Electronic Supplementary Material (ESI) for Dalton Transactions.
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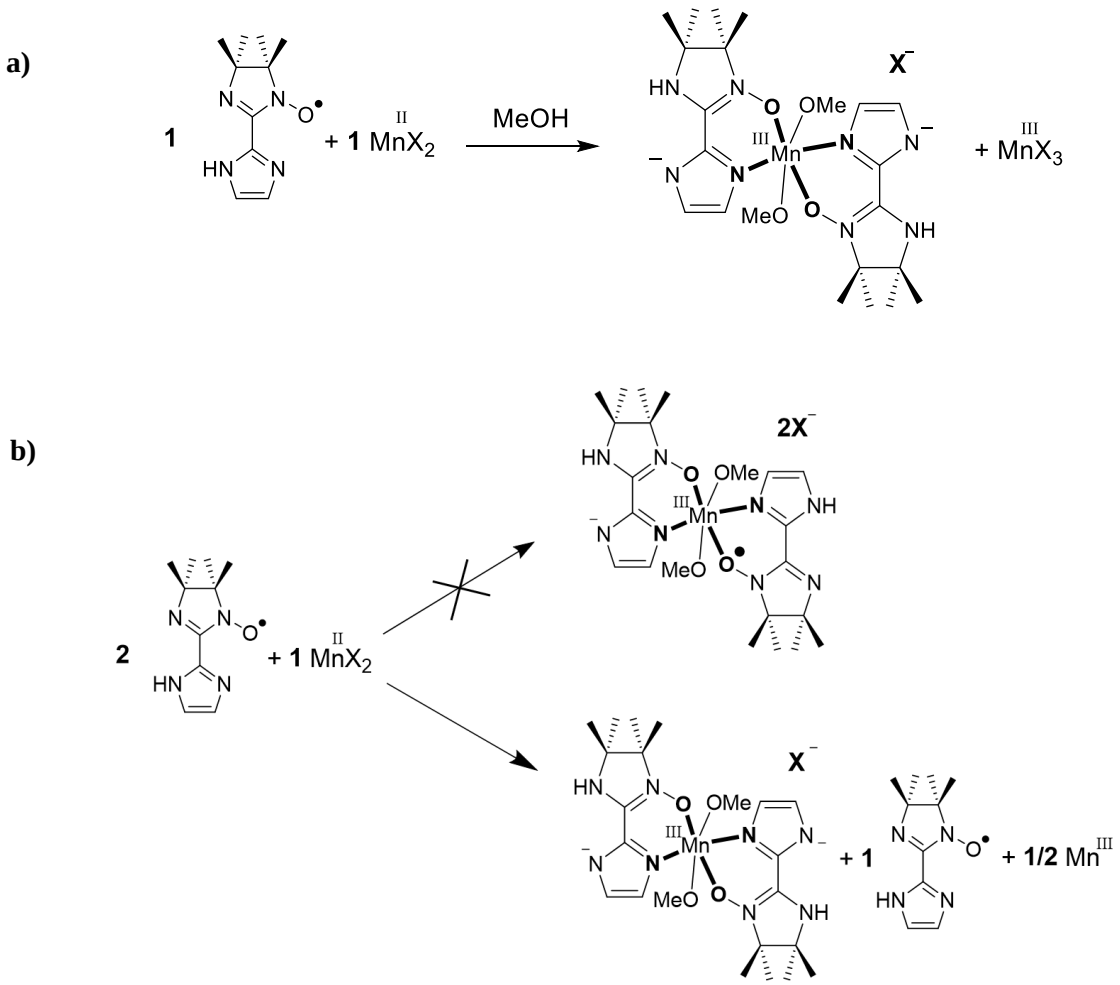
Electronic Supplementary Information



Scheme S1: Reaction schemes for different ratio of Mn(II) and imino nitroxide (IMImH) as reactants and X = OAc or ClO_4. a) ratio Mn(II):IMImH equal to 1:1 which give compounds **1** and **2**. b) ratio Mn(II):IMImH equal to 1:2 used in unsuccessful trials to have mixed complexes incorporating an imino nitroxide and its reduced form.

