

Title: Syntheses and Structural Characterizations of 24-Membered Di-Metal (Mn, Ni, Fe) Macrocylic Complexes and the C-S bond Formation between acetylacetonate and mercapto N-heterocycle

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1. Structures and Filled Drawing of Several Complexes

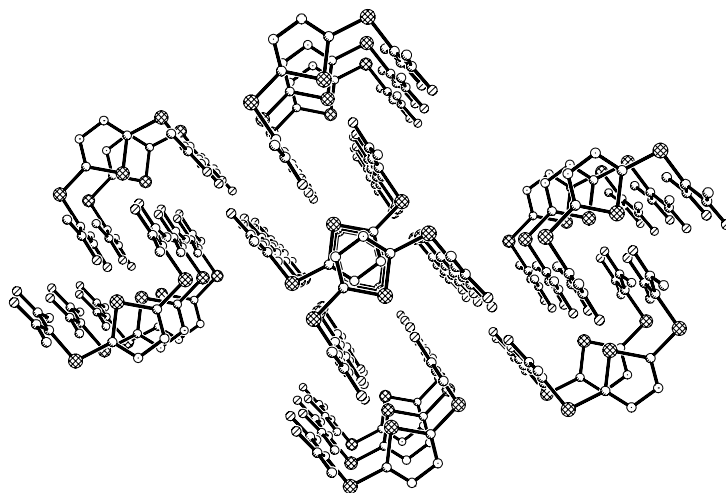


Figure S1. Packing diagram of H₂L.

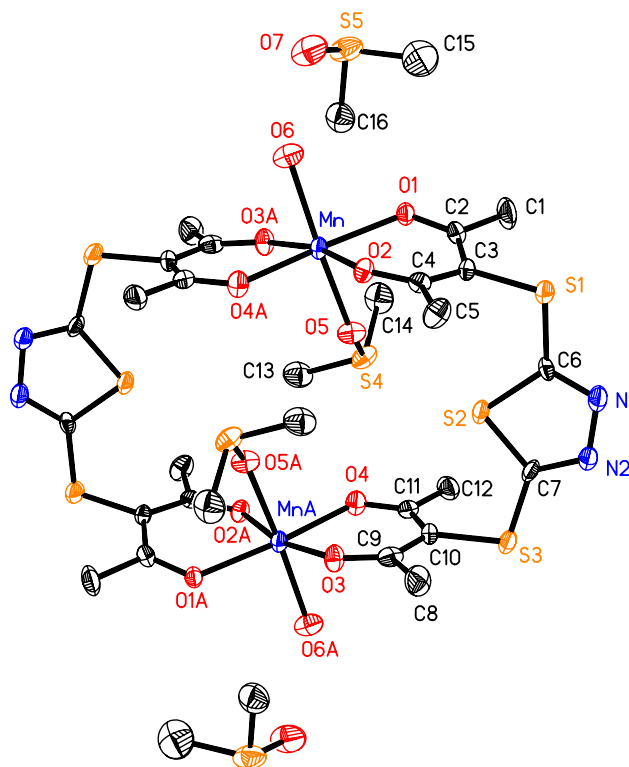


Figure S2 Structure of [MnL(H₂O)(dmsO)]₂·2dmsO (1)

