

Supporting Information

Superexchange coupling through diamagnetic $[\text{Fe}(\text{CO})_4]^{2-}$ bridging ligands in a xenophilic cluster.

Tobias Krämer,^a Zhenyang Lin,^b and John E. McGrady*^a

^aDepartment of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom; ^bDepartment of Chemistry, The Hong Kong University of Science and Technology, Hong Kong.

Coordinates of optimised (broken-symmetry) structure of **1**

Fe	-1.766534000	0.466131000	-1.281431000
Mn	0.052048000	-1.351002000	-0.536646000
O	1.025563000	-2.272161000	-2.291127000
O	-0.877574000	-3.270149000	0.017326000
O	-2.964592000	-0.992330000	0.965082000
O	-2.768428000	3.195913000	-0.961812000
O	0.494089000	0.784272000	-3.123006000
O	-3.619396000	-0.584387000	-3.295468000
C	2.470864000	-2.234144000	-2.538187000
C	2.648289000	-2.777606000	-3.953604000
C	1.330568000	-2.380736000	-4.632905000
C	0.318677000	-2.611787000	-3.518948000
C	-1.938113000	-3.893951000	-0.761824000
C	-2.811691000	-4.606966000	0.262022000
C	-1.779122000	-5.050071000	1.307318000
C	-0.828004000	-3.857972000	1.360099000
C	-2.426520000	-0.427841000	0.099251000
C	-2.354157000	2.118710000	-1.068990000
C	-0.359513000	0.634426000	-2.343785000
C	-2.889752000	-0.173639000	-2.503668000
H	2.959982000	-2.835784000	-1.760135000
H	2.797719000	-1.187635000	-2.451954000
H	2.760674000	-3.874103000	-3.939016000
H	3.535005000	-2.352945000	-4.446234000
H	1.105274000	-2.974612000	-5.530877000
H	1.342610000	-1.315748000	-4.911376000
H	-0.575951000	-1.977728000	-3.584237000

H	0.009912000	-3.670034000	-3.456848000
H	-1.473458000	-4.601874000	-1.470360000
H	-2.455845000	-3.105771000	-1.326233000
H	-3.374176000	-5.442844000	-0.179072000
H	-3.528322000	-3.896671000	0.702664000
H	-1.250448000	-5.955978000	0.968346000
H	-2.221967000	-5.263796000	2.290915000
H	-1.163528000	-3.091925000	2.074105000
H	0.216673000	-4.124120000	1.570438000
Fe	1.766535000	-0.466132000	1.281431000
Mn	-0.052047000	1.351002000	0.536646000
O	-1.025563000	2.272161000	2.291127000
C	-2.470864000	2.234146000	2.538185000
C	-2.648290000	2.777610000	3.953601000
C	-1.330571000	2.380737000	4.632904000
C	-0.318678000	2.611786000	3.518948000
H	0.575949000	1.977725000	3.584239000
H	-0.009910000	3.670032000	3.456848000
H	-1.105276000	2.974613000	5.530877000
H	-1.342614000	1.315749000	4.911376000
H	-2.760673000	3.874107000	3.939013000
H	-3.535007000	2.352951000	4.446231000
H	-2.959980000	2.835786000	1.760133000
H	-2.797721000	1.187637000	2.451953000
O	0.877575000	3.270149000	-0.017325000
C	1.938113000	3.893950000	0.761825000
C	2.811691000	4.606965000	-0.262021000
C	1.779123000	5.050071000	-1.307317000
C	0.828004000	3.857971000	-1.360098000
H	1.163529000	3.091924000	-2.074104000
H	-0.216673000	4.124119000	-1.570438000
H	1.250449000	5.955977000	-0.968345000
H	2.221967000	5.263795000	-2.290914000
H	3.374176000	5.442843000	0.179073000
H	3.528323000	3.896670000	-0.702663000
H	1.473459000	4.601873000	1.470361000
H	2.455845000	3.105770000	1.326233000
C	2.426521000	0.427841000	-0.099250000
O	2.964593000	0.992330000	-0.965081000
C	2.354157000	-2.118711000	1.068989000
O	2.768427000	-3.195914000	0.961810000
C	0.359514000	-0.634426000	2.343785000
O	-0.494088000	-0.784272000	3.123007000
C	2.889753000	0.173636000	2.503669000
O	3.619398000	0.584383000	3.295469000

