

Fig 1S. ^1H - ^1H -2D-ROESY spectrum on a cavitand ligand in CDCl_3 . The values of NOE between one H^a proton in a 3 or 5 position of the pyrimidyl groups and two protons, H^b and H^d , of the bridging methylene are shown in 0.25% and 0.49%, respectively.

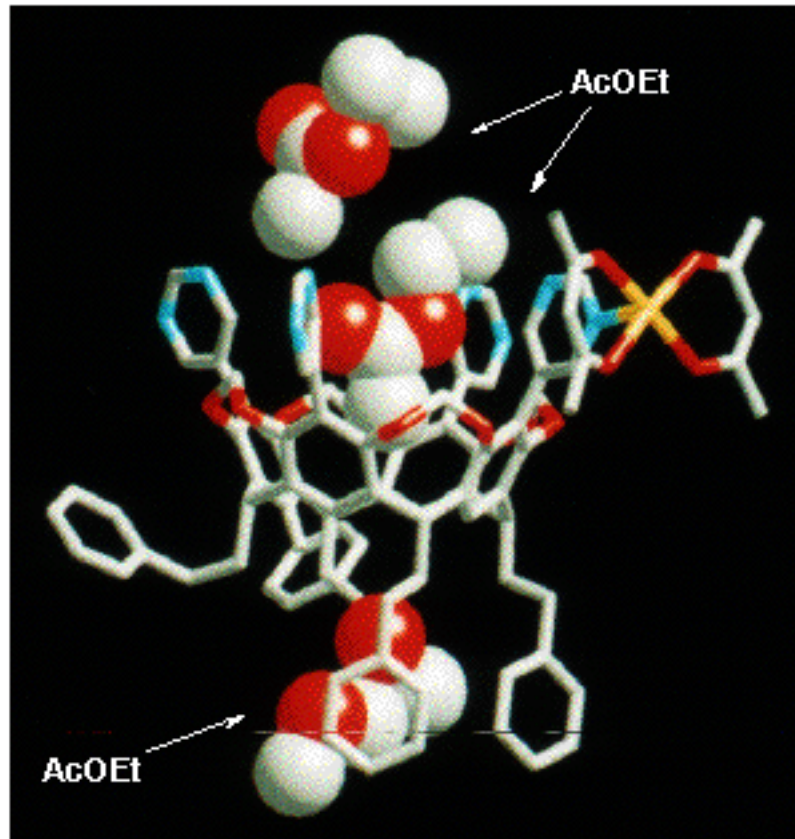


Fig. 2S The asymmetry unit of the crystal: The unit is constructed from a Mn complex with a cavitaand ligand, one AcOEt molecule into the cavitaand cavity and two AcOEt with heavy disordering. The white, red, blue and yellow atoms represent a carbon, an oxygen, a nitrogen atoms and a manganese (II) ions, respectively.