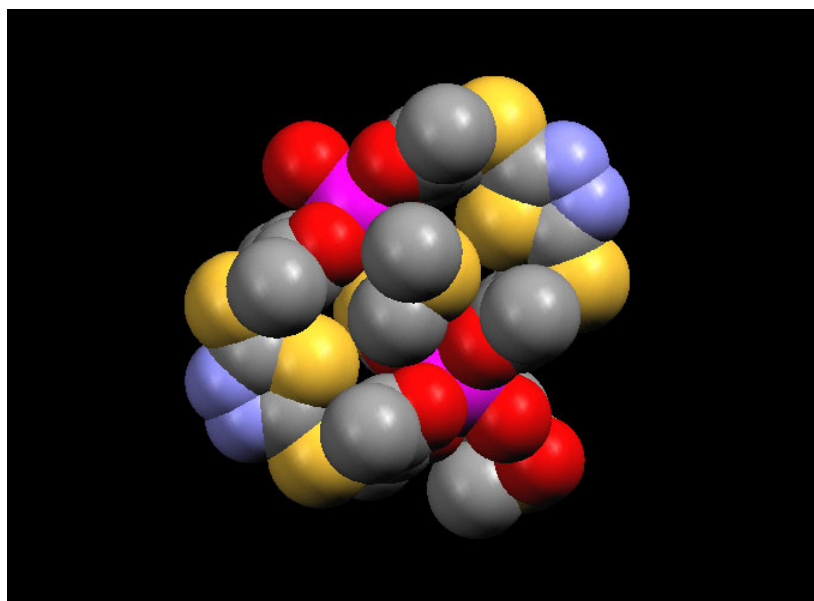


Figure S3. Filled drawing of **1**

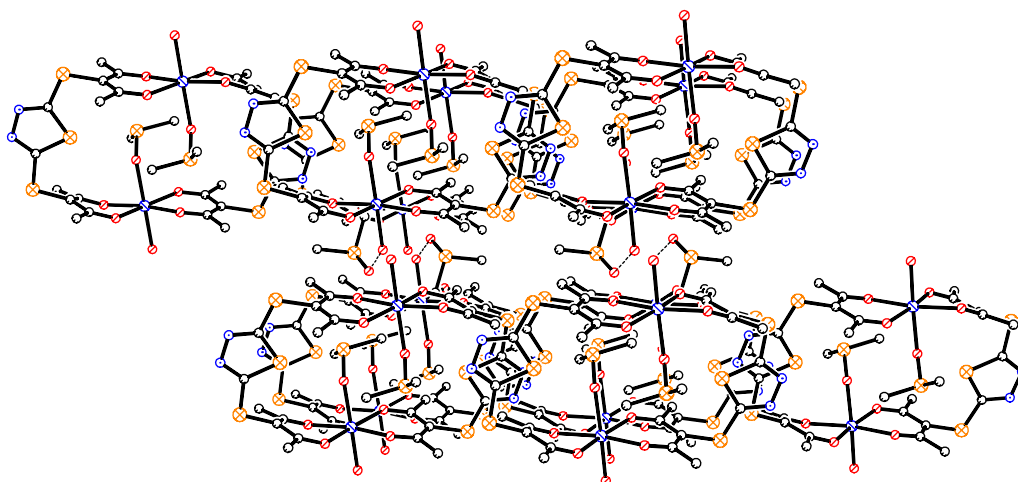


Figure S4 Packing diagram of **1**. Hydrogen bonding interactions between H₂O ligand and the solvate *dms**o* molecule outside the macrocycle are shown in dot lines. The adjacent thiadiazole rings overlap in a head-tail manner. Ligated *dms**o* exists in the channel formed by the overlapping cavities.

