The synthesis, characterization, DFT studies and catalytic activities of manganese (II) complex with 1,4-bis(2,2':6,2"-terpyridin-4'-yl) benzene

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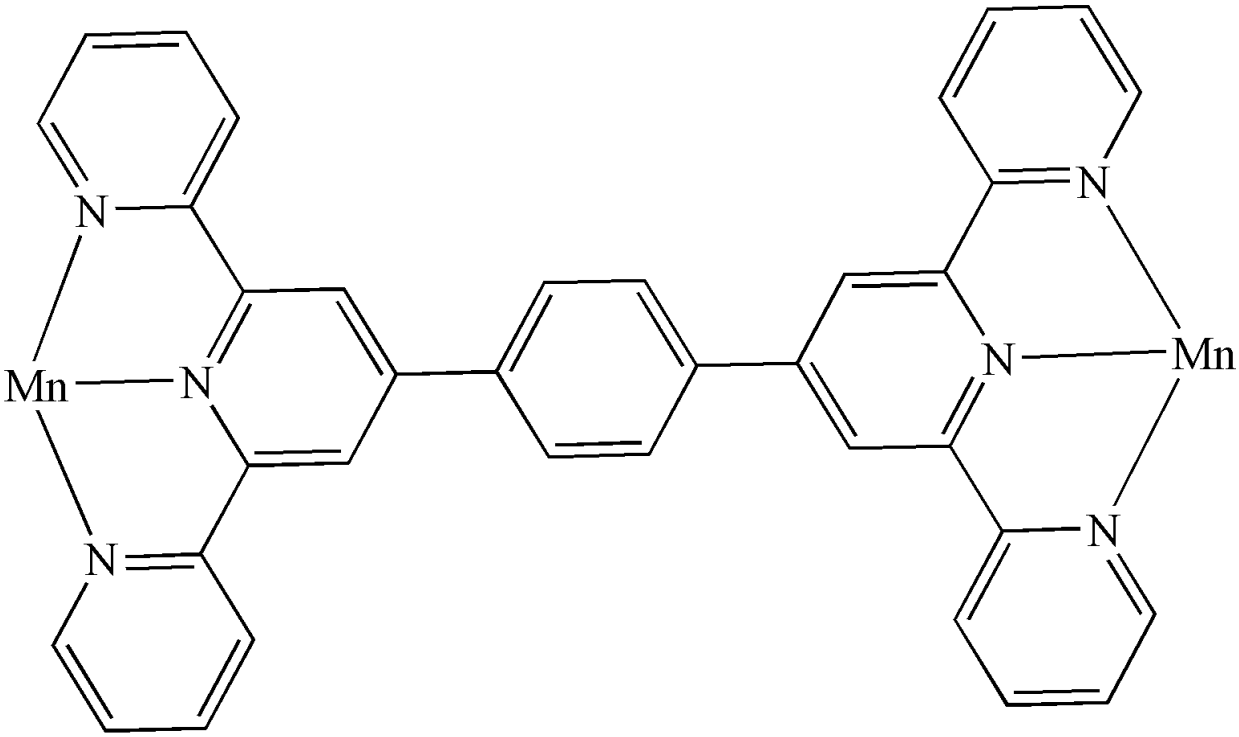
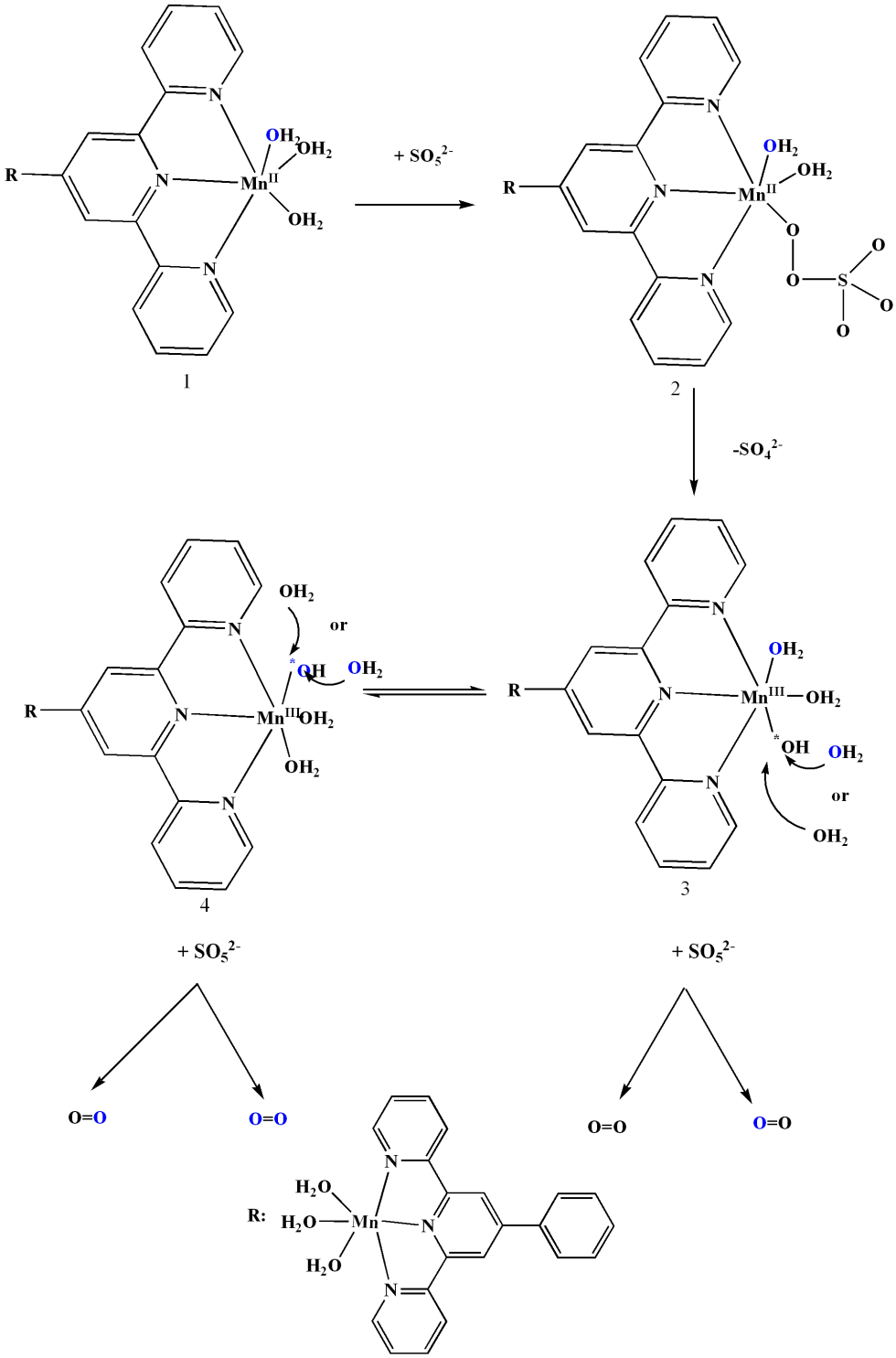


