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Supplementary Material

Necessity of Fine Tuning in Mo(IV) Bis(Dithiolene) Complexes to Warrant Nitrate Reduction

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Contents	Page number
Gas phase geometry optimized structures for the pentacoordinated species released in solution by **1**, **2** (figure 1) and **4** (figure 2).	2
Selected molecular orbitals for the pentacoordinated species, $\{[Mo^{IV}(NCS)(mnt)_2]^{1-}\}$(without geometry optimization) (figure 3)	3
Coordinates for the gas phase geometry optimized structure of the pentacoordinated species released in solution by **1**, **2** and **4**.	4-6
First few frequencies for the gas phase geometry optimized complexes (table 1)	6
Cyclic voltammetric traces and differential pulse polarographs of **1** and **2** (figure 4).	7
Cyclic voltammetric traces and differential pulse polarographs of **3** (figure 5).	8
^{31}P NMR spectroscopy of **1** in dichloromethane (figure 6).	8

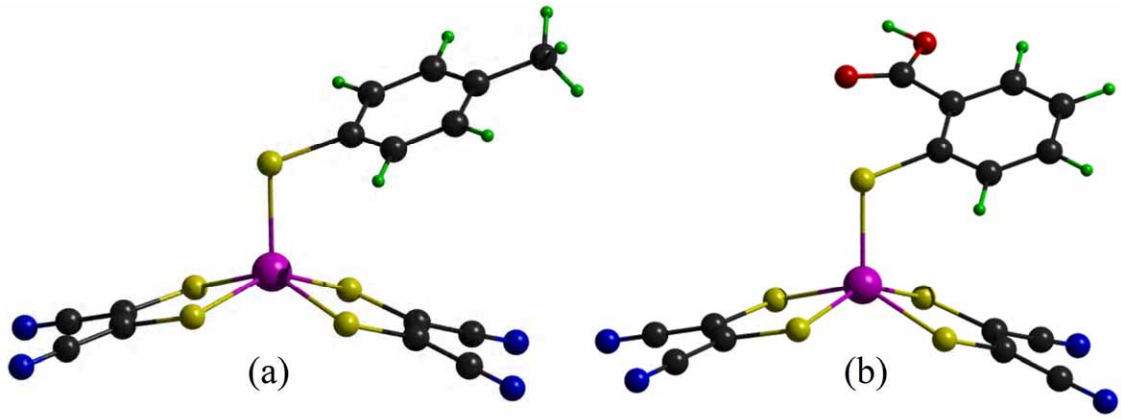

Figure 1. Gas phase geometry optimized structures (Diamond 3.1 e, Pov Ray generated view) for the penta-coordinated species released in solution by **1** (a), **2** (b), **5** (c) and **4** (d). Colour code: pink, Mo; yellow, S; red, O; blue, N; black, C, green, H.

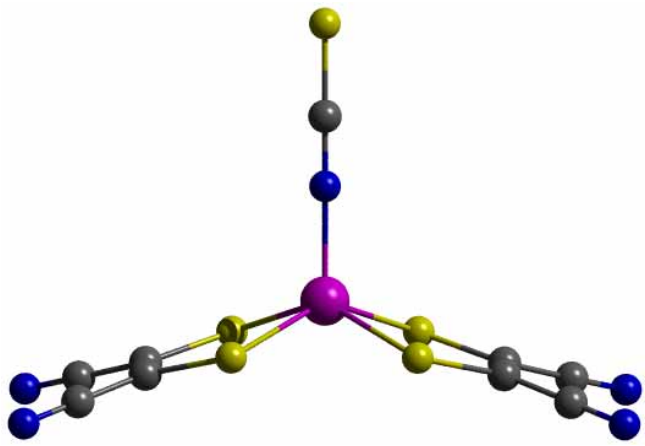

Figure 2. Gas phase geometry optimized structures (Diamond 3.1 e, Pov Ray generated view) for the penta-coordinated species released in solution by nd **4**. Colour code: pink, Mo; yellow, S; red, O; blue, N; grey, C.

