1.366(8)	C(2)-N(3)	1.326(5)	N(10)-C(11)	1.329(6)
N(3)-C(4)	1.350(8)	N(3)-C(4)	1.321(4)	N(3)-C(4)	1.316(9)
C(4)-N(5)	1.257(8)	C(4)-N(5)	1.287(4)	C(11)-N(12)	1.283(6)
N(8)-C(9)	1.272(8)	N(8)-C(9)	1.280(4)	N(8)-C(9)	1.268(6)
N(5)-Mn(1)-N(1)	85.0(2)	C(9)-N(10)	1.320(5)	C(9)-N(10)	1.331(6)
N(5)-Mn(1)-N(12)	90.6(2)	N(19)-Fe(1)-N(1)	91.30(11)	N(12)-Co(1)-N(1)	91.6(2)
N(1)-Mn(1)-N(12)	172.0(2)	N(19)-Fe(1)-N(15)	88.61(11)	N(12)-Co(1)-N(5)	178.00(18)
N(5)-Mn(1)-N(15)	173.4(2)	N(1)-Fe(1)-N(15)	91.08(12)	N(1)-Co(1)-N(5)	88.6(2)
N(1)-Mn(1)-N(15)	89.7(2)	N(19)-Fe(1)-N(12)	92.17(12)	N(12)-Co(1)-N(19)	87.67(17)
N(12)-Mn(1)-N(15)	95.0(2)	N(1)-Fe(1)-N(12)	176.09(11)	N(1)-Co(1)-N(19)	91.3(2)
N(5)-Mn(1)-N(8)	96.8(2)	N(15)-Fe(1)-N(12)	90.81(12)	N(5)-Co(1)-N(19)	94.31(18)
N(1)-Mn(1)-N(8)	89.2(2)	N(19)-Fe(1)-N(5)	87.28(11)	N(12)-Co(1)-N(8)	88.57(17)
N(12)-Mn(1)-N(8)	84.7(2)	N(1)-Fe(1)-N(5)	87.13(12)	N(1)-Co(1)-N(8)	89.79(19)
N(15)-Mn(1)-N(8)	87.1(2)	N(15)-Fe(1)-N(5)	175.48(11)	N(5)-Co(1)-N(8)	89.44(17)
N(5)-Mn(1)-N(19)	90.2(2)	N(12)-Fe(1)-N(5)	91.24(12)	N(19)-Co(1)-N(8)	176.12(16)
N(1)-Mn(1)-N(19)	98.7(2)	N(19)-Fe(1)-N(8)	177.27(12)	N(12)-Co(1)-N(15)	90.26(19)
N(12)-Mn(1)-N(19)	88.0(2)	N(1)-Fe(1)-N(8)	90.30(12)	N(1)-Co(1)-N(15)	178.10(19)
N(15)-Mn(1)-N(19)	86.6(2)	N(15)-Fe(1)-N(8)	89.15(11)	N(5)-Co(1)-N(15)	89.5(2)
N(8)-Mn(1)-N(19)	169.9(2)	N(12)-Fe(1)-N(8)	86.30(12)	N(19)-Co(1)-N(15)	88.5(2)
		N(5)-Fe(1)-N(8)	95.01(12)	N(8)-Co(1)-N(15)	90.52(18)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1

Table S2. Hydrogen bond interactions in **1**–**3** (Å, º).

Compound	*D*−H···*A*	Distances (Å)			Angles (º)
		D−H	H···*A*	*D*···*A*	*D*−H···*A*
1	N(1)-H(1)...O(1)	0.88	2.30	2.907(6)	126
	N(15)-H(15)...O(1)	0.88	2.30	2.940(6)	130
	N(8)-H(8)…O(1)	0.88	2.57	2.990(6)	110
	N(26)-H(26)...O(2)#1 [i]	0.88	2.16	2.874(6)	137
	N(40)-H(40)...O(2)#1 [i]	0.88	2.23	2.866(6)	129
	N(50)-H(50)...O(3)#2 [ii]	0.88	2.33	2.968(7)	129
	N(61)-H(61)...O(3)#2 [ii]	0.88	2.40	2.986(7)	125
	N(75)-H(75)...O(4)	0.88	2.27	2.876(6)	126
	N(82)-H(82)...O(4)	0.88	2.33	2.986(6)	132
2	N(1)-H(1)...O(2')#1 [iii]	0.86	2.20	2.946(4)	145
	N(1)-H(1)...O(2)#1 [iii]	0.86	2.36	3.117(5)	147
	N(12)-H(12)...O(1)#2 [iv]	0.86	2.15	2.941(4)	153
	N(12)-H(12)...O(1')#2 [iv]	0.86	2.21	2.954(5)	144
	N(15)-H(15)...O(2)#1 [iii]	0.86	2.64	3.066(4)	112
	N(19)-H(19)...O(1')#2 [iv]	0.86	2.37	2.948(5)	125
	N(19)-H(19)...O(1)#2 [iv]	0.86	2.54	3.061(5)	120
3	N(15)-H(15)...O(2)	0.89(4)	2.35(6)	3.062(7)	137(7)
	N(1)-H(1)...O(3)	0.90(4)	2.43(6)	2.997(7)	121(5)
	N(12)-H(12)...O(3)	0.89(4)	2.53(6)	3.009(7)	115(5)
	N(8)-H(8)...O(2)	0.89(4)	2.61(7)	3.057(8)	112(6)
	N(19)-H(19)...O(3)	0.89(4)	2.52(7)	3.194(8)	133(7)

Symmetry transformations used to generate equivalent atoms: (i) #1 x,y,z-1; (ii) #2 x,y-1,z; (iii) #1 -x+1,-y,-z+1; (iv) #2 -x+1,-y+1,-z+1.