Scheme 1S. A proposed structure of **1**.



Scheme 2S. A proposed mechanism for $^{36}O_2$ production from the reaction of SO_5^{2-} and **1**.

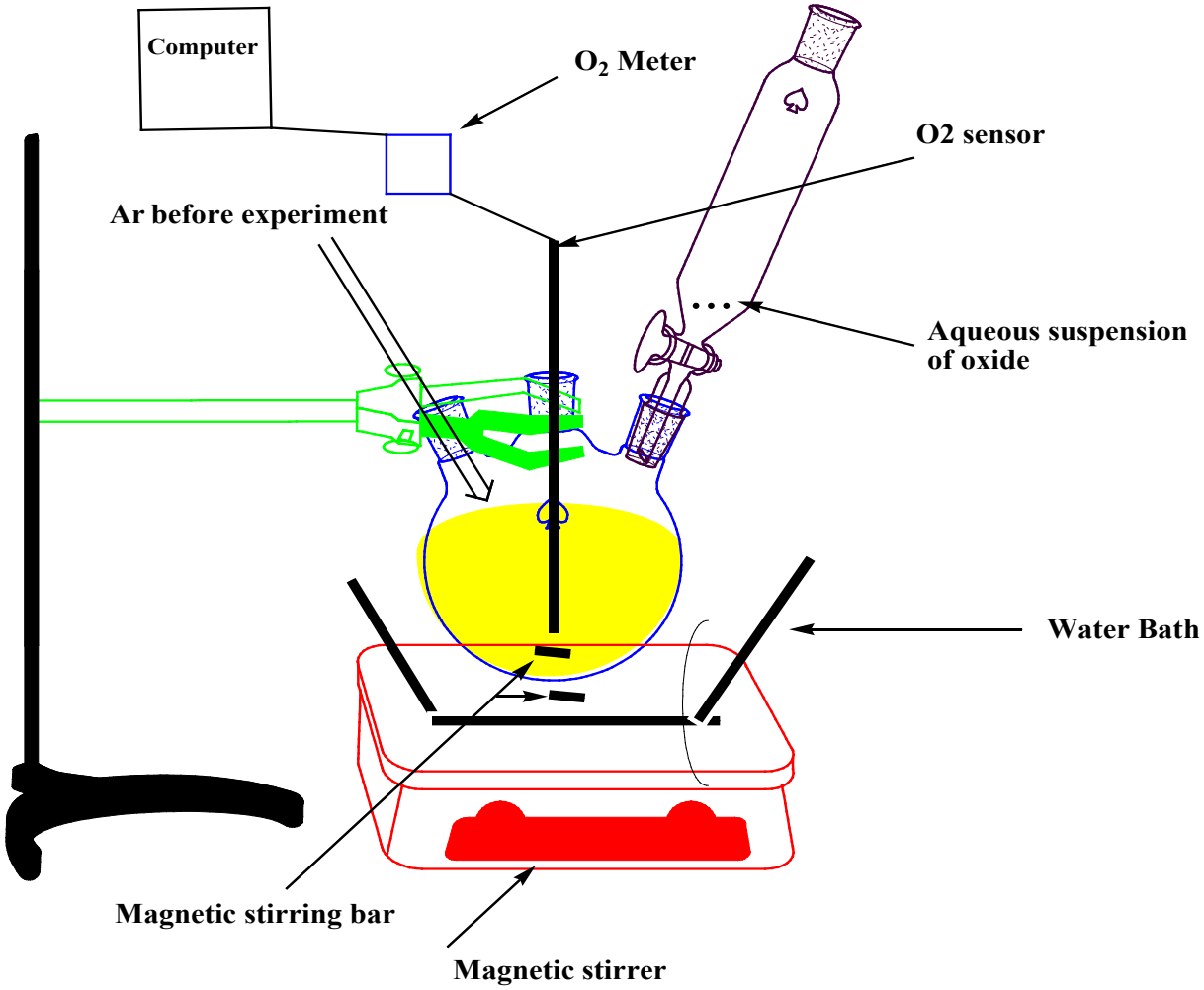


Fig. 1S. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) and **1**.

