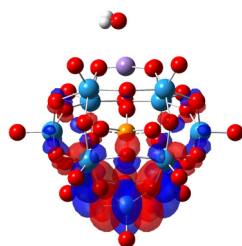
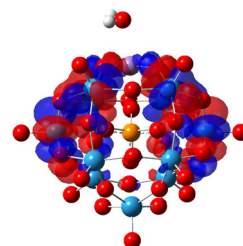


Figure S1. X-ray powder diffraction data for **2**.

2.198 eV

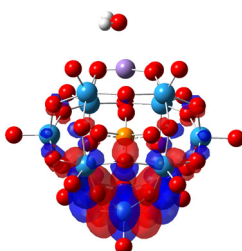


NTO(260 β)

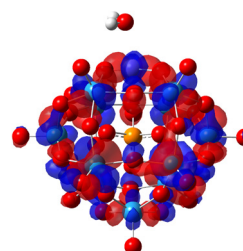


NTO(261 β)

2.601 eV

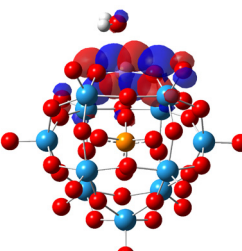


NTO(260 β)

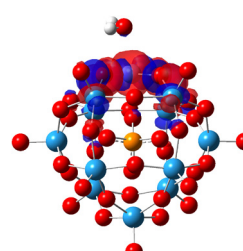


NTO(261 β)

3.625 eV



NTO(261 α)
from...



NTO(262 α)
to...

Figure S2. NTO analysis for $[(\text{Mn}^{\text{II}}(\text{H}_2\text{O}))\text{PW}_{11}\text{O}_{39}]^{5-}$. Color codes: Mn – purple, W – cyan, O – red, P – orange, H – white.

Table S1. Atomic ratios W/Mn for $[(\text{Mn}(\text{H}_2\text{O}))\text{PW}_{11}\text{O}_{39}]^{5-}$ peak calculated from HPLC-ICP-AES-data.

W/Mn	Mn 259.3 nm	Mn 260.5 nm	Mn 279.4 nm
W 209.8 nm	10.9±0.6	11.5±0.6	11.1±0.5
W 229.4 nm	11.3±0.5	11.2±0.5	11.5±0.6
W 239.7 nm	10.8±0.4	11.0±0.4	11.0±0.4

