Electronic Supplementary Information

Cerium(IV)-containing oxomolybdenum cluster with a unique $Ce_6Mo_9O_{38}$ core structure

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1. Complete experimental procedures and characterization data for complexes 1-5

General considerations

Unless otherwise stated, all manipulations were carried out in air. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 and 121.5 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P), respectively. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, U. K. The ligand NaL_{OEt}[1] was prepared according to a literature method.

Preparation of $[Ce(L_{OEt})_2(NO_3)_2]$ 1

To a solution (10 mL) of NaL_{OEt} (198 mg, 0.35 mmol) in water (10 mL) was added $[NH_3]_2[Ce(NO_3)_6]$ (97.2 mg, 0.18 mmol) in water (5 mL) dropwise over 5 min. The orange precipitate was collected, washed with water, and dried *in vacuo*. X-ray quality crystals were obtained by slow evaporation of a saturated CH_2Cl_2-hexane solution. Yield: 220 mg (93%). ^{1}H NMR ($CDCl_3$): δ 1.30 (t, 36H, CH_3), 4.08-4.12 (m, 24H, OCH_2), 5.12 (s, 10H, C_5H_5). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 121.1 (s). Anal. Calc. for $C_{34}H_{70}CeCo_2N_2O_{24}P_6$: C, 30.60; H, 5.29; N, 2.10. Found: C, 30.21; H, 5.42; N, 2.18. MS (FAB): *m/z* 1272 (M^+ - NO_3), 1210 (M^+ - $2NO_3$). IR (KBr, cm^{-1}): 1292 [ν(NO_3)].

Preparation of $[Ce(L_{OEt})_2(Cr_2O_7)]$ 2

To a solution of **1** (75 mg, 0.056 mmol) in water (18 mL) was added $Na_2Cr_2O_7 \cdot 2H_2O$ (18 mg, 0.060 mmol) in water (2 mL), and the mixture was stirred for 10 min. The orange solid was collected and recrystallized from CH_2Cl_2-hexane to give orange crystals which were suitable for X-ray diffraction. Yield: 72 mg (90%). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 36H, CH_3), 4.24-4.28 (m, 24H, OCH_2), 5.08 (s, 10H, C_5H_5). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 118.9 (s). IR (KBr, cm^{-1}): 861 sh, 964 sh [ν(Cr=O)]. Anal. Calc. for $C_{34}H_{70}CeCo_2Cr_2O_{25}P_6$: C, 28.62; H, 4.95. Found: C, 28.58; H, 4.89.

Preparation of [$H_4(L_{OEt}Ce)_6Mo_9O_{38}$] 3

To a solution of **1** (120 mg, 0.090 mmol) in water (30 mL) was added $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (37 mg, 0.30 mmol) in water (3 mL), and the mixture was stirred for 10 min. The yellow precipitate was collected, and re-dissolved in CH_2Cl_2-thf-hexane (v:v:v = 10:2:2), dried over with anhydrous Na_2SO_4. Slow evaporation of the filtrate gave orange crystals of **3** (yield: 45 mg, 57 %). The mother liquor was left to stand in air overnight to give yellow crystals identified as [$MoL_{OEt}(O)_2]_2(\mu$-O) **4** (yield: 28 mg, 46 %), which could be synthesised directly from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NaL_{OEt} (see below). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 108H, CH_3), 4.20 (m, 72H, OCH_2), 5.03 (s, 30H, C_5H_5). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 117.8 (s). IR (KBr, cm^{-1}): 845 [ν(Mo=O)]. MS (ESI): *m/z* 5510.1219 [M^+ - OH]. Anal. Calc. for $C_{102}H_{214}Co_6Ce_6Mo_9O_{92}P_{18}$: C, 22.16; H, 3.90; P, 10.54. Found: C, 22.78; H, 3.86; P, 10.54.