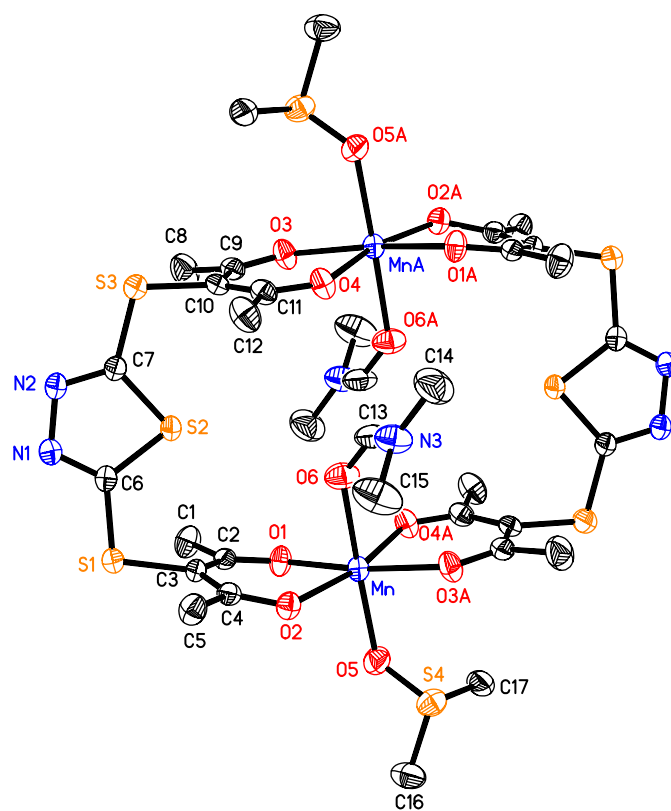


Figure S5 Structure of $[\text{MnL}(\text{dmf})(\text{dmsO})]_2$ (**4**)

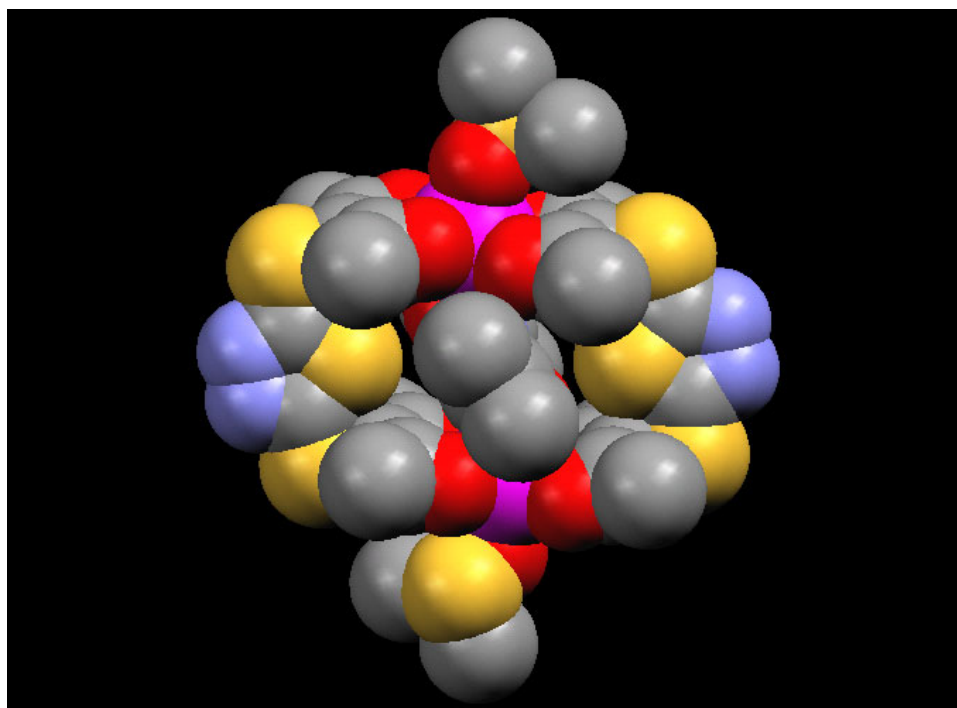


Figure S6. Filled Drawing of **4**

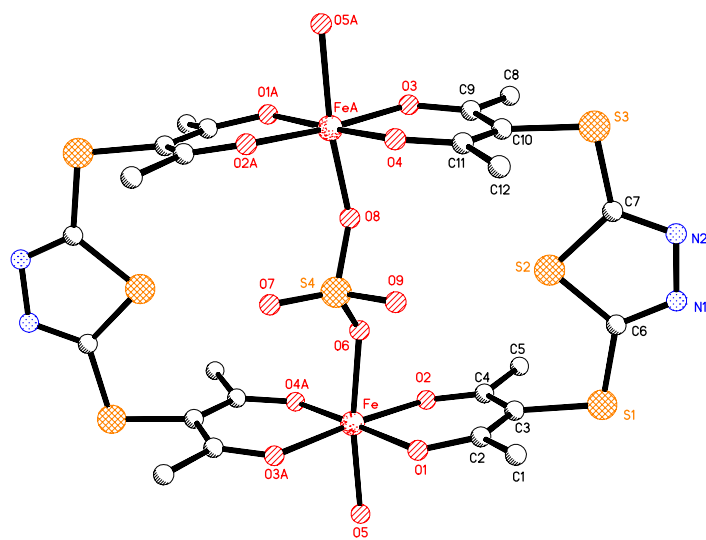


Figure S7. Rough structure of **7**. Disordered distribution of the atoms of the sulfate were found.