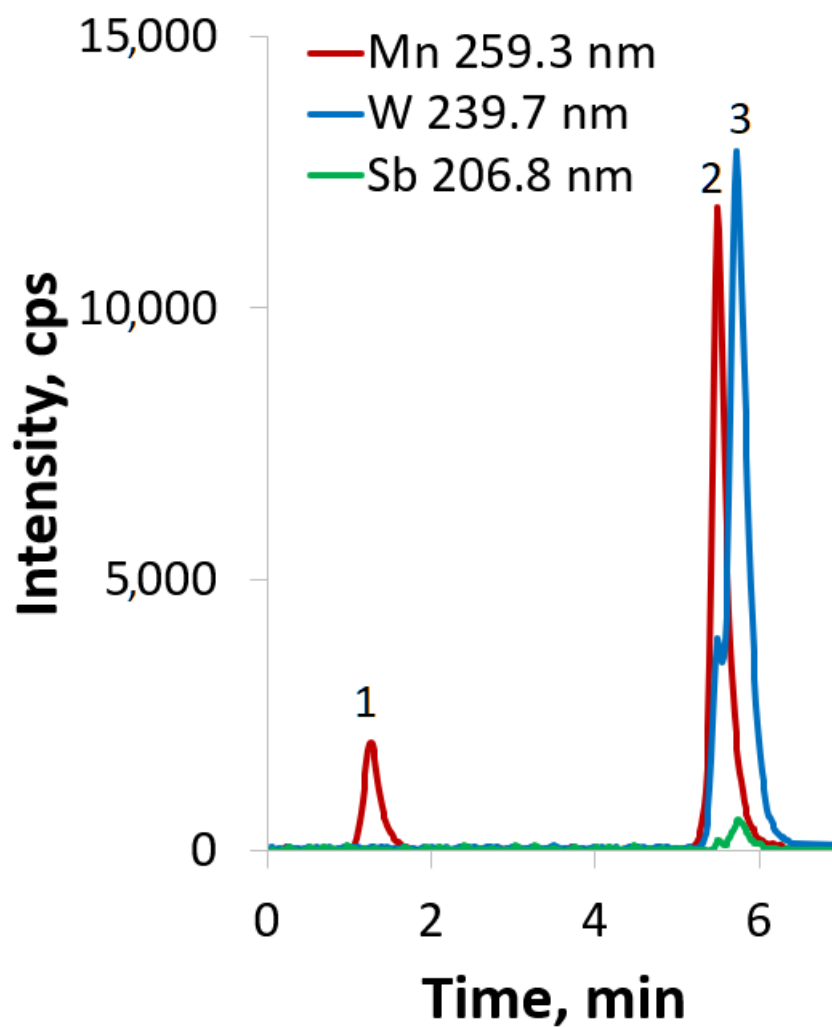


Figure S3. HPLC-ICP-AES chromatogram of **2** in water at natural pH scaled from the start of the elution.

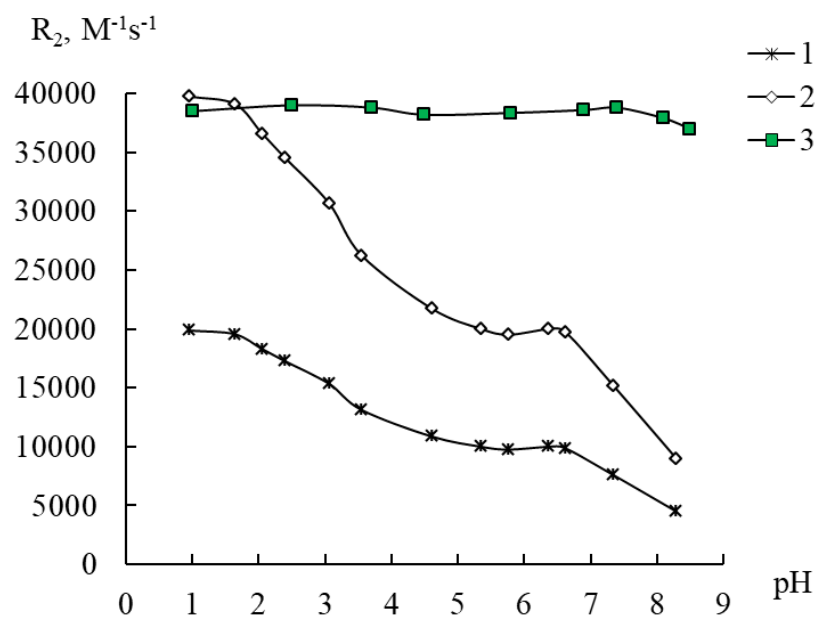


Figure S4. Dependence of the spin-spin relaxivity R_2 on pH in a 0.1 M solution of compound **3** in water. Calculations of relaxivity were carried out taking into account manganese(II) concentrations of 0.4 mM (1) and 0.2 mM (2). For comparison, data are presented for a MnCl_2 solution with a manganese(II) aqua ion content of 0.4 mM (3).

