

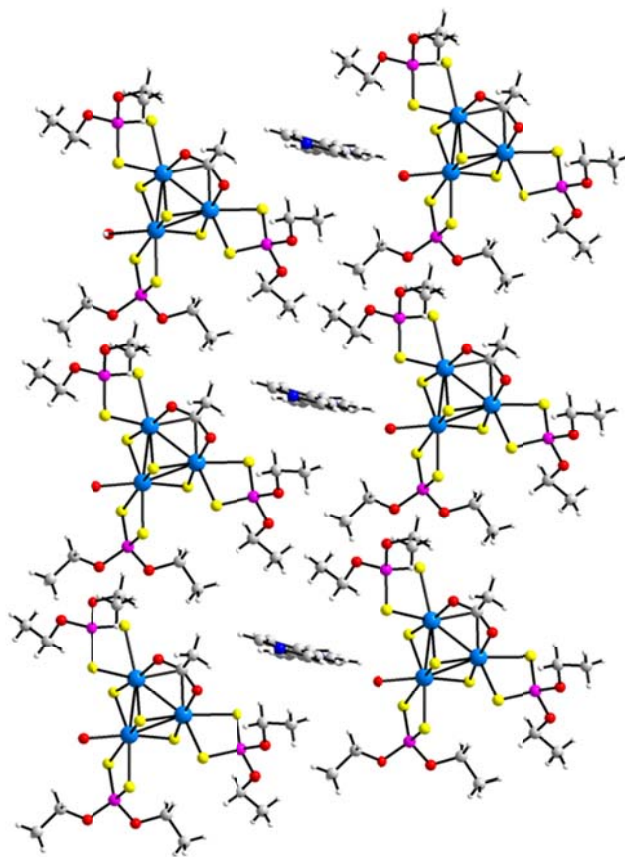
**Supplementary Information**

**Table S1.-** Values of  $k$  obtained for the fluxional process observed for the two  $\eta^2$ -dtp ligands of the two locked positions of species  $[\text{Mo}_3\text{S}_4(\eta^2\text{-dtp})_3(\eta^2(\mu)\text{-dtp})(\text{pyrazine})]$  in  $\text{CD}_2\text{Cl}_2$  solution at different temperatures.

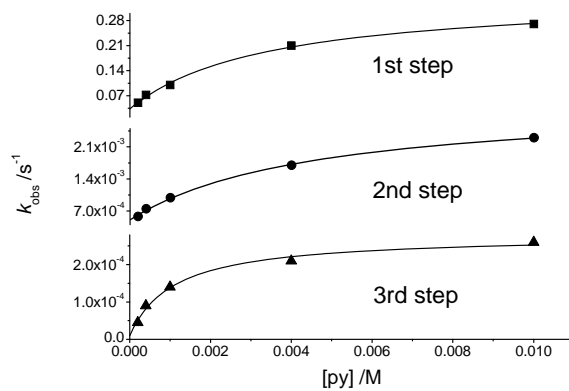
T /°C	$k_{\text{obs}} / \text{s}^{-1}$
-30	20
-25	37
-20	85
-10	300
0	800
10	1700
20	4500

**Table S2.-** Values of  $k_{\text{obs}}$  obtained for the reactions of the  $[\text{Mo}_3\text{S}_4(\eta^2\text{-dtp})_3(\eta^2(\mu)\text{-dtp})(\text{H}_2\text{O})]$  complex with pyridine in the indicated conditions of solvent and temperature,  $[\text{cluster}] = 2 \times 10^{-5}$  M.

Solvent	T /°C	[py] /M	$k_{\text{obs}} / \text{s}^{-1}$		
CHCl <sub>3</sub>	15	0.00020	0.050	0.00058	0.000045
		0.00040	0.072	0.00075	0.000090
		0.0010	0.10	0.00099	0.00014
		0.0040	0.21	0.0017	0.00021
		0.010	0.27	0.0023	0.00026
	25	0.00020	0.14		
		0.00040	0.17		
		0.0010	0.24		
		0.0040	0.39		
		0.010	0.49		
35	0.00060	0.43			
	0.0013	0.52			
	0.0025	0.67			
	0.0050	0.85			
	0.010	0.91			
CH <sub>3</sub> CN	25	0.00025	3.3		
		0.00050	3.2		
		0.0010	3.5		
		0.0040	3.8		
		0.0070	4.0		
CH <sub>3</sub> OH	25	0.0010	4.0		
		0.00025	3.3		
		0.0005	3.4		
		0.0010	3.5		
		0.0040	3.7		
		0.0070	3.8		
		0.010	3.9		



**Figure S1.**- Packing of the trinuclear clusters and the 1,2-bis(pyridyl)ethylene ligand in compound **5**.



**Figure S2.-** Dependence on the values of [py] of the observed rates constants obtained for the reaction of  $[Mo_3S_4(\eta^2\text{-dtp})_3(\eta^2(\mu)\text{-dtp})(H_2O)]$  with pyridine in chloroform and at 15 °C; [cluster] =  $2 \times 10^{-5}$  M.