2. IR spectra for the complexes

H₂L: IR (KBr pellet, cm⁻¹) 1549(s), 1390(s), 1253(m), 1061(s), 1022(m), 910(m), 752(w), 647(w), 536(w), 484(w).

1: IR (KBr pellet, cm⁻¹) 3419(m, br), 1587(s), 1383(s), 1336(s), 1053(m) 1026(s), 957(m), 903(w), 490(w).

2: IR (KBr pellet, cm⁻¹) 3400(m, br), 1674(s), 1649(s), 1587(s), 1383(s), 1336(m), 1051(m), 1018(w), 906(w), 498(w).

3: IR (KBr pellet, cm⁻¹) 1676(s), 1653(s), 1589(s), 1389(s), 1373(s), 1336(m), 1051(m), 1018(w), 901(w), 677(w), 490(w), 430(w).

4: IR (KBr pellet, cm⁻¹) 1660(s), 1591(s), 1383(s), 1335(m), 1063(m), 1014(s), 958(w), 646(w), 492(w).

5: IR (KBr pellet, cm⁻¹) 3400(br, m), 1578(s), 1375(s), 1333(s), 1070(s), 1020(m), 904(m), 648(w), 496(w), 440(w).

7: IR (KBr pellet, cm⁻¹) 3394(m,br), 1566(s), 1367(s), 1338(s), 1225(m), 1128(s), 1065(s), 1020(s), 980(m), 698(m), 667(m), 619(w), 600(m), 459(m).

8: IR (KBr pellet, cm⁻¹) 3373(m, br), 1564(s), 1365(s), 1338(s), 1221(m), 1126(m), 1065(s), 1022(m), 985(m), 735(m), 700(m), 652(m), 592(m), 498(m), 461(m).