Preparation of [$MoL_{OEt}(O)_2]_2(\mu$-O) 4

To a solution of $(NH_4)_6Mo_7O_{24}$ (150 mg, 0.12 mmol) in 1.8 M H_2SO_4 (30 mL) was added the solution of NaL_{OEt} (250 mg, 0.25 mmol) in water (30 mL) dropwise, and the yellow solution was stirred at room temperature for 20 min. The precipitate was collected, re-dissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4. Slow evaporation of the solvent afforded yellow crystals that were characterized as [$MoL_{OEt}(O)_2]_2(\mu$-$O)_2$ **4** by an X-ray diffraction study.[2] Yield: 80 mg (56 %). ^{1}H NMR ($CDCl_3$): δ 1.27 (m, 36H, CH_3), 4.17 (m, 24H, OCH_2), 5.03 (s, 10H, C_5H_5). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 113.9 (*pseudo* d), 123.8 (*pseudo* t). IR (KBr, cm^{-1}): 902 [ν(Mo=O)], 772, 631 [ν(Mo-O_b)]. MS (FAB): 1342 (M^+ + 1).

Preparation of [$H_4(L_{OEt}Zr)_6Mo_9O_{38}$] 5

[$Zr(L_{OEt})(CH_3CO_2)_3$] was prepared by refluxing [$L_{OEt}ZrF_3$][3] with trimethylsilyl acetate in CH_2Cl_2 under nitrogen and recrystallized from hexane. To a solution of [$Zr(L_{OEt})(CH_3CO_2)_3$] (100 mg) in water (30 mL) was added $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (18 mg) in water (3 mL), and the milky suspension was stirred overnight. The yellow precipitate was collected, re-dissolved in

CH_2Cl_2, and dried over anhydrous Na_2SO_4, and the solvent was evaporated to dryness. Recrystallization from $CHCl_3$-hexane afforded yellow crystals which were identified as $[H_4(L_{OEt}Zr)_6Mo_9O_{38}]$ **5** by an X-ray diffraction study. Yield: 10 mg (7 %). ^1H NMR ($CDCl_3$): δ 1.31 (t, 108H, CH_3), 4.14 (m, 72H, OCH_2), 5.12 (s, 30H, C_5H_5). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ 121.4 (s). IR (KBr, cm^{-1}): 860 [ν(Mo=O)].