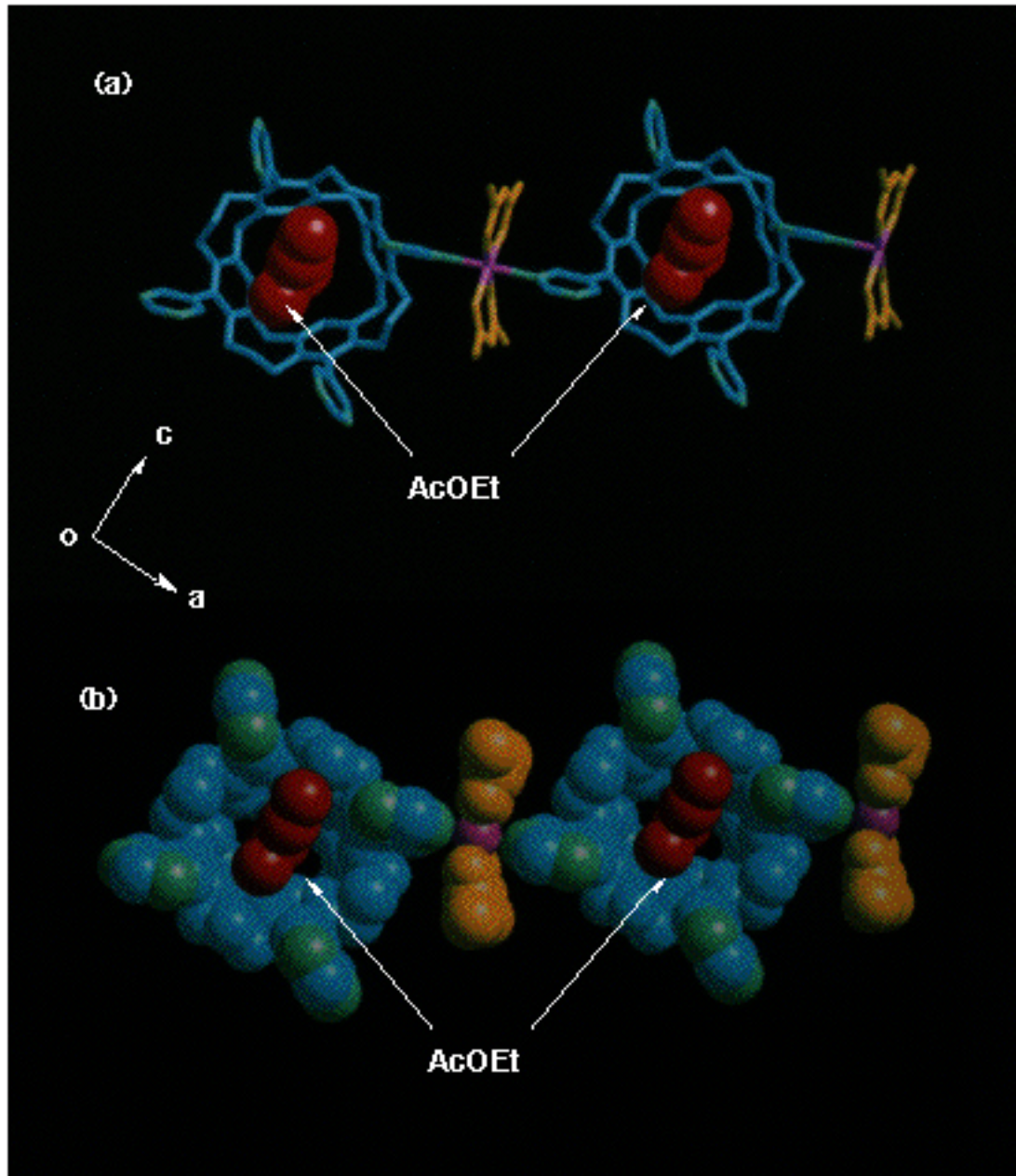
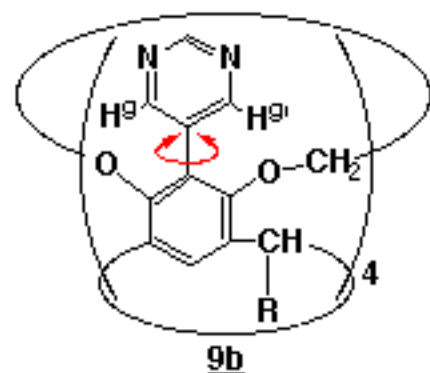


Fig. 3S the upper views of the one-dimensional Mn (II) coordination polymer with cavitaand ligands: (a) the coordination polymer is represented by a cylinder model (except for the included AcOEt molecules shown in a red ball model). The framework of the cavitaand ligand is shown in blue, and a manganese ion and acetylacetonate ligands are in magenta and yellow, respectively. (b) It is represented by a ball model based on van der Waal's radius.