^{BS}1 ($M_s = 0$): $E = -6665.67162757 E_h$ ($\langle S^2 \rangle = 4.97$)

^{HS}1 ($M_s = 5$): $E = -6665.66662998 E_h$ ($\langle S^2 \rangle = 30.03$), single-point on BS geometry

Coordinates of optimised (broken-symmetry) structure of 2

Cl	-1.386904000	0.409797000	-0.978485000
Mn	0.033152000	-1.542976000	-0.652373000
O	1.014689000	-2.118332000	-2.383151000
O	-0.939968000	-3.199893000	0.119874000
C	2.348801000	-2.770514000	-2.412662000
C	2.531030000	-3.210714000	-3.857809000
C	1.745245000	-2.149506000	-4.641927000
C	0.521298000	-1.924917000	-3.769109000
C	-2.069081000	-3.894450000	-0.547863000
C	-2.649449000	-4.803880000	0.524686000
C	-1.418850000	-5.163237000	1.369832000
C	-0.649156000	-3.852857000	1.420460000
H	2.331269000	-3.595311000	-1.686012000
H	3.086936000	-2.015639000	-2.100769000
H	2.101199000	-4.212171000	-4.016349000
H	3.592873000	-3.252235000	-4.138460000
H	1.469394000	-2.481757000	-5.652672000
H	2.328702000	-1.220273000	-4.738307000
H	0.090999000	-0.915587000	-3.829184000
H	-0.265271000	-2.675262000	-3.945914000
H	-1.649558000	-4.456767000	-1.396678000
H	-2.762999000	-3.124288000	-0.914169000
H	-3.141544000	-5.684425000	0.088180000
H	-3.396369000	-4.263934000	1.127577000
H	-0.820252000	-5.946289000	0.878477000
H	-1.679989000	-5.520785000	2.375848000
H	-1.010474000	-3.178858000	2.212512000
H	0.441054000	-3.965519000	1.500150000
Cl	1.418467000	-0.426114000	1.003372000
Mn	-0.001661000	1.526612000	0.677338000
O	-0.983322000	2.101719000	2.408134000
C	-2.317456000	2.753846000	2.437653000
C	-2.499628000	3.194173000	3.882769000
C	-1.713777000	2.133055000	4.666942000
C	-0.489863000	1.908424000	3.794085000
H	-0.059540000	0.899108000	3.854216000
H	0.296698000	2.658800000	3.970798000
H	-1.437888000	2.465399000	5.677646000
H	-2.297202000	1.203813000	4.763427000
H	-2.069813000	4.195654000	4.041198000
H	-3.561458000	3.235692000	4.163467000
H	-2.300000000	3.578580000	1.710928000
H	-3.055576000	1.998912000	2.125865000
O	0.971365000	3.183626000	-0.094816000
C	2.101223000	3.877541000	0.572320000
C	2.681129000	4.787087000	-0.500372000
C	1.449997000	5.147307000	-1.344374000

C	0.679652000	3.837298000	-1.394847000
H	1.039902000	3.163470000	-2.187528000
H	-0.410580000	3.950515000	-1.473474000
H	0.852168000	5.930461000	-0.852244000
H	1.710469000	5.505100000	-2.350476000
H	3.173986000	5.667251000	-0.063958000
H	3.427302000	4.247008000	-1.104070000
H	1.682539000	4.439751000	1.421622000
H	2.795110000	3.106997000	0.937880000

^{BS}2 ($M_s = 0$): $E = -4151.79873043 E_h$ ($\langle S^2 \rangle = 4.99$)

^{HS}2 ($M_s = 5$): $E = -4151.79711954 E_h$ ($\langle S^2 \rangle = 30.01$), single-point on BS geometry