SUPPLEMENTARY MATERIAL

Synthesis, structure and NMR studies of trinuclear Mo_3S_4 clusters coordinated with dithiophosphate and chiral carboxylate ligands

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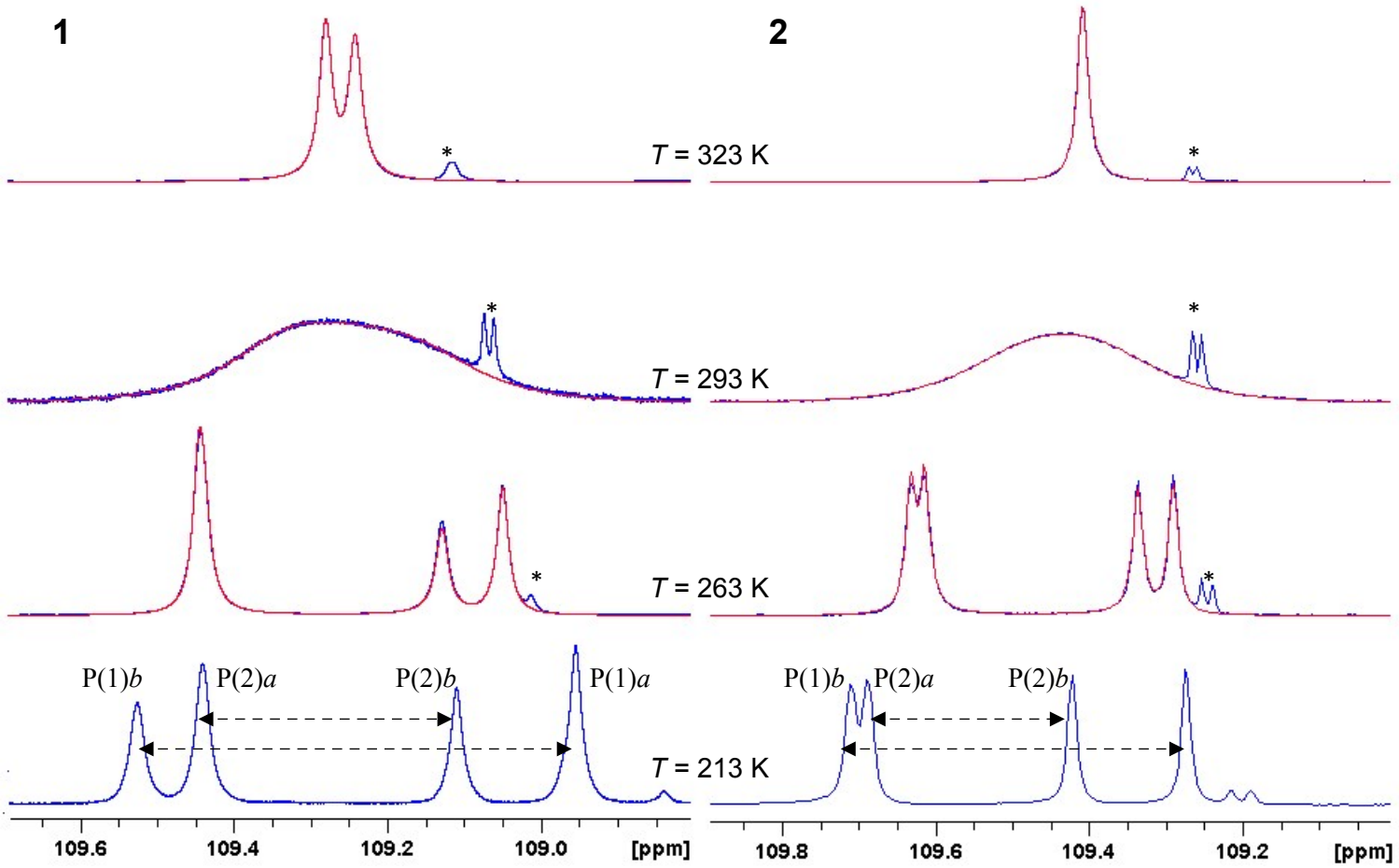

Figure S1. *Blue:* the fragments of the $^{31}P\{^{1}H\}$ NMR spectra, corresponding to P(1) and P(2) atoms in two isomers (*a*, *b*) of **1** and **2,** at various temperatures (the signals of unidentified impurities are marked by asterisks). *Red:* the spectra simulated for the *a*↔*b* exchange with rates listed in Table S1 in accordance with the schemes shown on low temperature spectra (213 K).

As mentioned in the main text, the resonances of P(3) atoms of two isomers are not resolved at all temperatures in **2**; in complex **1** the isomer interconversion results in a collapse of these resonances into single line at temperatures above -40°C. In this connection, we considered the temperature evolution of the fragments of the $^{31}P\{^{1}H\}$ NMR spectra (Figure S1), corresponding to P(1) and P(2) atoms, that allowed us to examine the rate of the isomer interchange for both compounds in the relatively large temperature intervals.

