Article:

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Dynamic-NMR and Quantum-Chemical Study of the Stereochemistry and Stability of the Chiral $MoO_2(acac)_2$ Complex in Solution

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Supplementary Information

Contains:

a) Representative Gaussian and Lorentzian fitting deconvolutions for line broadening analysis, NMR spectra including acetonitrile peak using toluene as a solvent, low temperature ^{1}H NMR data between 273 and 243 K and ln(*k*) against 1/*T* for $MoO_2(acac)_2$ in toluene.

b) Optimized SOGGA11X geometries with 6-31G+** and modified LANL2DZ on Mo.

c) Typical input file for GAMESS calculations.

d) Original Craven data set for benzene for $MoO_2(acac)_2$ exchange in solution. Craven, B. M.; Ramey E. C.; Wise, W. B. Lability and Stereochemistry of Dioxobis (2, 4-pentanedionato) Molybdenum (VI). Inorg. Chem. **1971**, 10, 2626–2628.

a) Representative Gaussian and Lorentzian fitting deconvolutions for line broadening analysis, NMR spectra including acetonitrile peak using toluene as a solvent, low temperature ^{1}H NMR data between 273 and 243 K and ln(*k*) against 1/*T* for $MoO_2(acac)_2$ in toluene.

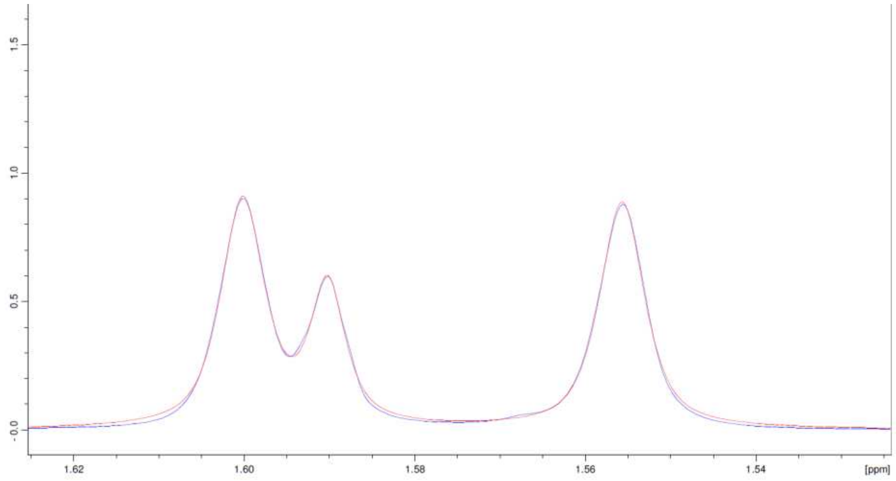

Figure S1. 500 MHz ^{1}H NMR, representative of a line broadening fitting for MoO_2acac_2 solution in benzene (C_6D_6, 10^{-2} M) at 315 K using a mixed shape Gaussian and Lorentzian function. Blue line: original spectrum; red line: fitted spectrum. Peaks left to right (δ, ppm): 1.60 (3H, s, CH_3), from bound acac signal A, 1.59 free Hacac (2 × 3H, s, CH_3) and 1.55 (3H, s, CH_3), from bound acac signal B.