2. DTA and TG curves determined for Several Complexes

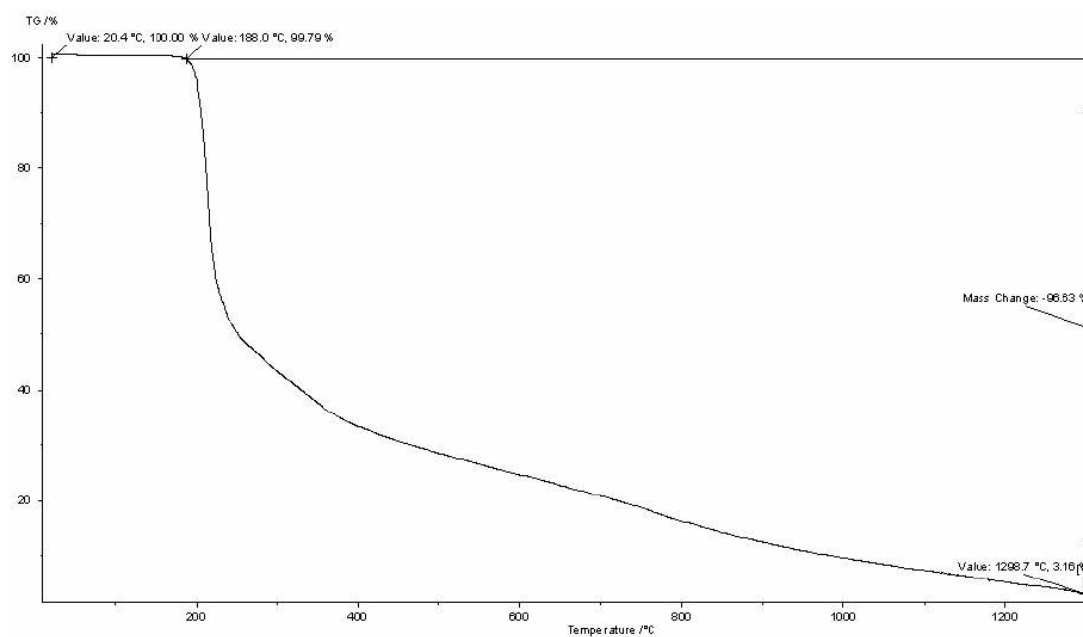


Figure S8. TG curve determined under dinitrogen atmosphere for H₂L

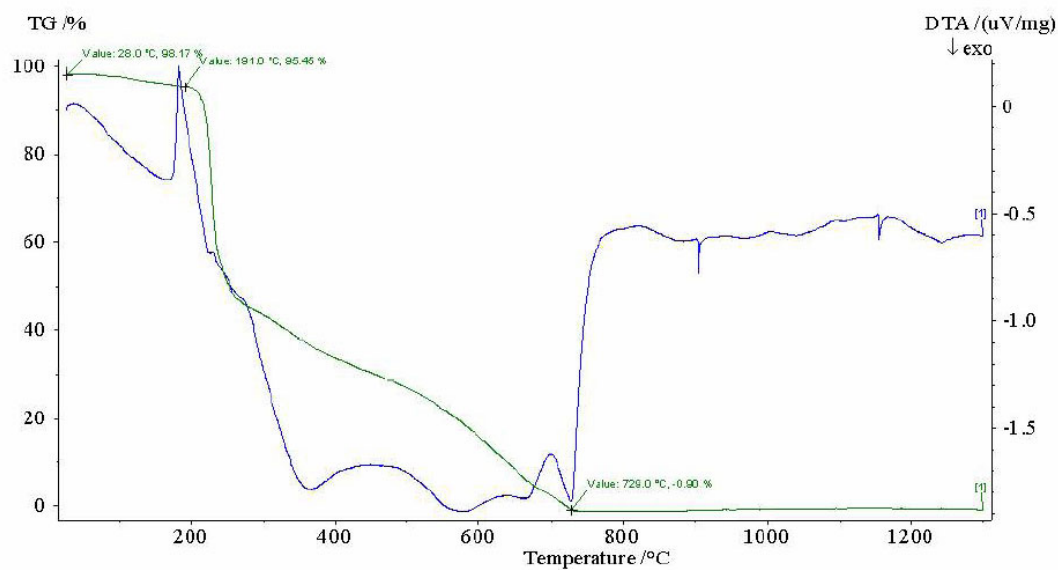