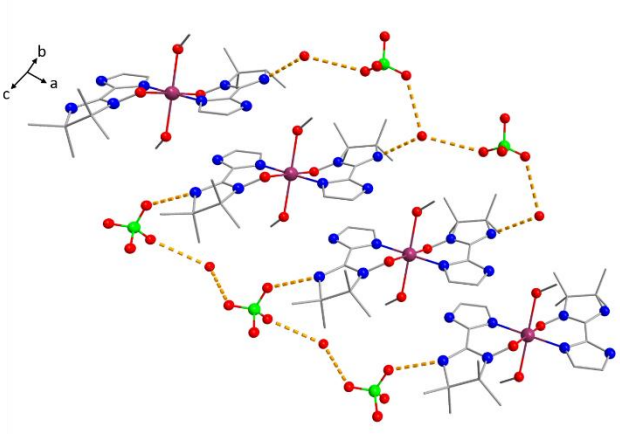
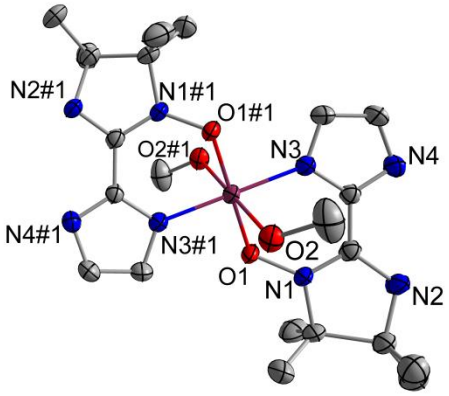
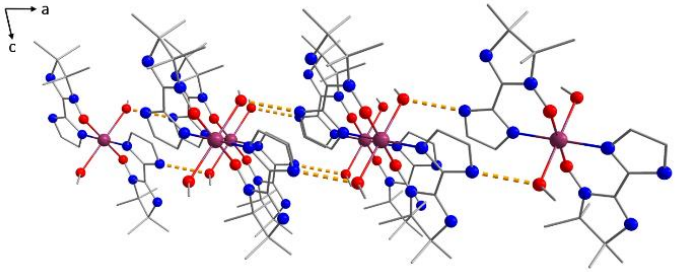


Figure S1: Intermolecular hydrogen bonds in compound **1**, drawn in orange dotted lines, between water molecules, perchlorate anions and nitrogen N2A/B, and between coordinated methanol molecules and nitrogen N4A/B. Hydrogen atoms are omitted for clarity. Each atom is depicted as follows: Mn, purple; O, red; N, blue; C, grey; Cl, green

a)



b)



c)

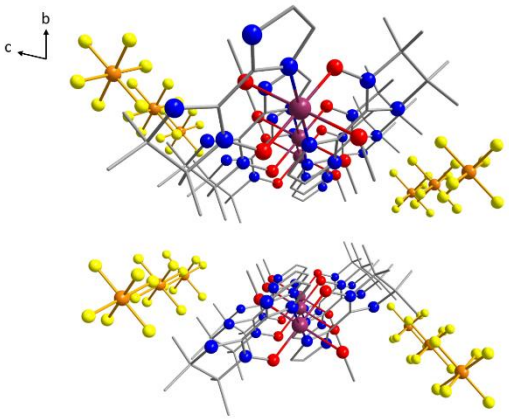


Figure S2: Crystal structure of complex **2** a) View of the complex with labels. b) Intermolecular hydrogen bonds between coordinated methanol molecules and imidazole moieties depicted in orange dotted lines. c) Crystal packing along the *a*-axis. Hydrogen atoms are omitted for clarity. Each atom is depicted as follows: Mn, purple; O, red; N, blue; C, grey; P, orange; F, yellow.