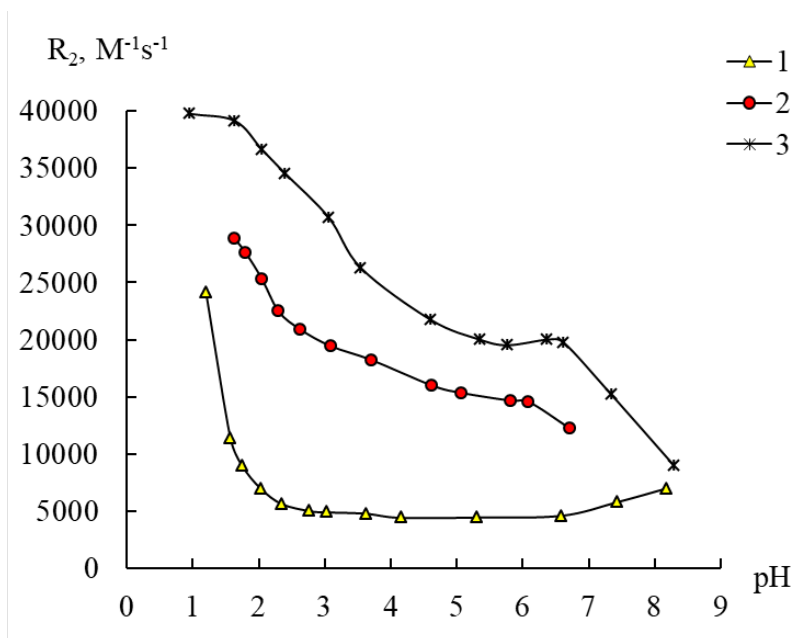


Figure S5. Changes in the relaxation efficiency R_2 (a) on the pH of solutions of compounds **1** (0.4 mM) (1), **2** (0.133 mM) (2), and **3** (0.1 mM) (3). CMn(II) 0.2 (3), 0.4 mM (1, 2).

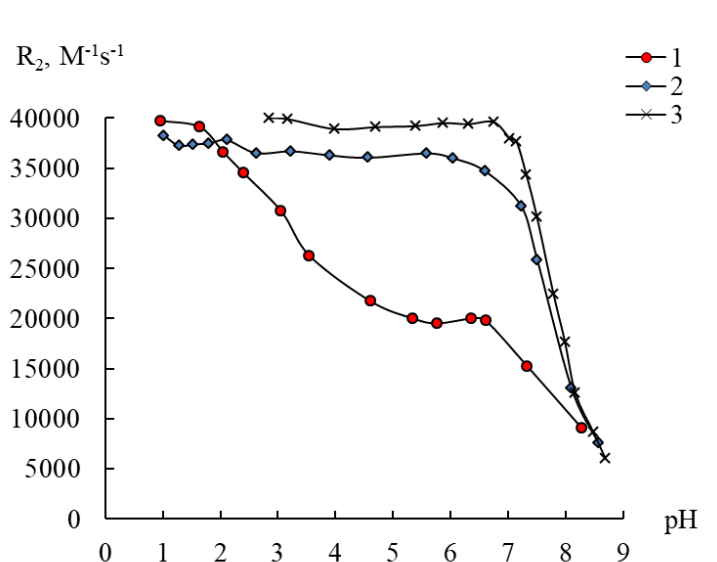


Figure S6. Changes in the relaxation efficiency R_2 on pH 0.1 mM solutions of compound **3** in water (1) and in PEI solution (2), and Mn(II) ions in PEI solution (3). $C_{\text{Mn(II)}}$ 0.2 (1, 2), 0.4 mM (3), C_{PEI} 10 mM (2, 3).