Figure S9. DTA and TG curves determined under air atmosphere for H₂L

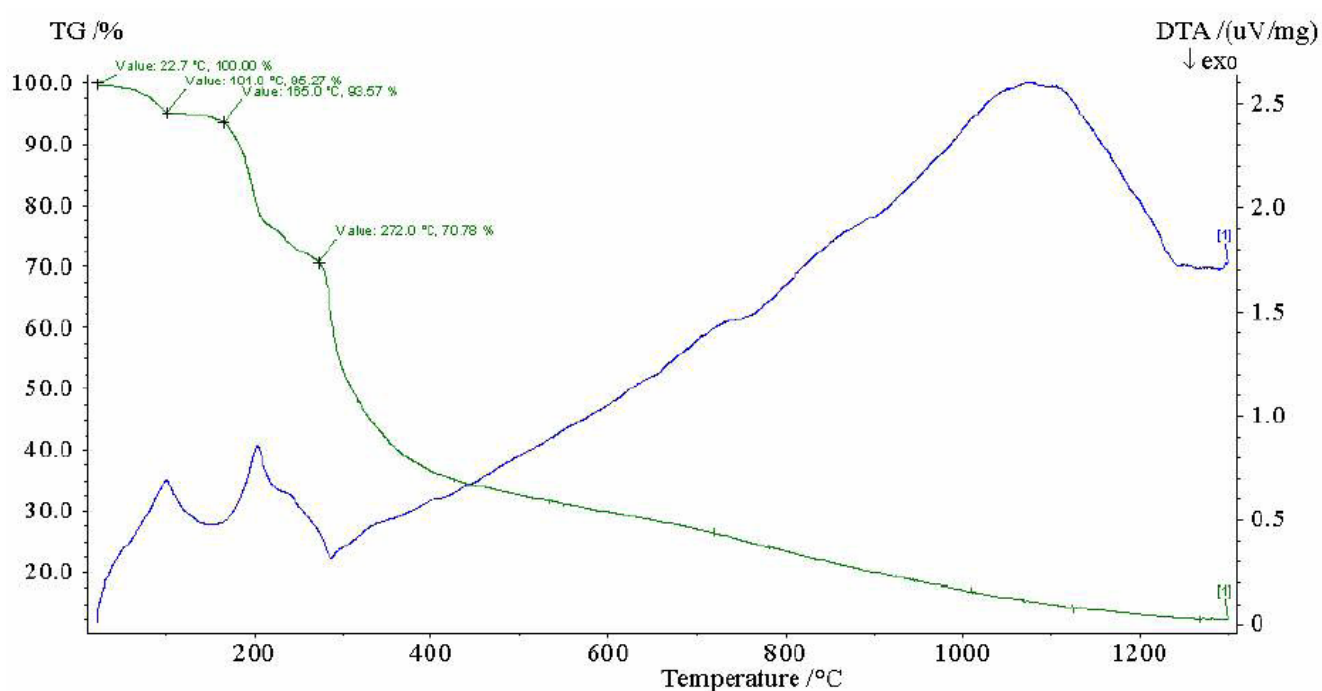


Figure S10. DTA and TG curves determined under dinitrogen atmosphere for 2

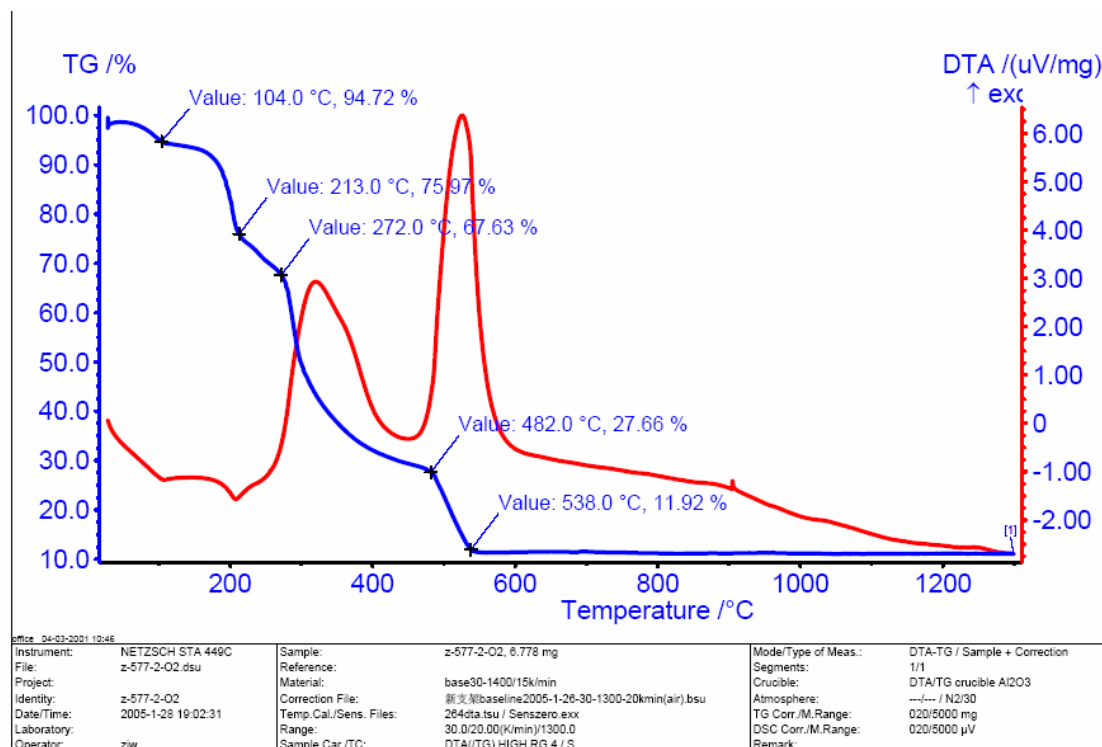