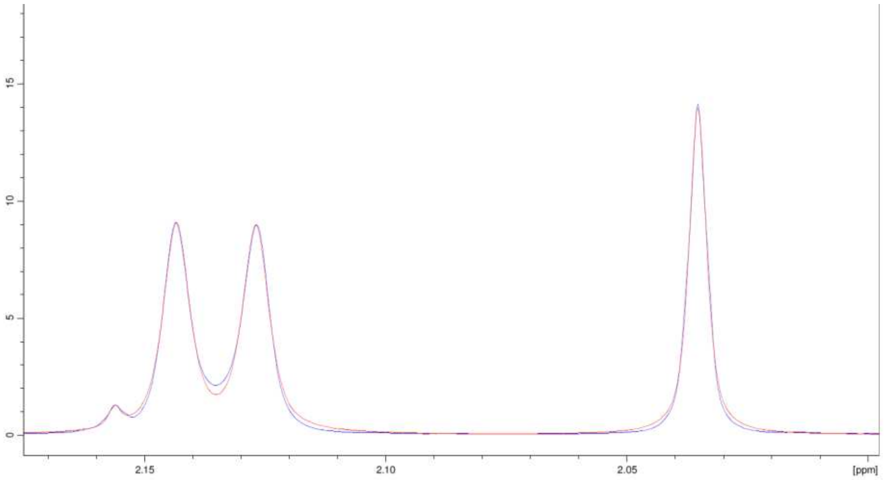

Figure S2. 500 MHz ^{1}H NMR, representative of a line broadening fitting for MoO$_2$(acac)$_2$ solution in chloroform (CDCl$_3$, 10^{-2} M) at 305 K using a mixed shape Gaussian and Lorentzian function. Blue line: original spectrum; red line: fitted spectrum. Peaks left to right (δ, ppm): 2.14 (3H, s, CH$_3$), from bound acac signal A, 2.13 (3H, s, CH$_3$), from bound acac signal B, and 2.03 free Hacac (2 × 3H, s, CH$_3$).

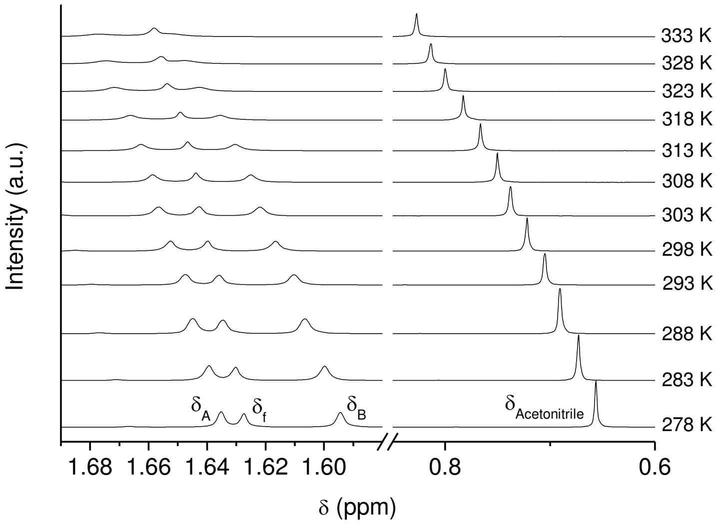

Figure S3. 500 MHz ^{1}H NMR, for MoO$_2$(acac)$_2$ solution in toluene (C$_7$D$_8$, 10^{-2} M) from 278 K to 333 K. last fittet point at 328 K due to free Hacac signal overlap with bound acac. Peaks left to right (δ, ppm): δ_A (3H, s, CH$_3$), from bound acac signal A, δ_f free Hacac (2 × 3H, s, CH$_3$), δ_B (3H, s, CH$_3$), from bound acac signal B, and $\delta_{Acetnonitrile}$ from CH$_3$CN internal standard.