Table S3. Cl···Cl interactions in **1**–**3.**

1				
Atom 1	**Atom 2**	**Length**	**SumRad**	**Symm. op.**
*Cl(7A)	Cl(34)	3.204(4)	<< 3.50	1+x,y,1+z
Cl(55)	Cl(15)	3.445(4)	< 3.50	x,1+y,z
Cl(57)	Cl(31)	3.300(3)	<< 3.50	x,y,1+z
*Cl(70)	Cl(5)	3.133(3)	<< 3.50	x,y,-1+z
*Cl(70)	Cl(38)	3.434(4)	< 3.50	x,1+y,z
Cl(1)	Cl(19)	3.454(3)	< 3.50	1+x,y,1+z
Cl(5)	*Cl(70)	3.133(3)	<< 3.50	x,y,1+z
Cl(6)	Cl(45)	3.431(3)	< 3.50	x,y,1+z
Cl(24)	Cl(44)	3.388(3)	< 3.50	-1+x,1+y,z
Cl(26)	Cl(44)	3.464(3)	< 3.50	-1+x,1+y,z
Cl(31)	Cl(57)	3.300(3)	<< 3.50	x,y,-1+z
Cl(34)	*Cl(7A)	3.204(4)	<< 3.50	-1+x,y,-1+z
Cl(36)	Cl(51)	3.181(3)	<< 3.50	-1+x,y,-1+z
Cl(38)	*Cl(70)	3.434(4)	< 3.50	x,-1+y,z
Cl(44)	Cl(24)	3.388(3)	< 3.50	1+x,-1+y,z
Cl(44)	Cl(26)	3.464(3)	< 3.50	1+x,-1+y,z
Cl(45)	Cl(6)	3.431(3)	< 3.50	x,y,-1+z
Cl(51)	Cl(36)	3.181(3)	<< 3.50	1+x,y,1+z
N(38)	Cl(7)	3.221(6)	< 3.30	-1+x,y,-1+z
N(3)	Cl(30)	3.225(6)	< 3.30	x,-1+y,1+z
Cl(7)	N(38)	3.221(6)	< 3.30	1+x,y,1+z
Cl(30)	N(3)	3.225(6)	< 3.30	x,1+y,-1+z
*Cl(7A)	Cl(34)	3.204(4)	<< 3.50	1+x,y,1+z
Cl(57)	Cl(31)	3.300(3)	<< 3.50	x,y,1+z
*Cl(70)	Cl(5)	3.133(3)	<< 3.50	x,y,-1+z
Cl(5)	*Cl(70)	3.133(3)	<< 3.50	x,y,1+z
Cl(31)	Cl(57)	3.300(3)	<< 3.50	x,y,-1+z
Cl(34)	*Cl(7A)	3.204(4)	<< 3.50	-1+x,y,-1+z
Cl(36)	Cl(51)	3.181(3)	<< 3.50	-1+x,y,-1+z
Cl(51)	Cl(36)	3.181(3)	<< 3.50	1+x,y,1+z
2				
Cl(4)	Cl(4)	3.155(2)	<< 3.50	1-x,1-y,1-z
Cl(8)	Cl(12)	3.433(3)	< 3.50	2-x,-y,-z
Cl(12)	Cl(8)	3.433(3)	< 3.50	2-x,-y,-z
Cl(9)	Cl(9)	3.430(2)	< 3.50	1-x,-y,-z
Cl(9)	Cl(15)	3.486(2)	< 3.50	1-x,-y,-z
Cl(15)	Cl(9)	3.486(2)	< 3.50	1-x,-y,-z
Cl(10)	Cl(14)	3.485(2)	< 3.50	1-x,-y,-z
Cl(14)	Cl(10)	3.485(2)	< 3.50	1-x,-y,-z
Cl(14)	Cl(14)	3.488(2)	< 3.50	-x,1-y,-z
3				
Cl(1)	Cl(7)	3.490(5)	< 3.50	-x,-y,1-z
Cl(7)	Cl(1)	3.490(5)	< 3.50	-x,-y,1-z
Cl(2)	Cl(5)	3.437(5)	< 3.50	-1-x,1-y,1-z
Cl(5)	Cl(2)	3.437(5)	< 3.50	-1-x,1-y,1-z
Cl(4)	Cl(4)	3.436(4)	< 3.50	-x,1-y,1-z
Cl(4)	Cl(8)	3.484(3)	< 3.50	-x,1-y,1-z
Cl(8)	Cl(4)	3.484(3)	< 3.50	-x,1-y,1-z
Cl(7)	Cl(7)	3.374(4)	< 3.50	1-x,-y,1-z
Cl(9)	Cl(18)	3.459(4)	< 3.50	1+x,y,z
Cl(18)	Cl(9)	3.459(4)	< 3.50	-1+x,y,z
Cl(16)	Cl(16)	3.178(4)	<< 3.50	-x,-y,-z