Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Electronic tuning of Mo_2(thioamidate)$_4$ complexes through π-system substituents and *cis/trans* isomerism

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Crystal Structure of 5

Data Collection

An orange crystal with approximate dimensions 0.055 x 0.053 x 0.025 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 20 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 10362 data were harvested by collecting 6 sets of frames with 0.5º scans in ω and φ with exposure times of 4 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [1]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement [2-4].

A successful solution by charge flipping provided most non-hydrogen atoms from the *E*-map [3]. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The dimolybdenum compound (Figure S1) resides on a crystallographic inversion center.

Thermal parameter restraints were required on the monothiosuccinimidato and acetate ligands to enable a computationally stable refinement.

The final least-squares refinement of 110 parameters against 1548 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0570 and 0.1337, respectively.

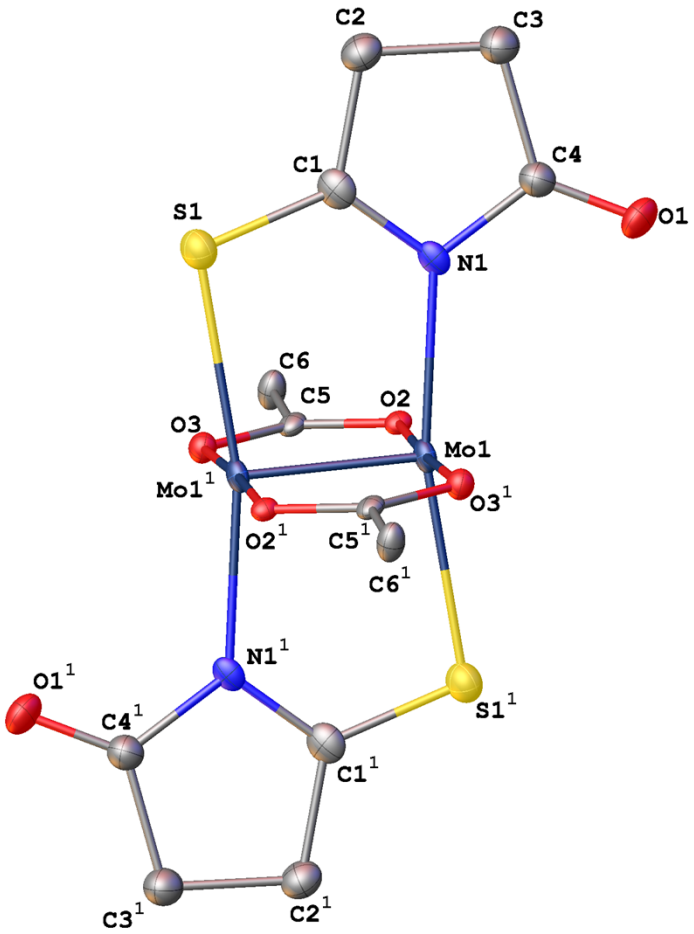

Figure S1. The structure of **5**. All atoms are drawn as 50% thermal probability ellipsoids. All hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **5**.

Empirical formula	$C_{12}H_{14}Mo_2N_2O_6S_2$
Formula weight	538.25
Temperature/K	100.0
λ/Å	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.450(2)
b/Å	8.227(3)
c/Å	18.268(8)
α/°	90
β/°	96.805(15)
γ/°	90
Volume/Å^3	813.3(6)
Z	2
ρ_{calc} mg/mm^3	2.198
μ/mm^{-1}	1.831
F(000)	528.0
Crystal size/mm^3	0.055 × 0.053 × 0.025
2Θ range for data collection	4.492 to 51.472°
Index ranges	$-6 \le h \le 6$, $-9 \le k \le 10$, $-19 \le l \le 22$
Reflections collected	10362
Independent reflections	1548[R(int) = 0.0395]
Data/restraints/parameters	1548/60/110
Goodness-of-fit on F^2	1.509
Final R indexes [I>=2σ (I)]	R_1 = 0.0570, wR_2 = 0.1328
Final R indexes [all data]	R_1 = 0.0606, wR_2 = 0.1337
Largest diff. peak/hole / e Å^{-3}	1.09/-1.08