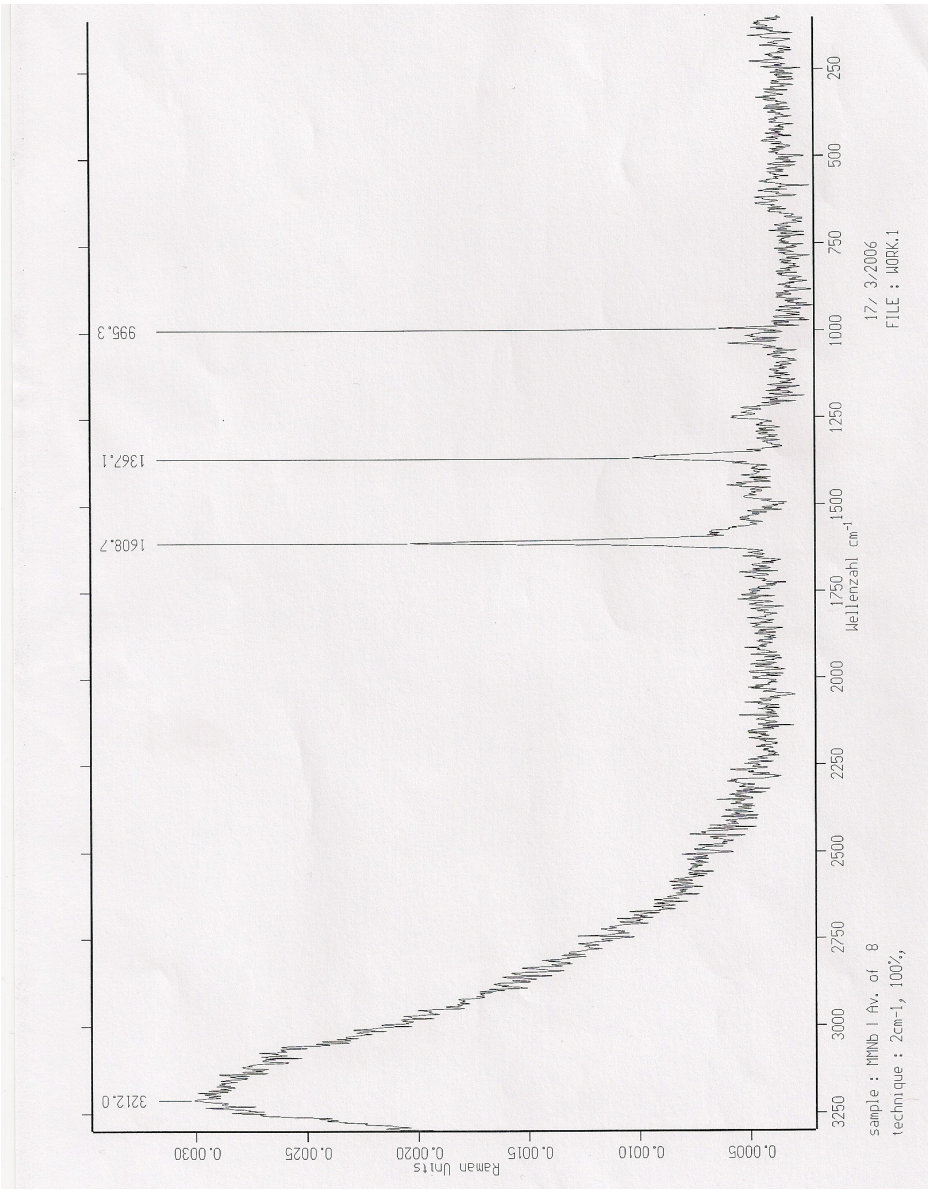


Fig. 2S. The Raman spectrum of **1** 120 s after reaction with oxone.