References

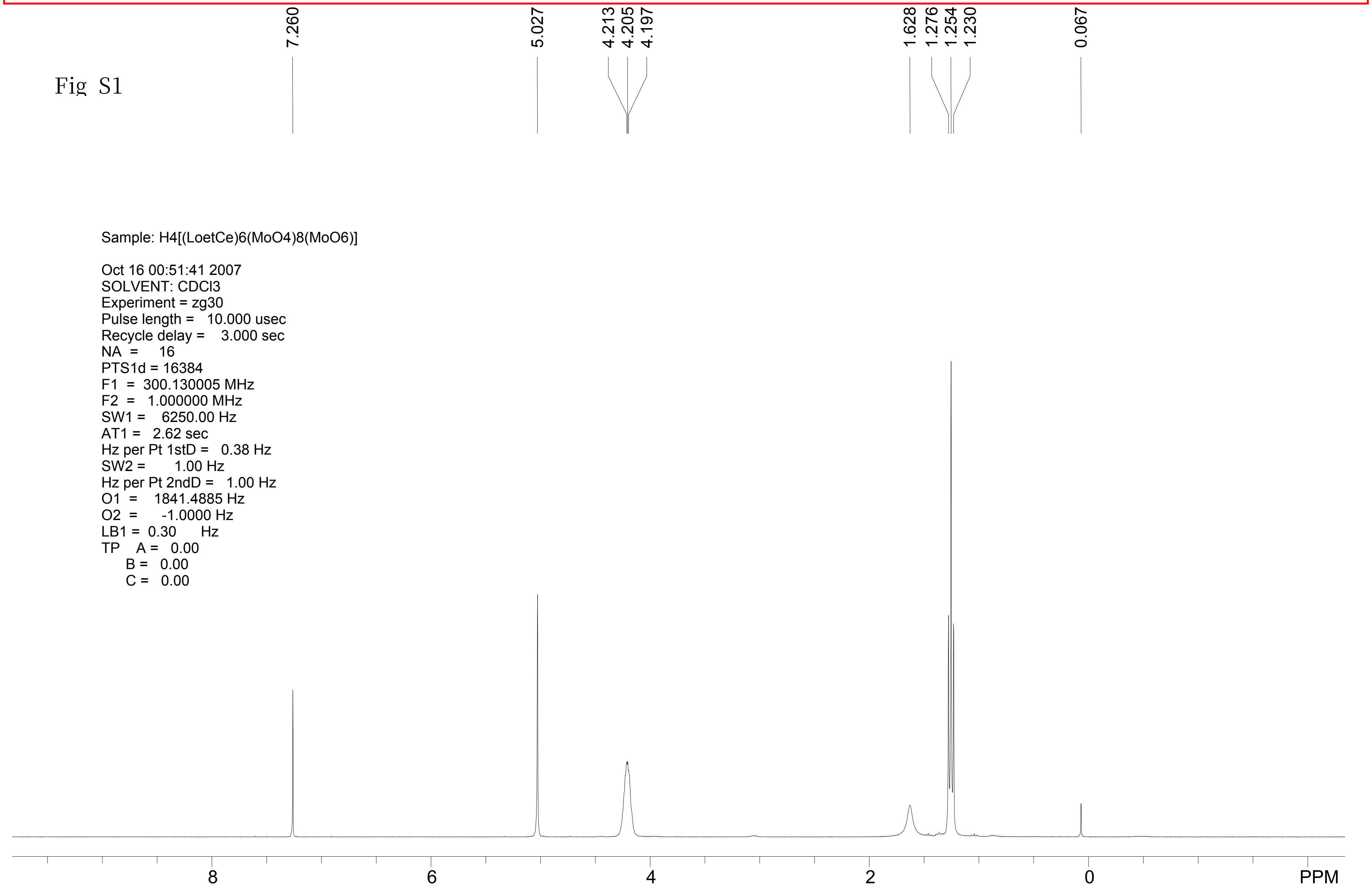
1 W. Kläui, *Z. Naturforsch*. 1979, **34 B**, 1403.

2 X.-Y. Yi, I. D. Williams and W.-H. Leung, unpublished results.

3 (a) T. C. H. Lam, E. Y. Y. Chan, W.-L. Mak, S. M. F. Lo, I. D. Williams, W.-T. Wong and W.-H. Leung, *Inorg. Chem.*, 2003, **42**, 1842. (b) Q.-F. Zhang, T. C. H. Lam, X.-Y. Yi, E. Y. Y. Chan, W.-Y. Wong, H. H. Y. Sung, I. D. Williams and W.-H. Leung, *Chem.-Eur. J.,* 2005, **11**, 101.

Figure S1 ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) spectrum of compound **3**. Resonances at ca. δ 7.26 and 1.6 ppm are due to $CHCl_3$ and water, respectively.

Fig S1



Sample: H4[(LoetCe)6(MoO4)8(MoO6)]