DFT Calculations

MO Picture

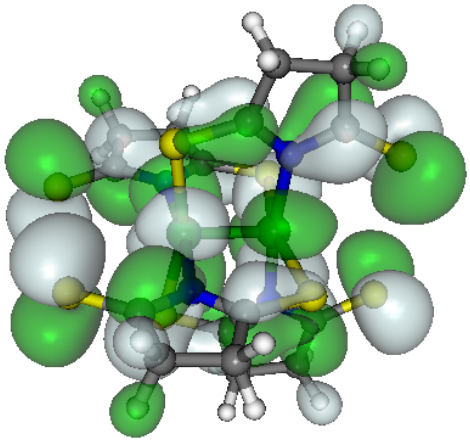

Figure S2. The δ* (LUMO) orbital of *trans*-2,2-$Mo_2(SNS5)_4$ (**2**).

Coordinates

trans-2,2-$Mo_2(SNO5)_4$ (**1a**)

Mo	0.00000	-0.00000	2.08617
S	-0.12019	2.49451	-0.35749
S	2.49432	0.12586	2.43783
O	-0.10854	2.26149	4.56953
O	2.26173	0.09972	-2.48931
N	-0.10531	2.13935	2.26663
N	2.13925	0.10267	-0.18615
C	-0.14560	3.00273	1.26238
C	-0.21277	4.44539	1.71773
H	-1.10927	4.92493	1.32167
H	0.64136	5.00280	1.32987
C	-0.21358	4.32409	3.24565
H	0.63716	4.81073	3.72367
H	-1.11581	4.71919	3.71389
C	-0.13793	2.82313	3.50359
C	3.00261	0.14578	0.81795
C	4.44541	0.21149	0.36271
H	5.00408	-0.63880	0.75711
H	4.92334	1.11167	0.75242
C	4.32457	0.20160	-1.16524
H	4.72458	1.09778	-1.64072
H	4.80714	-0.65564	-1.63587
C	2.82320	0.13025	-1.42328
Mo	0.00000	0.00000	0.00000
S	-2.49575	-0.12697	2.43991
S	0.12110	-2.49599	-0.34824
O	-2.25636	-0.12170	-2.48670
O	0.11760	-2.25684	4.57855
N	-2.13820	-0.10865	-0.18366
N	0.10693	-2.13814	2.27524
C	-3.00252	-0.15400	0.81955
C	-4.44404	-0.23185	0.36204
H	-5.00999	0.61533	0.75264
H	-4.91561	-1.13453	0.75365
C	-4.32087	-0.22628	-1.16578
H	-4.71551	-1.12583	-1.63935
H	-4.80683	0.62716	-1.63988
C	-2.81976	-0.14787	-1.42160
C	0.14923	-3.00261	1.27208
C	0.22407	-4.44441	1.72927
H	1.12789	-4.91622	1.34037
H	-0.62197	-5.00990	1.33563
C	0.21438	-4.32163	3.25713
H	-0.64350	-4.80302	3.72792
H	1.10995	-4.72161	3.73368
C	0.14271	-2.82000	3.51326

trans-2,2-$Mo_2(SNO6)_4$ (**1b**)