$T_c = -75^\circ\text{C}$
 $\Delta G^\ddagger = 40\text{kJ}\cdot\text{mol}^{-1}$

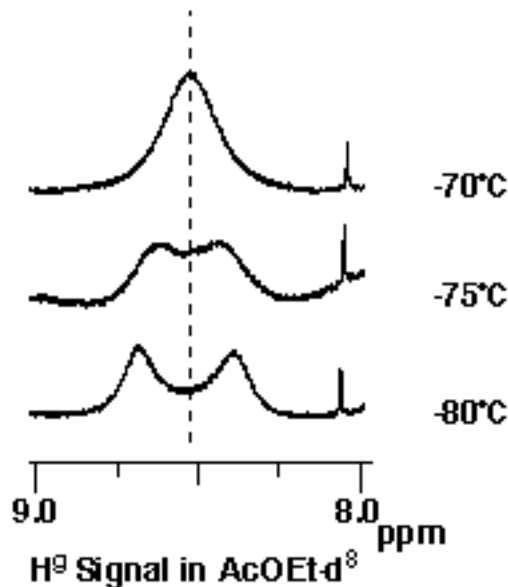


Fig. 5S the H^a signals in ¹H-NMR spectra in AcOEt-d⁸ depending upon the temperatures are indicated a coalescence phenomenon at -75°C. The activated energy of ~40 kJ/mol is estimated from the temperature.

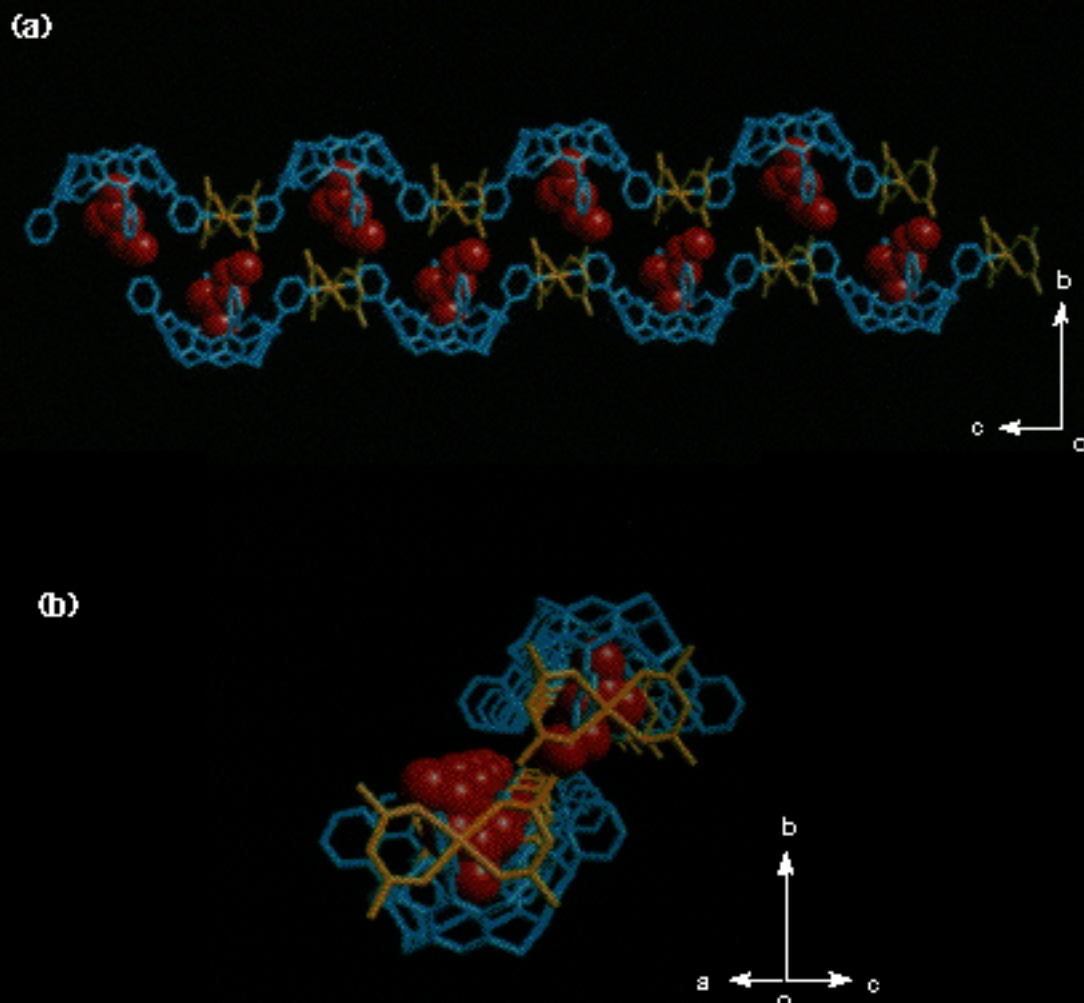


Fig. 6S (a) the projection through the a axis on two chains of the coordination polymers: It is understood that the cavitated ligands form no capsule formation. (b) The perspective view of two polymer chains along the diagonal lines in ac plane.