Oct 16 00:51:41 2007
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Recycle delay = 3.000 sec
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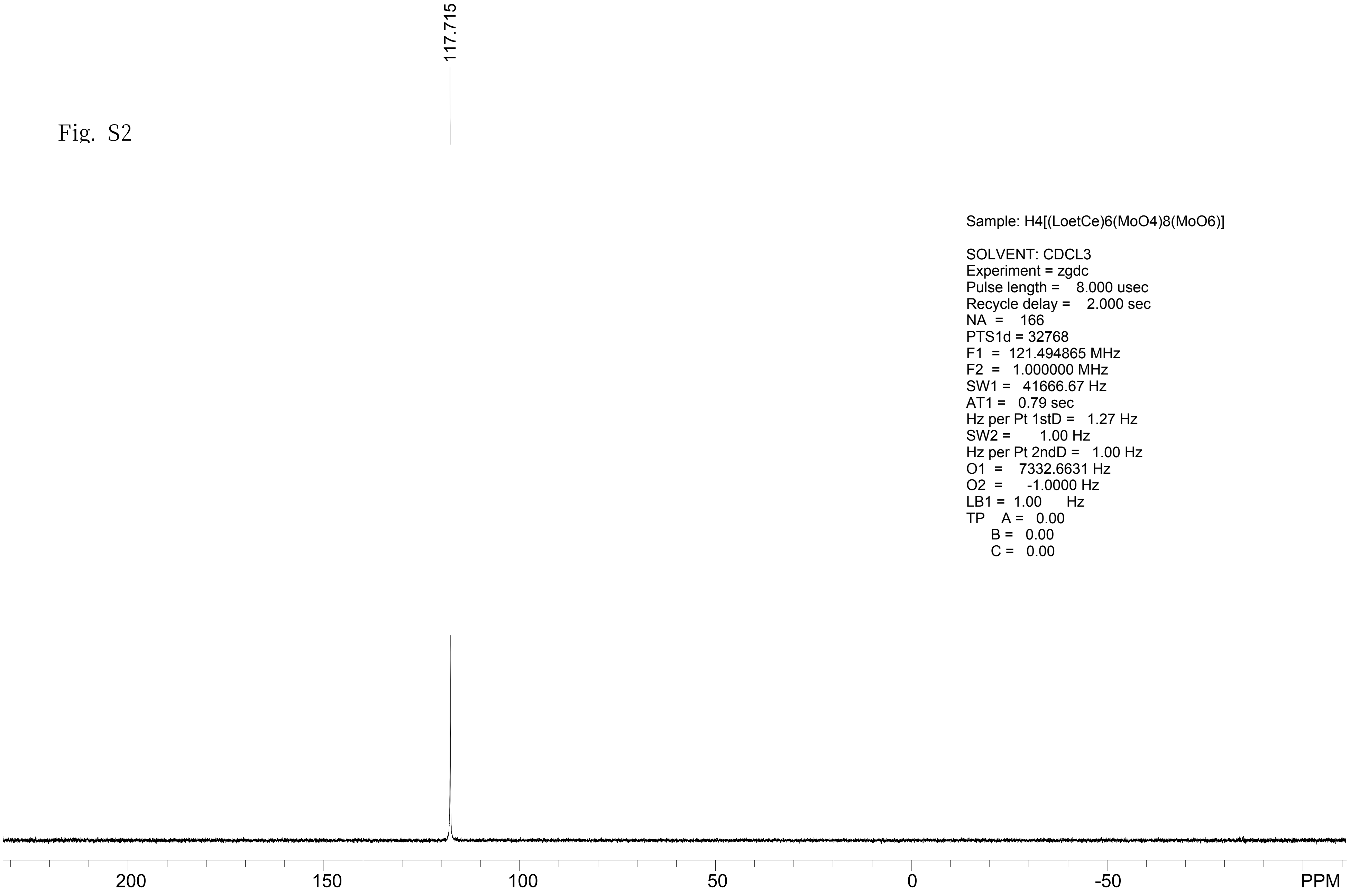
PTS1d = 16384
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6250.00 Hz
AT1 = 2.62 sec
Hz per Pt 1stD = 0.38 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 1841.4885 Hz
O2 = -1.0000 Hz
LB1 = 0.30 Hz
TP A = 0.00
B = 0.00
C = 0.00

Figure S2 $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz, 298 K) spectrum of complex **3**.

Fig. S2



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Sample: H4[(LoetCe)6(MoO4)8(MoO6)]

SOLVENT: CDCL3
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PTS1d = 32768
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F2  =   1.000000 MHz
SW1 =   41666.67 Hz
AT1 =   0.79 sec
Hz per Pt 1stD =   1.27 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    7332.6631 Hz
O2  =      -1.0000 Hz
LB1 =  1.00      Hz
TP    A =   0.00
      B =   0.00
      C =   0.00
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