Mo	0.00000	0.00000	0.00000
Mo	0.00000	0.00000	2.07456
S	1.42158	2.07493	-0.32682
S	-2.07351	1.42586	2.39692
S	-1.43546	-2.07121	-0.31669
S	2.07644	-1.42478	2.39501
O	1.01879	1.43518	4.49566
O	-1.46269	0.97018	-2.42411
O	-0.97193	-1.45584	4.50330
O	1.41864	-1.03050	-2.42533
N	1.25056	1.81875	2.28907
N	-1.81994	1.24680	-0.21848
N	-1.25133	-1.81495	2.29806
N	1.81113	-1.25816	-0.21986
C	1.74781	2.53436	1.28680
C	2.62237	3.74380	1.52807
H	3.66696	3.40811	1.53238
H	2.52318	4.42854	0.68650
C	2.29218	4.41697	2.85698
H	1.29814	4.87039	2.80188
H	2.99943	5.22299	3.06298
C	2.32413	3.37239	3.96661
H	1.97378	3.75785	4.92398
H	3.35102	3.02169	4.12559
C	1.48911	2.15308	3.63520
C	-2.54259	1.73549	0.78279
C	-3.79412	2.54809	0.53932
H	-3.94984	3.22308	1.38021
H	-4.64739	1.85832	0.53383
C	-3.72650	3.29422	-0.79000
H	-4.67607	3.79174	-0.99756
H	-2.96220	4.07494	-0.73440
C	-3.37914	2.30742	-1.89862
H	-4.21062	1.61019	-2.05766
H	-3.19036	2.79236	-2.85625
C	-2.16132	1.47119	-1.56511
C	-1.74683	-2.53523	1.29796
C	-2.57004	-3.77910	1.54444
H	-1.88778	-4.63836	1.55376
H	-3.24528	-3.93175	0.70320
C	-3.31717	-3.70029	2.87253
H	-3.82470	-4.64409	3.08217
H	-4.08989	-2.92811	2.81371
C	-2.32814	-3.35974	3.98124
H	-2.81234	-3.16303	4.93766
H	-1.63976	-4.19787	4.14367
C	-1.47923	-2.15122	3.64531
C	2.52608	-1.75969	0.78109
C	3.72485	-2.64815	0.53774

H	3.37813	-3.68917	0.54385
H	4.41617	-2.55010	1.37409
C	4.39247	-2.33554	-0.79809
H	4.85908	-1.34713	-0.75315
H	5.18778	-3.05454	-1.00498
C	3.33961	-2.36158	-1.90010
H	2.97311	-3.38470	-2.04762
H	3.72315	-2.02494	-2.86308
C	2.13471	-1.50685	-1.56660

trans-2,2-$Mo_2(SNS5)_4$ (**2**)

Mo	0.00000	-0.00000	2.13360
Mo	0.00000	0.00000	-0.00000
S	-0.62741	2.38420	2.50093
S	-1.97312	-0.52803	4.93500
S	-2.38155	-0.63443	-0.37090
S	1.96828	0.51080	4.94169
S	2.38378	0.63394	-0.36277
S	-0.51641	1.97188	-2.80458
S	0.63202	-2.38245	2.50109
S	0.53234	-1.96836	-2.80409
N	0.55453	-2.07112	-0.13916
N	-0.54801	2.07211	-0.13950
N	-2.07188	-0.55372	2.26989
C	2.73059	0.71230	3.48693
C	-2.72991	-0.73512	3.47819
N	2.07227	0.54448	2.27688
C	1.12682	-4.17446	-1.09571
H	2.09785	-4.38150	-1.56727
H	0.39674	-4.84393	-1.57195
C	-4.17391	-1.13479	3.22400
H	-4.84857	-0.41260	3.70466
H	-4.37334	-2.11026	3.68981
C	1.15732	-4.30086	0.43942
H	0.44371	-5.04267	0.82795
H	2.14665	-4.57952	0.83197
C	2.91207	0.76660	1.24523
C	-4.30039	-1.15886	1.68888
H	-4.58038	-2.14589	1.29160
H	-5.04101	-0.44228	1.30346
C	4.30759	1.12850	1.70151
H	4.59622	2.11769	1.31590
H	5.04185	0.41003	1.30765
C	-1.13581	4.30569	0.43901
H	-0.41763	5.04156	0.83036
H	-2.12412	4.59137	0.82903
C	-0.76840	2.91111	0.89324
C	-0.71972	2.73130	-1.34860
C	0.77832	-2.90917	0.89365