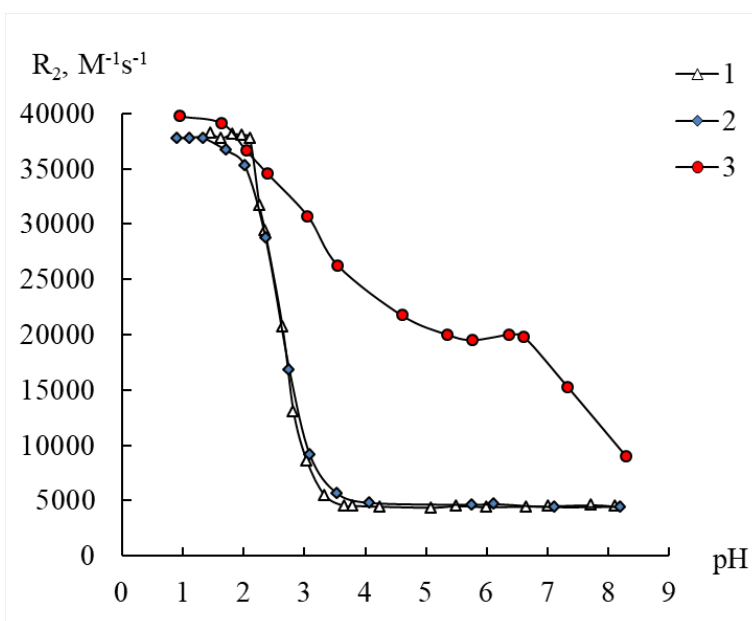


Figure S7. Changes in relaxation efficiency R_2 on pH of Mn(II)-EDTA systems (1), compound **1** – EDTA (2), aqueous solution of **1** (3). $C_{\text{Mn(II)}}$ 0.2 (2), 0.4 mM (1, 3), C_{EDTA} 1 mM (1, 2).

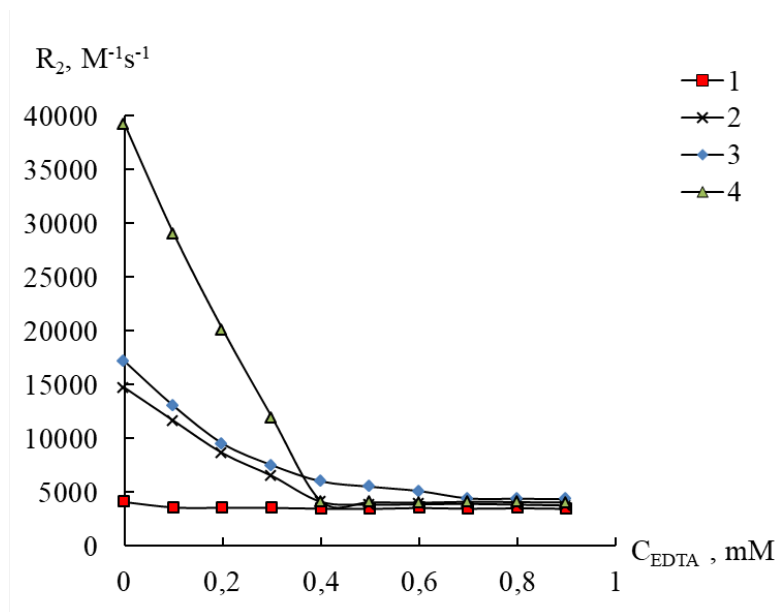


Figure S8. Change in the relaxation efficiency R_2 on the content of EDTA in solutions of compounds **1-3** (1-3) and in an aqueous solution of aqua ions Mn(II) (4), $C_{\text{Mn(II)}}$ 0.2 (3), 0.4 mM (1, 2, 4), pH 5.5.