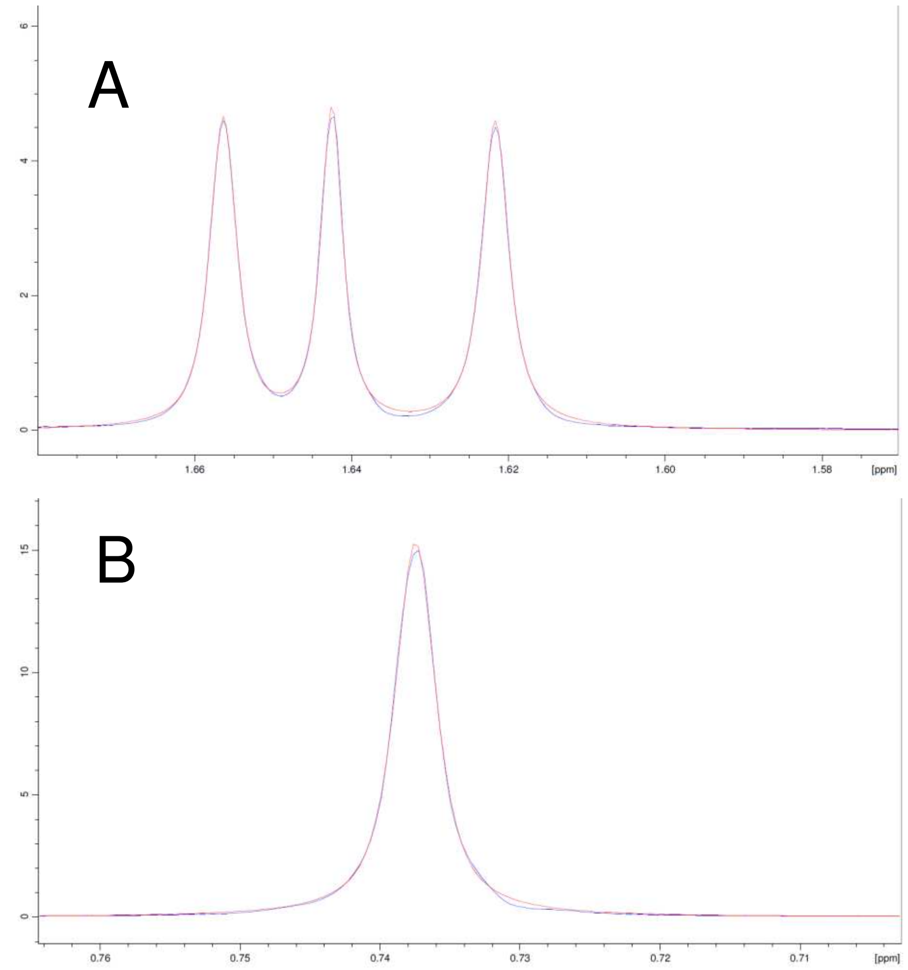

Figure S4. 500 MHz ^{1}H NMR, representative of a line broadening fitting for $MoO_2(acac)_2$ solution in toluene (C_7D_8, 10^{-2} M) at 303 K using a mixed shape Gaussian and Lorentzian function. Blue line: original spectrum; red line: fitted spectrum. (A) Peaks left to right (δ, ppm): 1.66 (3H, s, CH_3), from bound acac signal A, 1.64 free Hacac (2 × 3H, s, CH_3) and 1.62 (3H, s, CH_3), from bound acac signal B. (B) 0.74, signal of CH_3CN internal standard.

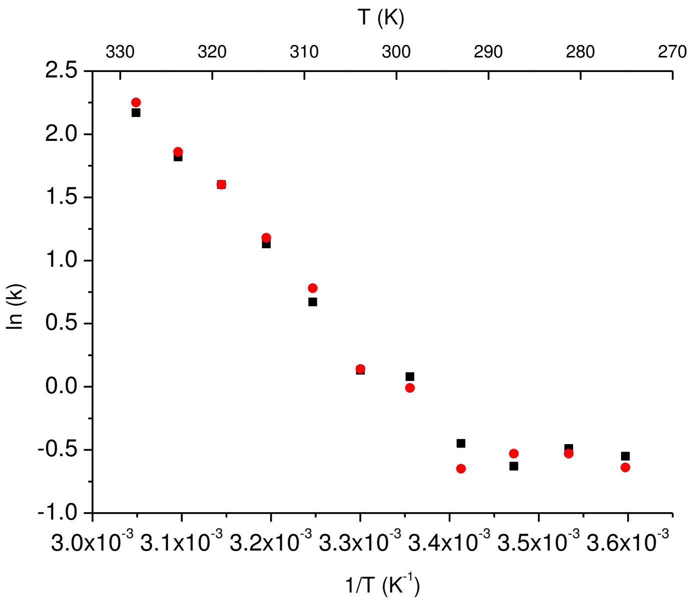

Figure S5. ln (*k*) versus 1/*T* for the equilibrium of $MoO_2(acac)_2$ in toluene (C_7D_8) solution from 278 to 328 K. Data from line broadening analysis using: (■) free Hacac ligand as internal standard, and (●) CH_3CN as internal standard in the same sample. A linear correlation in observed for the range 290-330K. However, below 290 K no significant changes in line broadening are observed.