C	-1.10177	4.18021	-1.09601
H	-2.06970	4.39490	-1.57043
H	-0.36499	4.84439	-1.56933
C	4.18144	1.08831	3.23647
H	4.84148	0.34551	3.70633
H	4.40148	2.05263	3.71566
C	-2.90858	-0.77928	1.23635
C	0.73489	-2.72815	-1.34819

cis-2,2-$Mo_2(SNO5)_4$ (**4a**)

Mo	-0.00000	0.00000	2.08248
S	0.56201	-2.43233	-0.34436
S	2.41782	0.63133	-0.33489
O	0.36729	-2.26609	4.58387
O	2.17198	0.72947	4.59268
N	0.49692	-2.09259	2.28279
N	2.08266	0.53024	2.29156
C	0.68439	-2.93076	1.27040
C	0.99426	-4.34392	1.72020
H	1.97286	-4.65034	1.34690
H	0.26507	-5.04080	1.30447
C	0.93205	-4.24258	3.24782
H	0.17326	-4.88279	3.69842
H	1.87889	-4.47168	3.73865
C	0.57541	-2.78352	3.51683
C	2.91368	0.75355	1.28060
C	4.30813	1.13630	1.73295
H	4.57894	2.11341	1.32995
H	5.03822	0.42233	1.34853
C	4.19160	1.12599	3.26071
H	4.82439	0.37710	3.73918
H	4.42090	2.08501	3.72556
C	2.72982	0.77862	3.52695
Mo	0.00000	0.00000	0.00000
S	-0.56202	2.43234	2.42684
S	-2.41782	-0.63133	2.41737
O	-0.36730	2.26609	-2.50139
O	-2.17198	-0.72945	-2.51020
N	-0.49692	2.09259	-0.20031
N	-2.08266	-0.53024	-0.20907
C	-0.68439	2.93076	0.81208
C	-0.99427	4.34392	0.36228
H	-1.97286	4.65033	0.73558
H	-0.26508	5.04080	0.77801
C	-0.93207	4.24258	-1.16533
H	-0.17328	4.88279	-1.61594
H	-1.87891	4.47167	-1.65616
C	-0.57540	2.78352	-1.43435
C	-2.91368	-0.75354	0.80188
C	-4.30813	-1.13628	0.34954
H	-4.57895	-2.11340	0.75253

H	-5.03822	-0.42232	0.73396
C	-4.19160	-1.12597	-1.17822
H	-4.82439	-0.37708	-1.65670
H	-4.42092	-2.08499	-1.64308
C	-2.72982	-0.77862	-1.44447

cis-2,2-$Mo_2(SNO5)_4 \cdot 2MeOH$ (**4a**·2MeOH)

Mo	0.00000	-0.00000	0.00000
S	-0.32348	-2.48129	2.30886
S	2.45617	-0.46880	-0.18739
O	-0.39174	-2.32547	-2.63518
O	2.34901	-0.32684	4.75673
N	-0.35637	-2.12808	-0.31846
N	2.13701	-0.32496	2.44106
C	-0.43620	-2.98350	0.69988
C	-0.63572	-4.42119	0.26708
H	-1.56788	-4.81222	0.67827
H	0.16884	-5.04713	0.65607
C	-0.64204	-4.32090	-1.25821
H	0.16715	-4.87422	-1.73624
H	-1.57363	-4.65402	-1.71726
C	-0.45468	-2.83296	-1.54353
C	2.97130	-0.51818	1.42040
C	4.40132	-0.77462	1.84833
H	5.05648	0.00177	1.44922
H	4.75349	-1.72445	1.44355
C	4.30889	-0.75831	3.37381
H	4.55873	-1.71512	3.83439
H	4.93421	-0.00091	3.84748
C	2.84275	-0.44653	3.66351
Mo	0.00000	0.00000	2.13129
S	0.34193	2.48781	-0.15462
S	-2.46782	0.45067	2.29704
O	0.33854	2.34054	4.79127
O	-2.34803	0.39175	-2.64986
N	0.33399	2.13605	2.47709
N	-2.13854	0.34886	-0.33630
C	0.42480	2.99122	1.45060
C	0.61100	4.42903	1.88970
H	1.52363	4.84304	1.45900
H	-0.21658	5.04087	1.52673
C	0.65034	4.32081	3.41431
H	-0.12392	4.89779	3.92077
H	1.60652	4.61682	3.84870
C	0.42659	2.83988	3.68886
C	-2.97539	0.53066	0.69331
C	-4.40177	0.80046	0.26081
H	-5.07397	0.05370	0.68573
H	-4.72994	1.77142	0.63531
C	-4.31539	0.74286	-1.26435