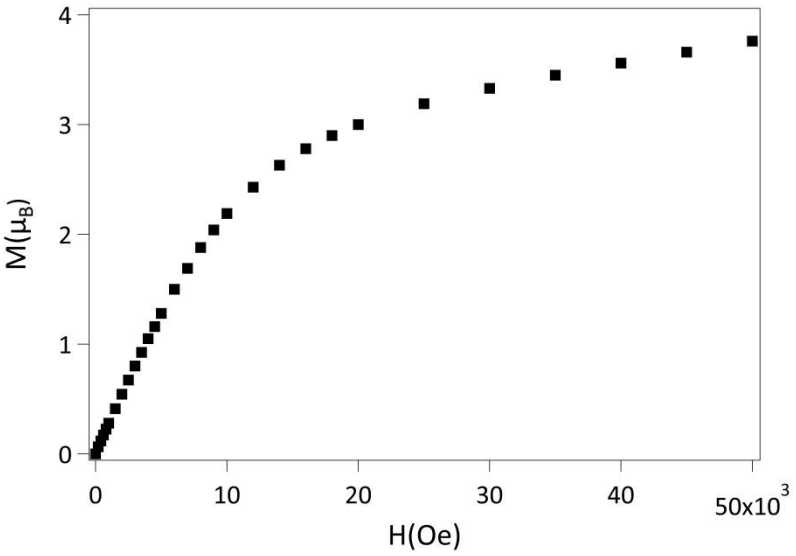


Figure S3: Magnetization of compound **1** at 2 K.

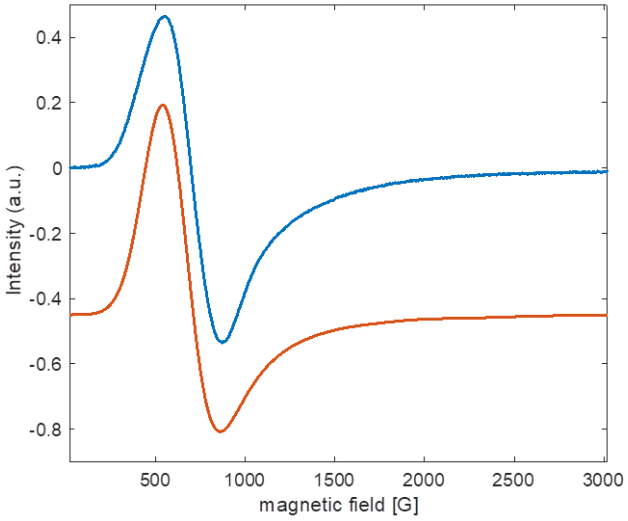


Figure S4: Experimental (top/blue) EPR spectra in parallel mode (T = 26K) for compound **1** and simulation (down/orange) EPR spectra with following values: S = 2, g = [2.07 1.98 1.95], E/D = 0.2, IDI = 2 cm^{-1}

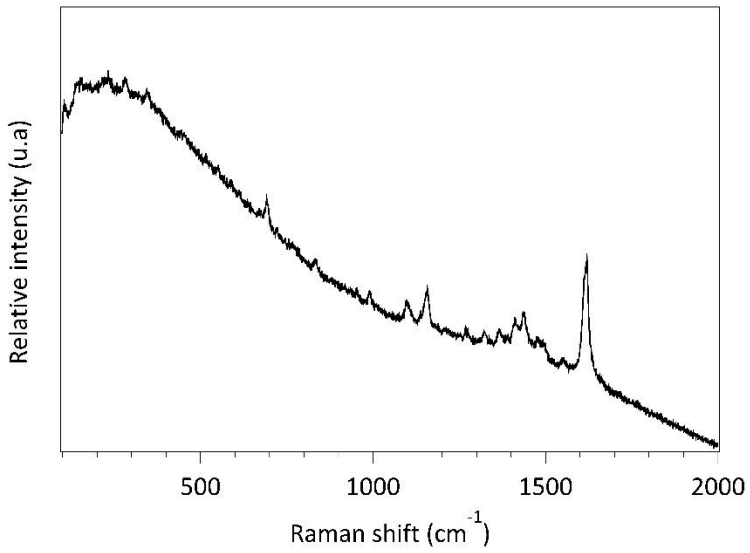


Figure S5: Raman spectra of non-coordinated radical IMImH at 293 K with 785 nm excitation