Figure S11. DTA and TG curves determined under air atmosphere for 2

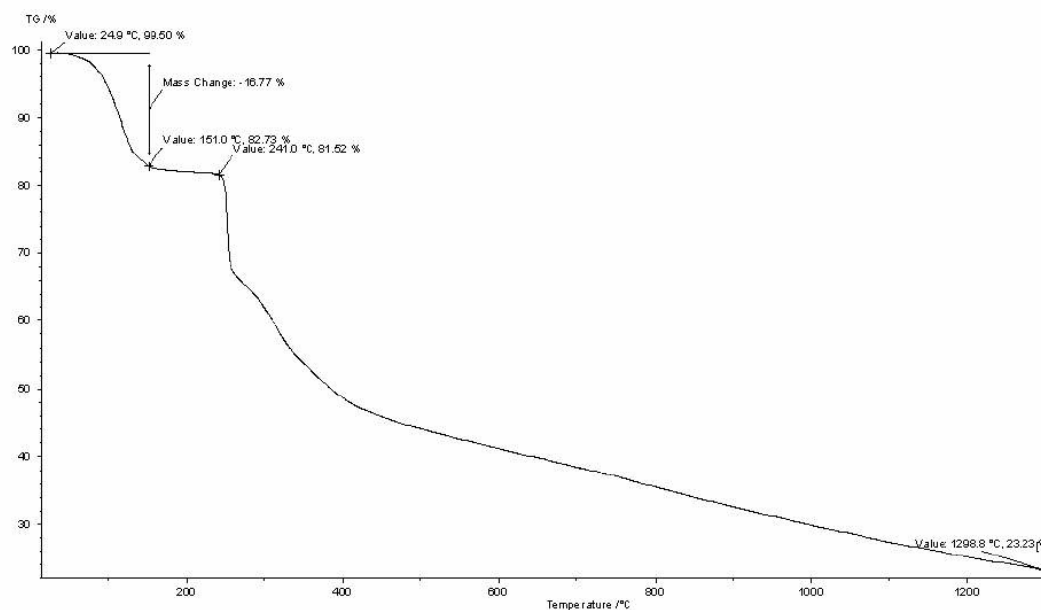


Figure S12. TG curve determined under dinitrogen atmosphere for **5**

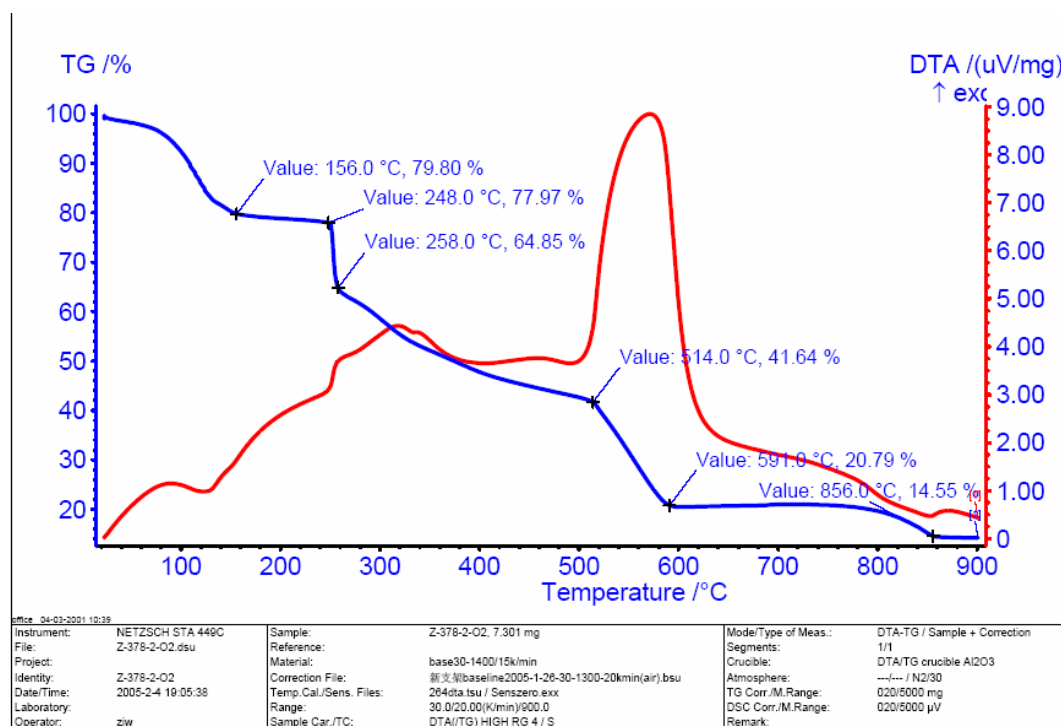