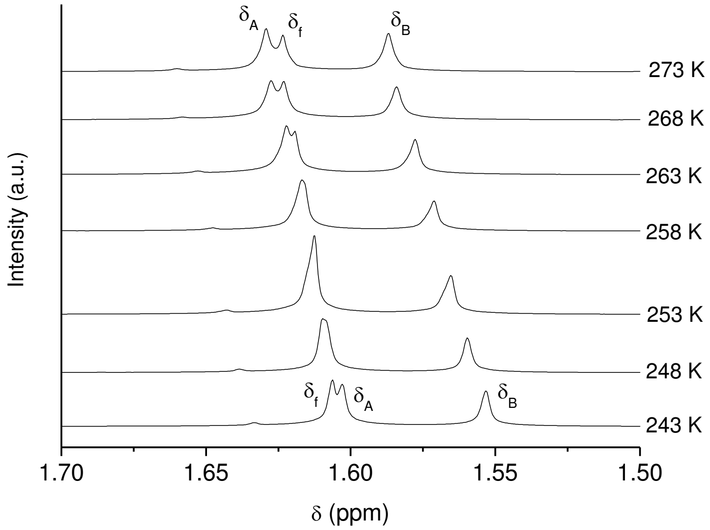

Figure S6. 500 MHz ^1H NMR, for $MoO_2(acac)_2$ solution in toluene (C_7D_8, 10^{-2} M) from 273 K to 243 K. Please note the shift and peak signal inversion of the free Hacac by cooling the solution. For the signal at 273K, peaks left to right (δ, ppm): δ_A (3H, s, CH_3), from bound acac signal A, δ_f free Hacac (2 × 3H, s, CH_3), δ_B (3H, s, CH_3), from bound acac signal B.

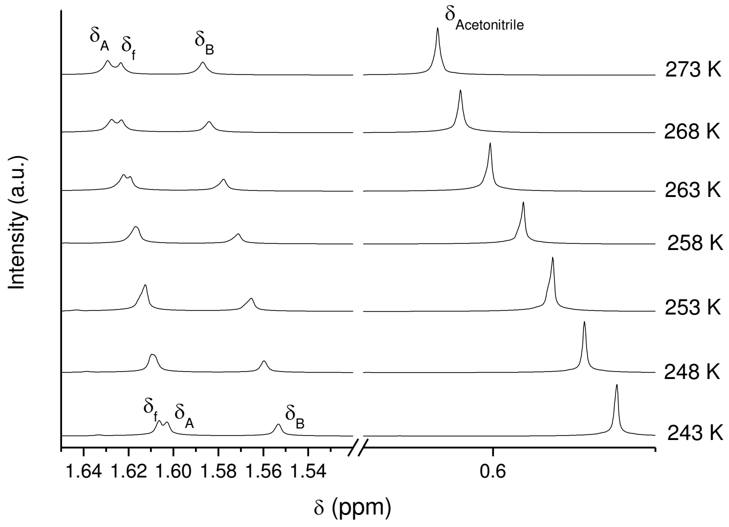

Figure S7. 500 MHz ^{1}H NMR, for $MoO_2(acac)_2$ solution in toluene (C_7D_8, 10^{-2} M) from 273 K to 243 K. Scale expanded with respect to Figure S5 to show the presence of acetonitrile. For the signal at 273K, peaks left to right (δ, ppm): δ_A (3H, s, CH_3), from bound acac signal A, δ_f free Hacac (2 × 3H, s, CH_3), δ_B (3H, s, CH_3), from bound acac signal B, and $\delta_{Acetnonitrile}$ from CH_3CN internal standard.