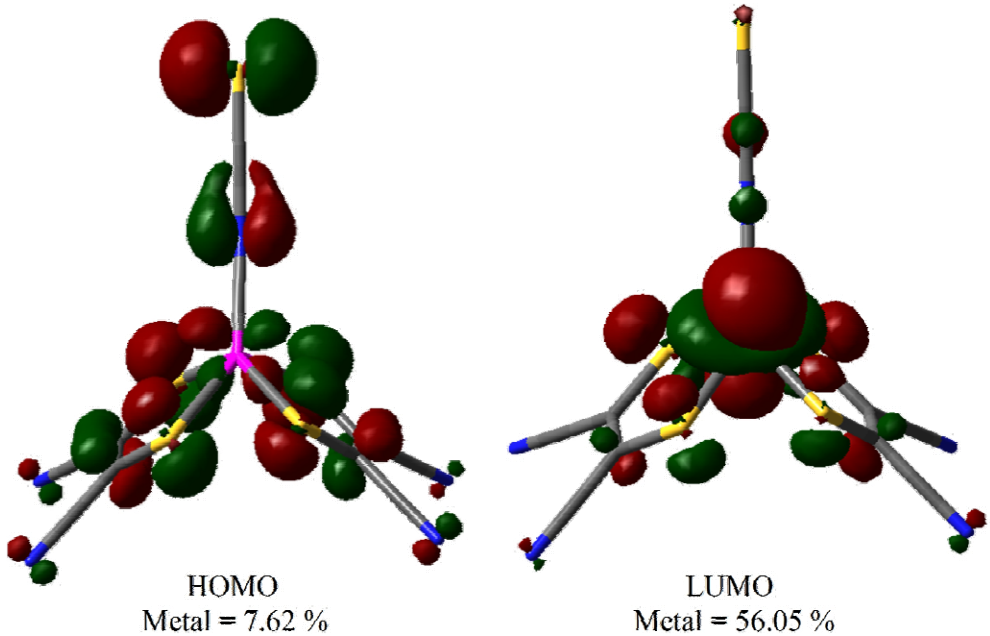

Figure 3. Selected molecular orbitals for the penta-coordinated species, $\{[Mo^{IV}(NCS)(mnt)_2]^{1-}\}$ (without optimization). Colour codes: pink, Mo; yellow, S; blue, N; grey, C. Isosurface cut off value = 0.04.

Coordinates for the gas phase geometry optimized structure of {[$Mo^{IV}(SC_6H_4$-*p*-Me)$(mnt)_2]^{1-}$}

Mo	-0.69930900	-0.03306900	-0.04297900
S	0.40177000	1.50676200	-1.46510700
S	0.54920300	1.00586400	1.66821300
S	-2.51112300	0.14854800	-1.55480800
S	-2.40814900	-0.25512900	1.58188900
S	0.14220000	-2.17203100	-0.37597100
N	3.12029000	4.03755500	-1.70795500
N	3.31378600	3.38301400	2.43389800
N	-6.18798700	-0.24585600	-2.00835800
N	-6.05000100	-0.77406700	2.15751800
C	1.58246700	2.36179500	-0.46811400
C	2.43240700	3.29319600	-1.13233500
C	1.64791600	2.14533000	0.88375100
C	2.56725700	2.83946700	1.72271300
C	-3.94070200	-0.35217000	0.71419400
C	-5.11197300	-0.57937500	1.49374200
C	-3.98626600	-0.17977800	-0.64546100
C	-5.20737000	-0.21480300	-1.37914700
C	1.93888400	-2.09105100	-0.28218800
C	2.69969800	-1.52699300	-1.31246800
H	2.20178900	-1.06407300	-2.15829500
C	4.09160900	-1.54304700	-1.23940500
H	4.66908900	-1.09356500	-2.04456400
C	4.75845700	-2.11665000	-0.14822400
C	3.98274400	-2.68770900	0.86904500
H	4.47463600	-3.14265900	1.72639600
C	2.58971800	-2.67828400	0.80969500
H	2.00545200	-3.12038600	1.61113500
C	6.26651900	-2.08869700	-0.05727200
H	6.73070600	-2.17716500	-1.04609900
H	6.64625200	-2.90310000	0.56956500
H	6.61986000	-1.14628800	0.38263500

Coordinates for the gas phase geometry optimized structure of {[$Mo^{IV}(SC_6H_4$-*o*-COOH)$(mnt)_2]^{1-}$}

Mo	-0.67850900	0.23874100	-0.12215800
S	0.18632000	2.23382000	-1.06855300
S	-2.59870800	0.67840600	-1.42769400
S	0.22564100	-1.66102800	-1.09983600
S	-2.25050700	-0.54114400	1.47102900
S	0.66799300	0.80538700	1.72995100
O	3.21686500	-4.08285100	1.28785700
H	2.75123000	-4.82772900	1.71104100
O	1.20037000	-4.04480700	0.30457600
C	2.01980000	-1.50579800	-1.06059300
C	1.61919000	2.21863300	1.26259700
C	1.40565600	2.83661100	0.05726600
C	-3.83114900	-0.51210800	0.69201300
N	-5.80781900	-1.44713100	2.08137300
N	-6.27161700	0.15104500	-1.77558000
C	2.85165800	-2.40457600	-0.34966800
C	4.24487900	-2.21657400	-0.38021700
H	4.87088700	-2.90108800	0.18004400
C	-3.98526200	0.01033700	-0.56687700
N	2.71776400	4.93579500	-0.70615600
C	2.61493100	-0.47232900	-1.79743400
H	1.97692700	0.22101900	-2.33392900
C	2.57721200	2.69626700	2.20342500
C	2.30734600	-3.56057800	0.41396100
C	-5.25179300	0.08353900	-1.21524500
N	3.36024000	3.05553400	2.98846800
C	3.99786900	-0.31008500	-1.82487700
H	4.42818900	0.50588800	-2.39936700
C	2.13173900	3.99625000	-0.34223000
C	-4.93020600	-1.02030700	1.44435300
C	4.82004200	-1.18266300	-1.11031500
H	5.89899100	-1.05740800	-1.11866200