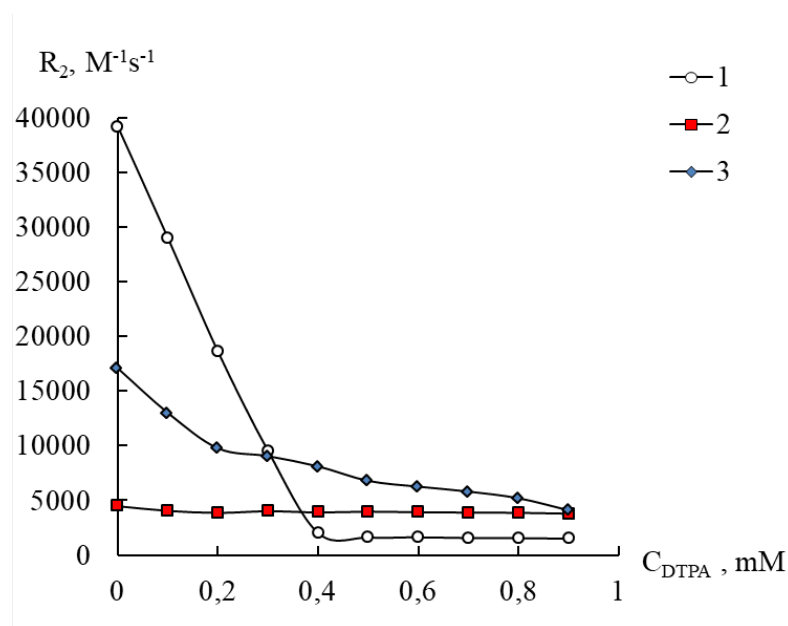


Figure S9. Dependence of the relaxation efficiency R_2 on the concentration of DTPA in aqueous solutions of Mn(II) (1) and compounds **1** (2) and **3** (3). $C_{\text{Mn(II)}}$ 0.2 (3), 0.4 mM (1, 2), pH 5.5.

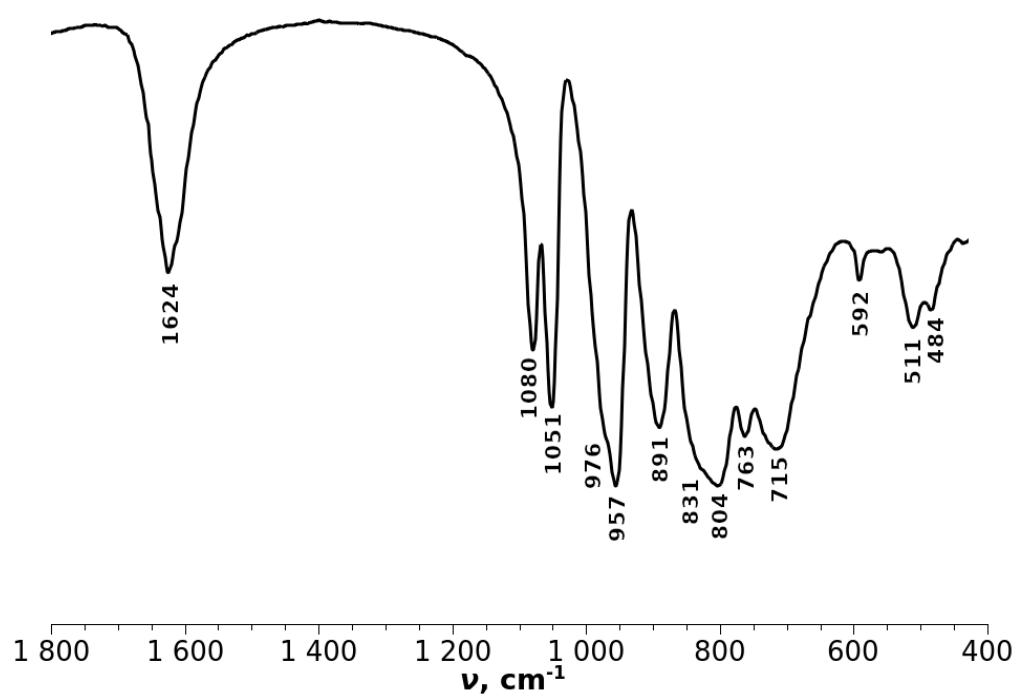


Figure S10. IR spectrum of complex 1.