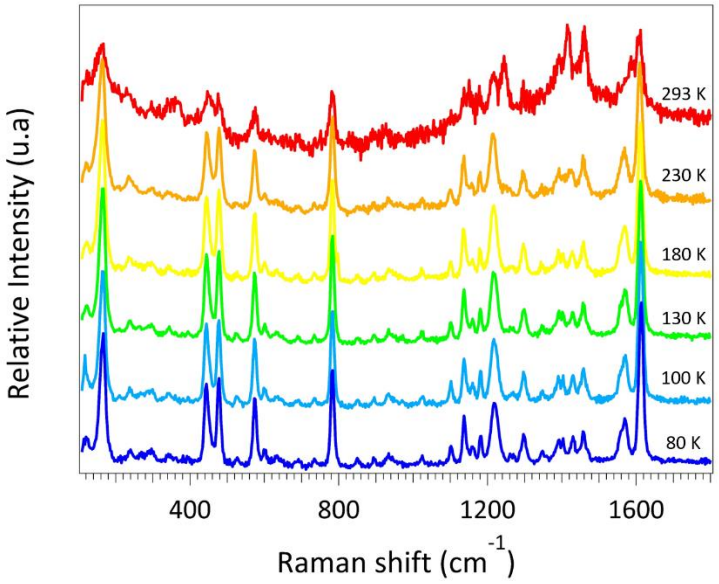


Figure S6: Raman spectra of compound **1** at several temperatures top from 293 K to 80K with 785 nm excitation

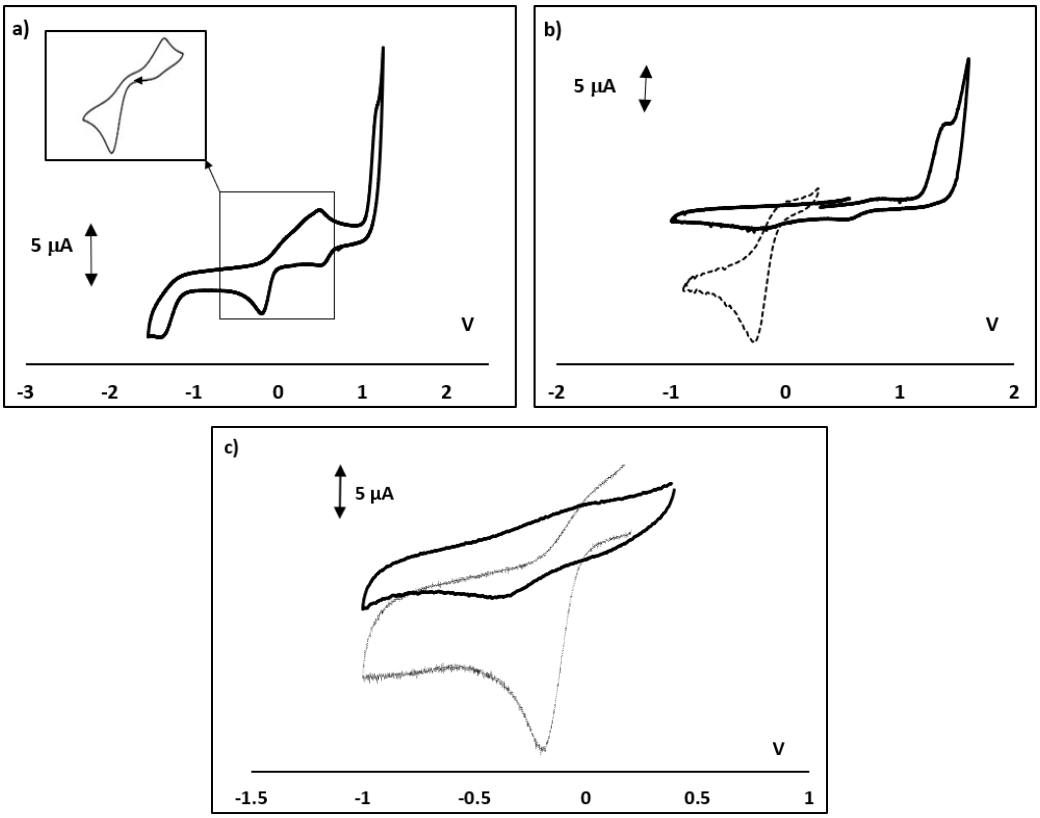


Figure S7: Cyclic voltammetry of non-coordinated radical IMImH at 0,1 V/s. a) In methanol solution and inset corresponds to a limited zone of the ECE process described in the manuscript. b) In CH_2Cl_2 solution (bold) and after addition of 20% of Methanol (dotted). c) Cyclic voltammetry focused on a limited potential region: before addition of Mn^{2+} (thin) and after addition of 1 eq of Mn^{II} (bold)