Coordinates for the gas phase geometry optimized structure of $\{[Mo^{IV}(NCS)(mnt)_2]^{1-}\}$

Mo	0.00029300	0.25746200	-0.00025200
S	1.59096500	-0.49280400	-1.57908800
S	1.59131600	-0.49122900	1.57916400
S	-1.59021100	-0.49317000	-1.57912800
S	-1.58974400	-0.49329000	1.57917400
S	-0.00646200	5.01311000	-0.00021700
N	5.12195500	-1.55235500	-2.10660100
N	5.12208300	-1.55148000	2.10692200
N	-5.12000000	-1.55684100	-2.10631200
N	-5.11947700	-1.55658600	2.10729700
N	-0.00028900	2.22314400	-0.00052200
C	3.05847500	-0.90151500	-0.68377700
C	4.20217200	-1.26590400	-1.45082400
C	3.05866600	-0.90095000	0.68391800
C	4.20237800	-1.26491000	1.45108600
C	-3.05706800	-0.90385300	-0.68366800
C	-4.20057200	-1.26907700	-1.45061400
C	-3.05690000	-0.90400100	0.68401500
C	-4.20005200	-1.26942900	1.45132300
C	-0.00310400	3.42356100	-0.00035300

Table 1. First few frequencies for the gas phase optimized complexes.

Optimized complexes	$\{[Mo^{IV}(SC_6H_4\text{-}p\text{-}Me)(mnt)_2]^{1-}\}$	$\{[Mo^{IV}(SC_6H_4\text{-}o\text{-}COOH)(mnt)_2]^{1-}\}$	$\{[Mo^{IV}(NCS)(mnt)_2]^{1-}\}$
First few frequencies	14.2091	10.6105	17.6107
	19.2047	18.6997	22.1455
	32.0571	28.3368	27.7891
	33.3197	31.9902	31.9827
	40.4835	36.3154	58.0963
	49.2091	40.3527	77.9563
	52.4071	51.6835	97.0461
	62.0784	70.0522	97.5836
	79.4244	75.9062	110.711
	96.2456	97.1435	115.856