Figure S13. DTA and TG curves determined under air atmosphere for **5**

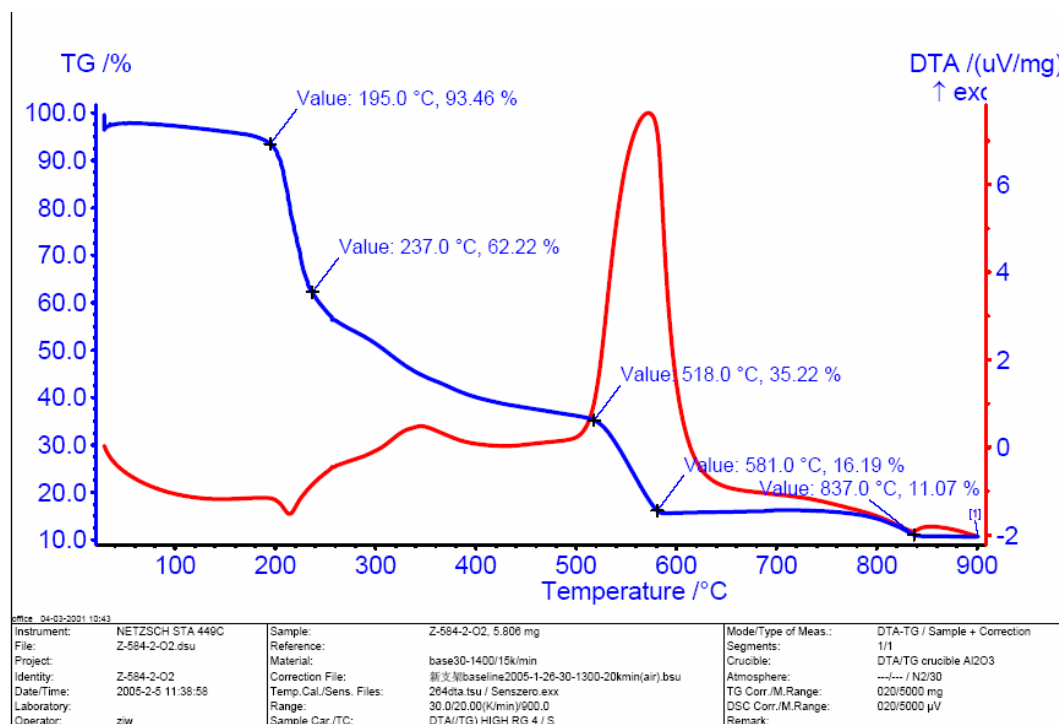


Figure S14. DTA and TG curves determined under air atmosphere for [MnL(dmf)(dmsO)] (4)