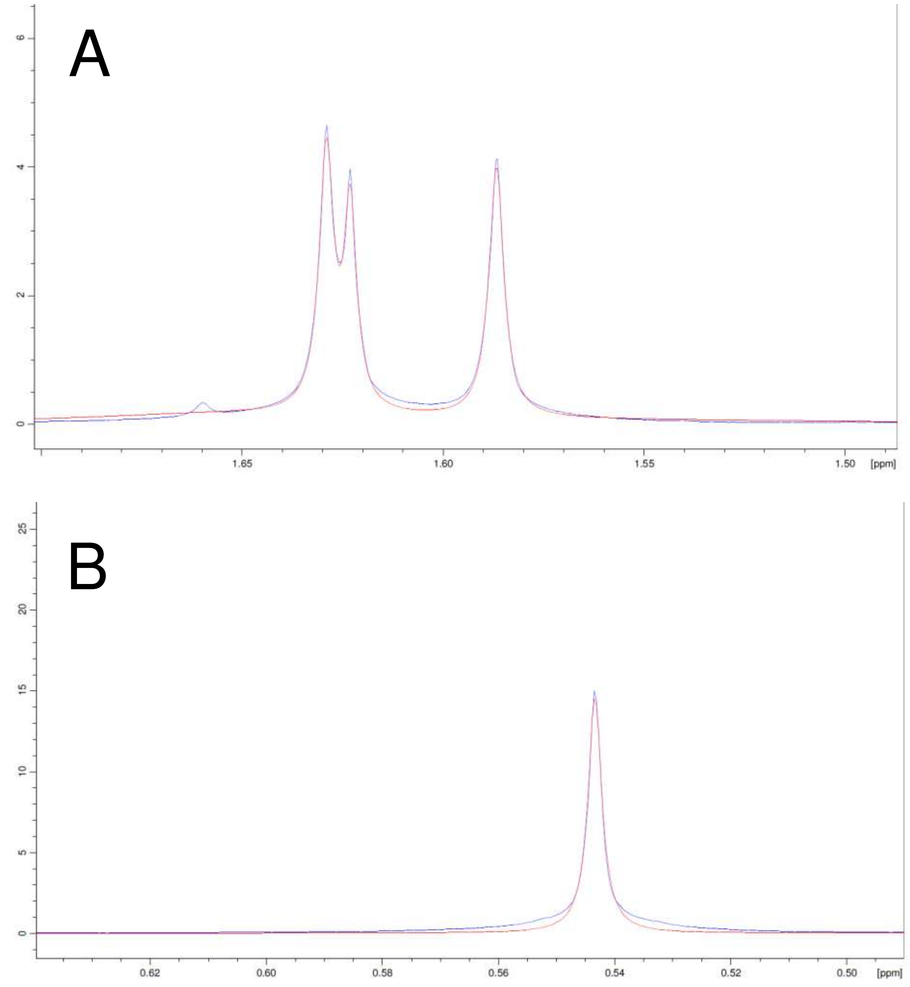

Figure S8. 500 MHz ^{1}H NMR, representative of a line broadening fitting for $MoO_2(acac)_2$ solution in toluene (C_7D_8, 10^{-2} M) at 268 K using a mixed shape Gaussian and Lorentzian function. Blue line: original spectrum; red line: fitted spectrum. (A) Peaks left to right (δ, ppm): 1.63 (3H, s, CH_3), from bound acac signal A, 1.62 free Hacac (2 × 3H, s, CH_3) and 1.59 (3H, s, CH_3), from bound acac signal B. (B) 0.54, signal of CH_3CN internal standard.

b) Optimized SOGGA11X geometries with 6-31G+** and modified LANL2DZ on Mo (Cartesian, in Ångstrom, only symmetry unique atoms are given; in GAMESS format: label, charge, coordinates):

(i) Ground state, C_2 symmetry:

MO	42.0	0.0000000000	0.0000000000	-0.0816788103
O	8.0	1.0657492827	-0.8161703635	-1.1107347350
O	8.0	1.0340923021	-0.8852189576	1.7044682878
O	8.0	-1.2714849339	-1.5291530977	0.3241886884
C	6.0	-1.2355942786	-2.5662348676	1.0964047617
C	6.0	0.8270059445	-1.9616011074	2.3181882196
C	6.0	-2.3919589735	-3.5041308875	0.8871860649
C	6.0	-0.2630778178	-2.8324861364	2.0466582472
C	6.0	1.8100434331	-2.3172789000	3.4052021756
H	1.0	-3.3288531515	-2.9625996396	1.0573884855
H	1.0	-2.3452299705	-4.3701586241	1.5513469637
H	1.0	-2.3971328176	-3.8430239593	-0.1545535057
H	1.0	-0.3578761406	-3.7390476885	2.6324704540
H	1.0	1.8577139610	-1.4959457660	4.1281140058
H	1.0	2.8066607444	-2.4167880579	2.9610565044
H	1.0	1.5509946796	-3.2441093478	3.9227414675

(ii) Transition state TS1, C_{2v} symmetry:

MO	42.0	0.0000000000	0.0000000000	-0.4563229183
O	8.0	1.4395302048	0.0000000000	-1.3441772185
O	8.0	-0.0000000000	2.0918631775	-1.3130721583
O	8.0	-0.0000000000	1.2137911025	1.2015194021
C	6.0	-0.0000000000	2.4781944429	1.4931258468
C	6.0	-0.0000000000	3.2435443422	-0.8236410141
C	6.0	-0.0000000000	3.5057030565	0.5745349308
C	6.0	-0.0000000000	-4.3875193281	-1.8064294164
C	6.0	-0.0000000000	-2.7475690365	2.9726841994
H	1.0	-0.0000000000	5.3624247210	-1.3124315184
H	1.0	0.8819850964	4.3033331613	-2.4500355291
H	1.0	-0.0000000000	3.8174742338	3.1941530451
H	1.0	0.8822564356	2.2815947537	3.4249603198
H	1.0	0.0000000000	4.5306917086	0.9246417795

(iii) Transition state TS2a, C_{2v} symmetry:

MO	42.0	0.0000000000	0.0000000000	-1.0120845760
O	8.0	0.0000000000	1.2775932298	0.1015334691
O	8.0	1.4062352963	1.2211316008	-2.0669087669
C	6.0	1.2428502981	2.4670870464	-2.2904827776
C	6.0	0.0000000000	3.1195716478	-2.3534670208
H	1.0	0.0000000000	4.1803247744	-2.5765180692
C	6.0	2.5111949208	3.2393854657	-2.5415168649
H	1.0	2.3218910441	4.2755863291	-2.8311796047
H	1.0	3.0897913553	2.7378670468	-3.3240646819
H	1.0	3.1176029261	3.2247291255	-1.6286003495

(iv) Transition state TS2b, C_{2v} symmetry:

MO	42.0	-0.0000000000	0.0000000000	-0.7128276752
O	8.0	1.2537804642	0.0000000000	0.4119895969
O	8.0	1.3036409943	1.4004210957	-1.7166840627
C	6.0	1.2147619046	2.5530811004	-2.2500147119
C	6.0	-0.0000000000	3.1975794451	-2.5146304788
H	1.0	-0.0000000000	4.1846932145	-2.9608330651
C	6.0	2.5278164836	3.1973413714	-2.6080466284
H	1.0	2.3960278725	4.1731420131	-3.0821886774
H	1.0	3.0803109943	2.5349380999	-3.2830537701
H	1.0	3.1302054642	3.3095700541	-1.7000682572

c) Typical input file for GAMESS calculations, including full $ECP and $DATA groups:

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 $CONTRL ICUT=11 NPRINT=-5 $END
 $SCF DIRSCF=.TRUE. $END
 $DFT NRAD=99 NLEB=590 NRAD0=99 NLEB0=590 $END !hybrid
 $STATPT OPTTOL=1E-6 NSTEP=250 HSSEND=.TRUE. $END !Tight optimization; default is 1E-4!
 $FORCE METHOD=SEMINUM NVIB=2 VIBSIZ=0.01 SCLFAC=1.0 PROJCT=.TRUE. $END
 $SYSTEM TIMLIM=200000 MWORDS=80 MEMDDI=10 $END
 $GUESS GUESS=HUCKEL $END
 $ECP
  Mo-ECP GEN     28     3
  5      ----- f-ul potential     -----
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    -20.2080084       1    147.8982938
   -106.2116302       2     45.7358898
    -41.8107368       2     13.2911467
     -4.2054103       2      4.7059961
  3      ----- s-ul potential     -----
      2.8063717       0    110.2991760
     44.5162012       1     23.2014645
     82.7785227       2      5.3530131
  4      ----- p-ul potential     -----
      4.9420876       0     63.2901397
     25.8604976       1     23.3315302
    132.4708742       2     24.6759423
     57.3149794       2      4.6493040
  5      ----- d-ul potential     -----
      3.0054591       0    104.4839977
     26.3637851       1     66.2307245
    183.3849199       2     39.1283176
     98.4453068       2     13.1164437
     22.4901377       2      3.6280263
  O-ECP NONE
  O-ECP NONE
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  H-ECP NONE
 $END
 $DATA
TS2b, DFT/6-31G+**/modified LANL2DZ; B3LYP staring geometry
Cnv 2

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S   4
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  2     0.1309000000E+01     -0.1136008000E+01
  3     0.4500000000E+00     -0.1161159000E+01
  4     0.1681000000E+00      0.1006479000E+01
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P   3
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P   4
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  4     0.7800000000E-01      0.7801960100E+00
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D   1
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   D      1
     1           0.8000000000  1.00000000

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   D      1
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C          6.0   0.0000000000   3.2607530138  -2.4832751559
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   D      1
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C          6.0   2.5348130948   3.2619734958  -2.5928722659
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   L      1
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   D      1
     1           0.8000000000  1.00000000

H          1.0   2.4056268757   4.2732264970  -2.9878613277
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   S      1
     1           0.0360000000  1.00000000

H          1.0   3.0701813333   2.6515585971  -3.3294228515
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  S     1
    1          0.0360000000  1.00000000

H         1.0   3.1562958759   3.2972565183  -1.6910176249
  N31    6
  S     1
    1          0.0360000000  1.00000000

 $END
```

d) Original Craven data set for $MoO_2(acac)_2$ exchange in benzene solution. Craven, B. M.; Ramey E. C.; Wise, W. B. Lability and Stereochemistry of Dioxobis (2, 4-pentanedionato) Molybdenum (VI). Inorg. Chem. **1971**, 10, 2626–2628.

Data collected using a Varian A60 HA-100 spectrometer operating at 60 MHz. '…' entries are reported as in the original paper.

Temp (K)	$\Delta\nu_{A,B}$ Hz	$W_{1/2}$, observed, Hz A	$W_{1/2}$, observed, Hz B	CH_3CN $W_{1/2}$ (ref) Hz	Ay $W_{1/2}$ (cor from inhom), Hz	Intrinsic $W_{1/2}$, Hz	Cor $W_{1/2}$, Hz	τ, sec
287.7	2.8	0.90	0.85	0.45	0.42	0.42	0	
294.2	2.6	0.80	0.85	0.42	0.45	0.39	0.06	
300.2	2.42	1.03	1.05	0.48	0.56	0.38	0.18	0.89
302.2	2.35	1.10	1.10	0.44	0.63	0.35	0.28	0.58
305.7	2.25	1.10	1.20	0.40	0.75	0.33	0.42	0.39
309.2	2.14	…	3.28	0.50	2.78	0.31	2.48	0.18
311.2	…	3.15		0.45	2.71	0.30	2.41	0.145
317.2	…	2.70		0.35	2.35	0.28	2.07	0.11
323.2	…	1.95		0.42	1.53	0.24	1.29	0.092
328.2	…	1.23		0.50	0.73	0.21	0.52	0.072
333.2	…	0.77		0.45	0.32	0.19	0.13	
338.7	…	0.60		0.40	0.20	0.15	0.05	
344.7	…	0.52		0.39	0.13	0.13	0	