H	-4.60892	1.66907	-1.75951
H	-4.90791	-0.05901	-1.70727
C	-2.84232	0.47733	-1.54487
O	-0.65133	-0.21374	4.64545
H	-0.17091	0.57411	4.96583
C	-0.66381	-1.23111	5.64217
H	-1.17368	-0.88471	6.54637
H	0.34980	-1.54913	5.89606
H	-1.21523	-2.07834	5.23772
O	0.38214	0.57653	-2.50938
H	-0.51258	0.35161	-2.83024
C	1.35686	0.29939	-3.51029
H	2.32947	0.57132	-3.10345
H	1.17555	0.89937	-4.40732
H	1.36087	-0.75996	-3.77605

cis-2,2-$Mo_2(SNO6)_4$ (**4b**)

Mo	0.00000	-0.00000	2.08315
S	1.28562	2.12342	2.39091
S	-2.14131	1.25795	2.38644
O	1.17895	1.34255	-2.41322
O	-1.74418	0.53331	-2.41071
N	1.13893	1.85882	-0.21948
N	-1.89674	1.07608	-0.22556
C	1.56980	2.61811	0.78841
C	2.30078	3.91938	0.55444
H	2.91853	4.14312	1.42306
H	1.55164	4.71879	0.49140
C	3.11590	3.88152	-0.73414
H	3.54863	4.86196	-0.94279
H	3.94840	3.18073	-0.62236
C	2.21403	3.43279	-1.87804
H	1.45347	4.19795	-2.07570
H	2.75554	3.27541	-2.81009
C	1.48242	2.14674	-1.55503
C	-2.64589	1.52180	0.78245
C	-3.95975	2.23026	0.54784
H	-4.14501	2.91409	1.37549
H	-4.76312	1.48379	0.57650
C	-3.96973	2.94149	-0.80084
H	-4.94893	3.38378	-0.99472
H	-3.24536	3.76122	-0.78958
C	-3.60552	1.93600	-1.88454
H	-3.44855	2.39647	-2.86034
H	-4.41516	1.20821	-2.01290
C	-2.35677	1.14077	-1.55672
Mo	0.00000	0.00000	0.00000
S	-1.28562	-2.12342	-0.30776

S	2.14131	-1.25795	-0.30329
O	-1.17886	-1.34260	4.49639
O	1.74416	-0.53334	4.49387
N	-1.13893	-1.85882	2.30264
N	1.89674	-1.07608	2.30871
C	-1.56980	-2.61811	1.29474
C	-2.30075	-3.91940	1.52871
H	-2.91852	-4.14314	0.66010
H	-1.55160	-4.71880	1.59173
C	-3.11585	-3.88156	2.81731
H	-3.54855	-4.86201	3.02597
H	-3.94837	-3.18078	2.70555
C	-2.21397	-3.43281	3.96120
H	-1.45338	-4.19796	4.15883
H	-2.75546	-3.27546	4.89327
C	-1.48241	-2.14674	3.63818
C	2.64589	-1.52180	1.30070
C	3.95975	-2.23026	1.53531
H	4.14501	-2.91409	0.70766
H	4.76312	-1.48379	1.50666
C	3.96972	-2.94150	2.88399
H	4.94892	-3.38379	3.07787
H	3.24535	-3.76123	2.87272
C	3.60551	-1.93602	3.96769
H	3.44853	-2.39650	4.94349
H	4.41514	-1.20824	4.09606
C	2.35676	-1.14078	3.63987