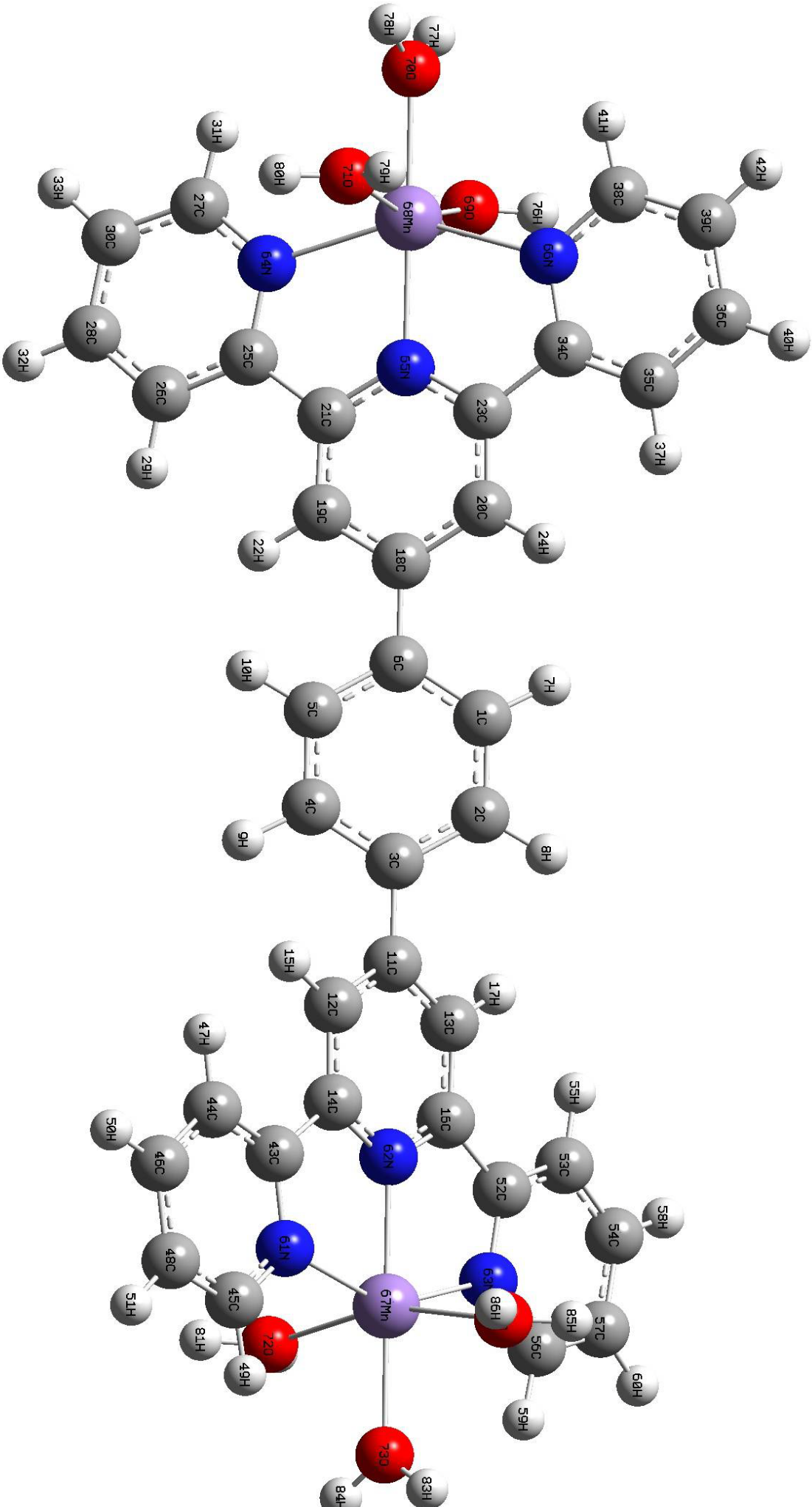


Fig. 3S: Atom numbers and labels used in optimization of structures of **1** and **3**.

Table 1S. Optimized structural parameters of species **1** and **3** using B3LYP/SBKJC method. The units for bond lengths (A-B) are Å and for bond (A-B-C) and dihedral angles (A-B-C-D) are degrees.

Structural property	1	3	Structural property	1	3
Mn68-N64	2.24	2.03	O69-Mn68-N65	100.0	97.9
Mn68-N65	2.19	1.94	O69-Mn68-N66	92.6	93.8
Mn68-N66	2.24	2.02	O70-Mn68-N64	105.6	99.0
Mn68-O69	2.25	1.76	O70-Mn68-N65	179.8	178.8
Mn68-O70	2.18	2.01	O70-Mn68-N66	105.8	99.8
Mn68-O71	2.25	2.05	O71-Mn68-N64	92.5	88.4
C25-N64	1.38	1.40	O71-Mn68-N65	99.4	94.2
C27-N64	1.37	1.37	O71-Mn68-N66	92.8	89.0
C21-C25	1.51	1.49	C25-N64-C27	119.2	120.2
C21-N65	1.37	1.38	C21-N65-C23	121.3	122.1
C23-N65	1.37	1.38	C34-N66-C38	119.2	120.3
C23-C34	1.51	1.49	O69-Mn68-N64-C25	99.8	93.5
C34-N66	1.38	1.40	O69-Mn68-N65-C23	89.8	90.9
C38-N66	1.37	1.37	O69-Mn68-N66-C38	80.3	80.1
N64-Mn68-N65	74.3	80.5	O71-Mn68-N64-C27	81.4	88.2
N65-Mn68-N66	74.3	80.5	O71-Mn68-N64-C21	89.4	91.0
O69-Mn68-O70	80.2	83.2	O71-Mn68-N64-C34	99.0	96.6
O70-Mn68-O71	80.4	84.7	N64-C25-C21-N65	1.0	-1.4
N64-Mn68-N66	148.5	160.7	N65-C23-C34-N66	0.0	1.0
O69-Mn68-O71	160.6	167.9	N65-C23-C20-C18	0.0	0.5
O69-Mn68-N64	92.6	92.7	C20-C18-C6-C1	34.8	24.9

Table 2S: Mülliken charges in atomic units and pure spin values [α (↑) –β (↓)] of Mn, O, and N atoms in one side of structures of **1** and **3**.

Mülliken charge	1	3	α (↑) –β (↓)	1	3
Mn68	1.00	0.07	Mn68	4.85	3.00
N64	0.24	0.26	N64	0.01	-0.04
N65	0.36	0.38	N65	0.01	-0.08
N66	0.24	0.28	N66	0.01	-0.04
O69	-0.58	-0.29	O69	0.01	0.10
O70	-0.57	-0.48	O70	0.01	0.02
O71	-0.58	-0.50	O71	0.01	0.01