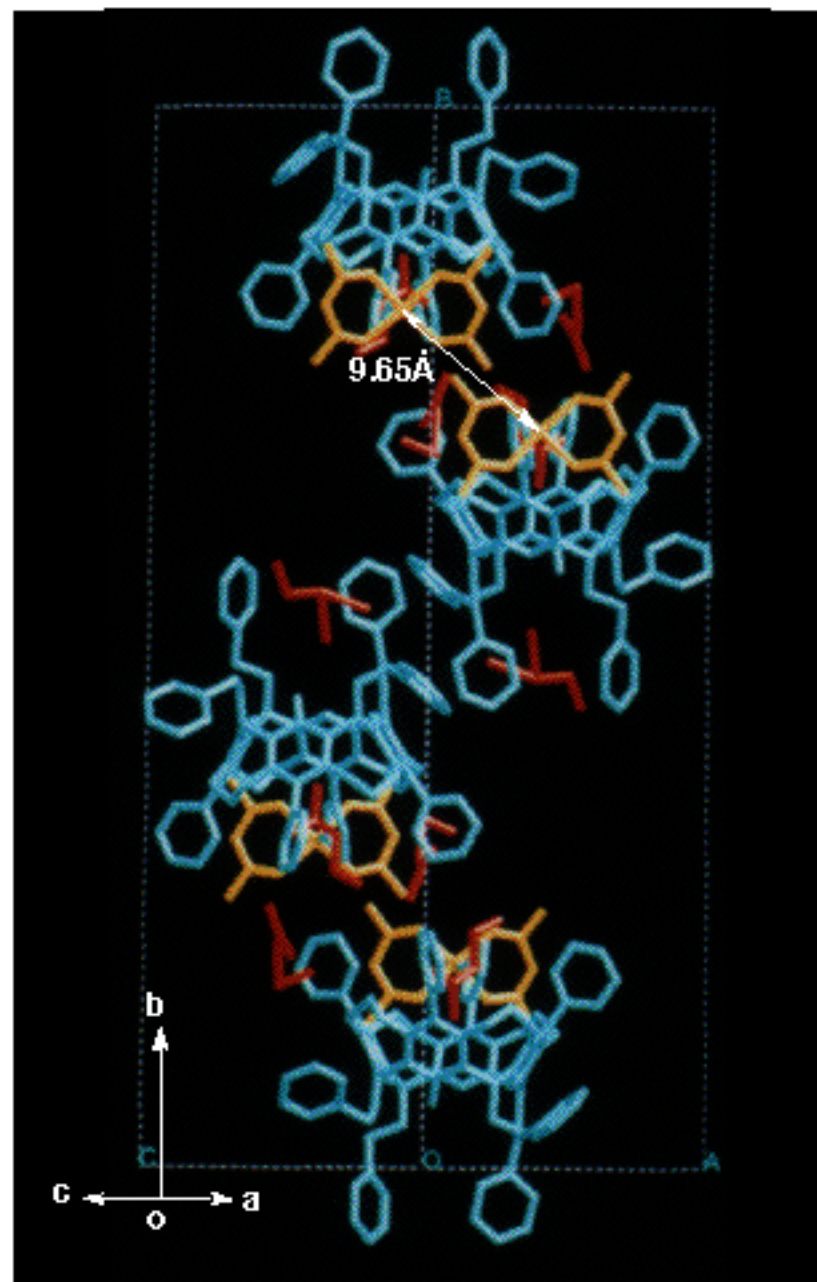


Fig 7S the locations of the coordination polymers in crystal: The one-dimensional polymer chains are directed to a diagonal line in the *ac* plane. The cavitaad ligands, AcOEt molecules and acetylacetonato Mn (II) complexes are shown in blue, red and yellow lines, respectively.