Table S1. Values of the py-dtp exchange rates, *k*, at different temperatures for the compounds **1** and **2** in $CDCl_3$ solution

T/K	*k*/s^{-1}	
	1	**2**
263	5.7	5.8
273	18.6	20.5
283	63	67
288	116	109
290	143	
293	211	172
295	291	
301		430
302	594	
323	2590	2250

Table S2. Rates of the py-flip at different temperatures for **1** and **2** in CD_2Cl_2 solution

1		**2**	
T/K	*k*/s^{-1}	*T*/K	*k*/s^{-1}
213	19.2	213	19.8
218	37.1	223	79
228	151	228	153
238	523	233	299
		243	906

Table S3. Selected bond angles (°) for **1-2**

Angle (º)	**1**	**2**	Angle(º)	**1**	**2**
Mo2-Mo1-Mo3	60.55(2)	60.90(1)	**S1-Mo1-S2**	104.97(5)	105.44(5)
Mo1-Mo2-Mo3	58.57(2)	58.22(2)	**S1-Mo1-S4**	108.57(5)	108.68(5)
Mo1-Mo3-Mo2	60.88(2)	60.87(2)	**S1-Mo1-S5**	158.36(5)	158.52(5)
Mo2-Mo1-S1	53.99(3)	53.76(3)	**S1-Mo1-S6**	83.76(5)	83.20(5)
Mo2-Mo1-S2	52.95(4)	53.35(3)	**S2-Mo1-S4**	94.39(5)	93.62(5)
Mo2-Mo1-S4	96.82(4)	97.29(3)	**S2-Mo1-S5**	89.53(5)	88.83(5)
Mo2-Mo1-S5	142.47(4)	142.13(4)	**S2-Mo1-S6**	98.19(5)	101.24(5)
Mo2-Mo1-S6	103.69(4)	104.73(3)	**S4-Mo1-S5**	85.75(5)	85.84(5)
Mo3-Mo1-S1	54.83(3)	54.86(3)	**S4-Mo1-S6**	159.49(5)	157.87(5)
Mo3-Mo1-S2	99.94(4)	99.82(4)	**S5-Mo1-S6**	78.25(5)	78.23(5)
Mo3-Mo1-S4	54.30(4)	54.38(3)	**S1-Mo2-S2**	104.21(5)	104.54(5)

Mo3-Mo1-S5	139.31(4)	139.51(4)	**S1-Mo2-S3**	105.22(4)	104.67(5)
Mo3-Mo1-S6	137.81(4)	136.78(4)	**S1-Mo2-S7**	88.01(4)	161.43(5)
Mo1-Mo2-S1	53.50(4)	53.60(3)	**S1-Mo2-S8**	162.43(5)	87.25(4)
Mo1-Mo2-S2	52.64(3)	52.59(3)	**S2-Mo2-S3**	98.93(5)	98.19(5)
Mo1-Mo2-S3	97.88(4)	97.76(4)	**S2-Mo2-S7**	92.43(5)	87.52(4)
Mo1-Mo2-S7	102.37(4)	140.10(3)	**S2-Mo2-S8**	86.60(5)	160.85(5)
Mo1-Mo2-S8	139.23(4)	140.83(4)	**S3-Mo2-S7**	159.72(5)	87.14(5)
Mo3-Mo2-S1	53.87(3)	53.68(3)	**S3-Mo2-S8**	86.33(4)	93.18(5)
Mo3-Mo2-S2	98.11(4)	97.11(3)	**S7-Mo2-S8**	77.57(4)	77.68(4)
Mo3-Mo2-S3	52.99(3)	52.81(4)	**S1-Mo3-S3**	105.66(5)	104.81(5)
Mo3-Mo2-S7	141.85(3)	139.95(4)	**S1-Mo3-S4**	108.01(5)	108.53(5)
Mo3-Mo2-S8	139.32(3)	102.03(3)	**S1-Mo3-S9**	83.43(5)	83.48(5)
Mo1-Mo3-S1	54.52(4)	54.74(3)	**S1-Mo3-S10**	159.03(5)	158.59(5)
Mo1-Mo3-S3	99.92(4)	99.96(4)	**S3-Mo3-S4**	93.74(5)	94.40(5)
Mo1-Mo3-S4	54.06(3)	54.34(3)	**S3-Mo3-S9**	101.32(5)	99.72(5)
Mo1-Mo3-S9	136.67(4)	137.12(4)	**S3-Mo3-S10**	87.26(5)	89.10(5)
Mo1-Mo3-S10	140.65(4)	139.72(4)	**S4-Mo3-S9**	157.97(5)	158.52(5)
Mo2-Mo3-S1	54.06(3)	53.73(3)	**S4-Mo3-S10**	87.08(5)	86.07(5)
Mo2-Mo3-S3	53.26(3)	52.91(3)	**S9-Mo3-S10**	77.78(5)	78.10(5)
Mo2-Mo3-S4	96.90(3)	97.24(3)			
Mo2-Mo3-S9	104.98(4)	104.18(4)			
Mo2-Mo3-S10	140.44(4)	141.97(4)			