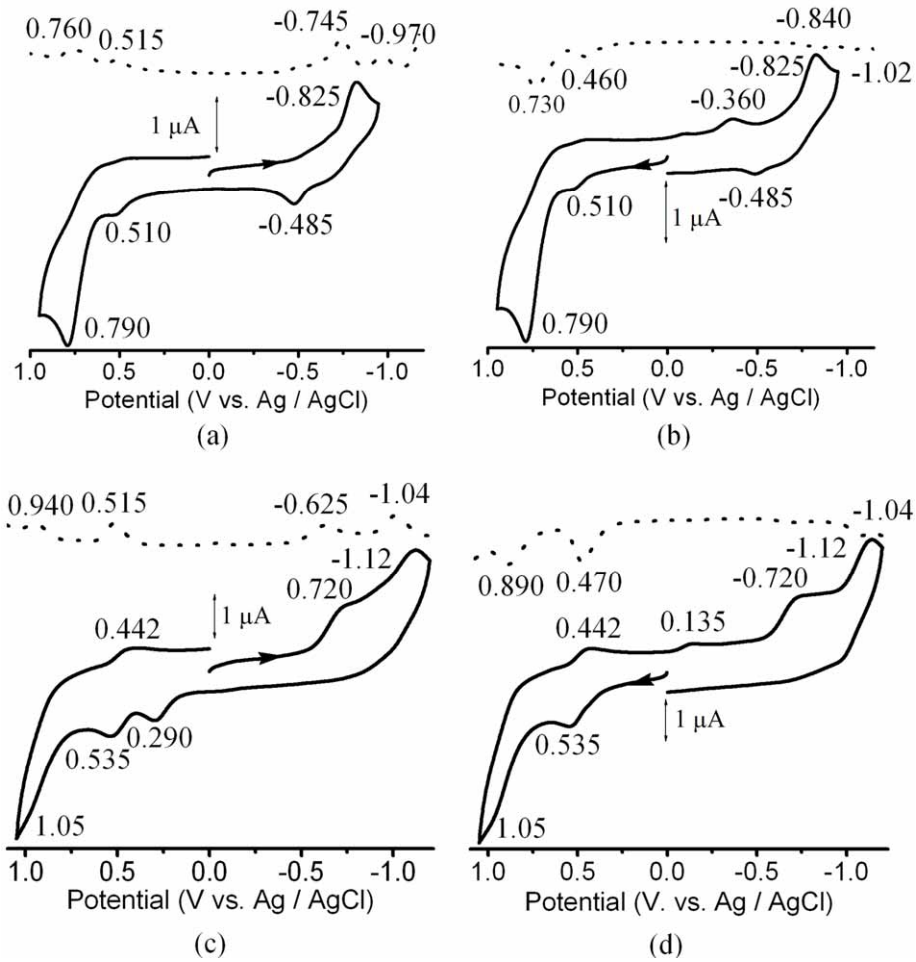

Figure 4. Cyclic voltammetric traces (scan rate = 100 mV/sec) and differential pulse polarographs (scan rate = 20 mV/sec, pulse width = 50 ms, pulse period = 200 ms, pulse amplitude = 50 mV) of **1** and **2** in presence of 5 equivalent PPh_3 in dichloromethane. (a) Oxidative and (b) reductive scan of **1**; (c) oxidative and (d) reductive scan of **2**.

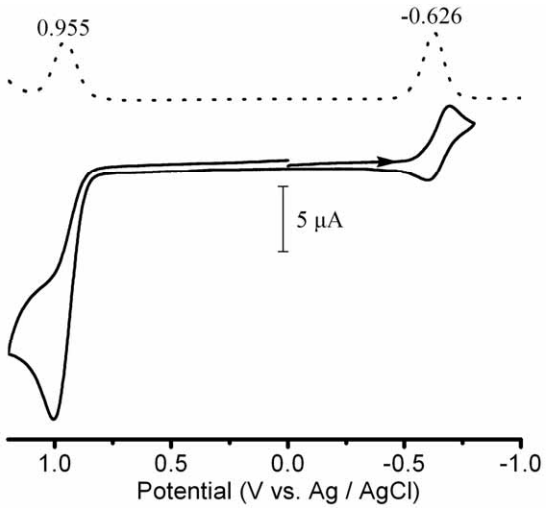

Figure 5. Cyclic voltammetric traces (scan rate = 100 mV/sec) and differential pulse polarographs (scan rate = 20 mV/sec, pulse width = 50 ms, pulse period = 200 ms, pulse amplitude = 50 mV) of **3** in dichloromethane.

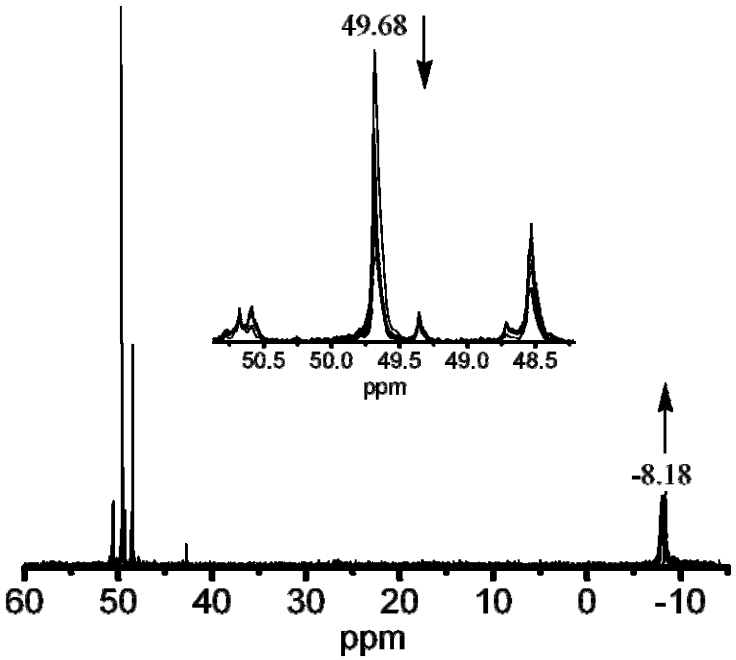

Figure 6. ^{31}P NMR spectroscopic results of **1** in dichloromethane (proton decoupled). Total time = 2 hours. Elapsed time = 15 minutes. Inset: Signal due to PPh_3 bound to molybdenum has been expanded to show its decrease in intensity with time.