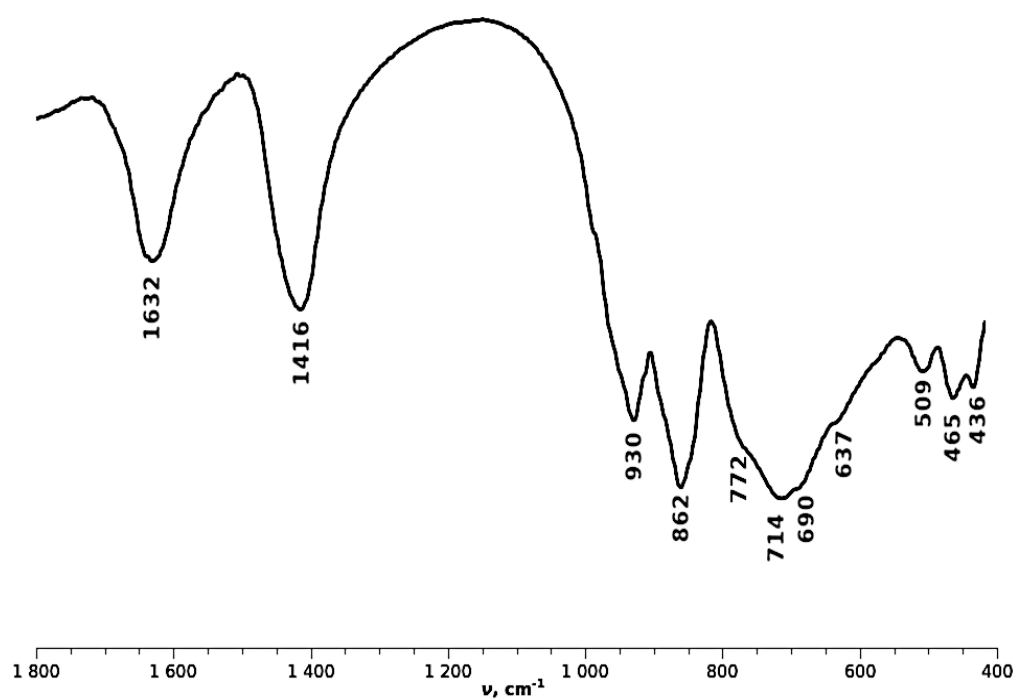


Figure S11. IR spectrum of complex 2.

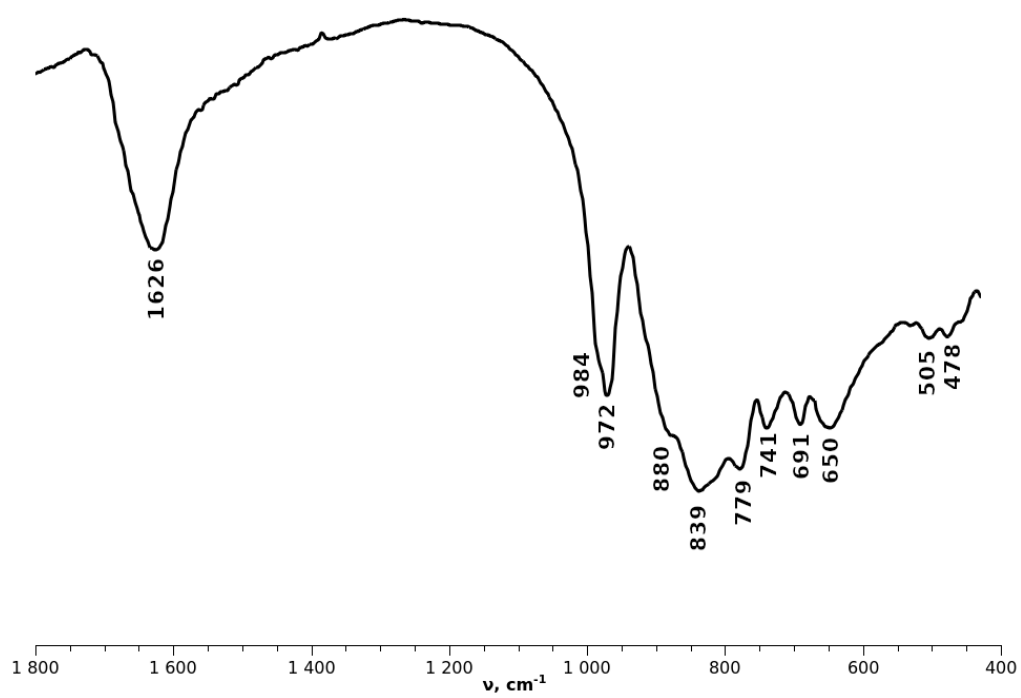


Figure S12. IR spectrum of complex 3.