

Tuning the nuclearity of $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ -based assemblies by playing with the degree of flexibility of bis-thiosemicarbazones ligands

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Part 1 : MALDI-TOF Spectra

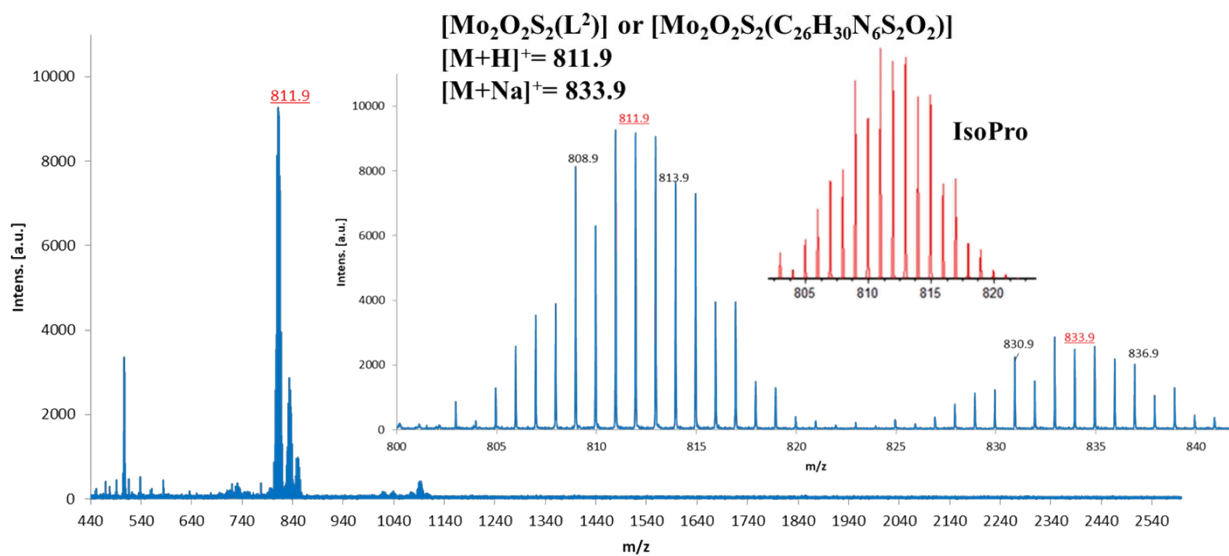


Figure S1 MALDI-TOF spectrum for $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^2)]$ complex

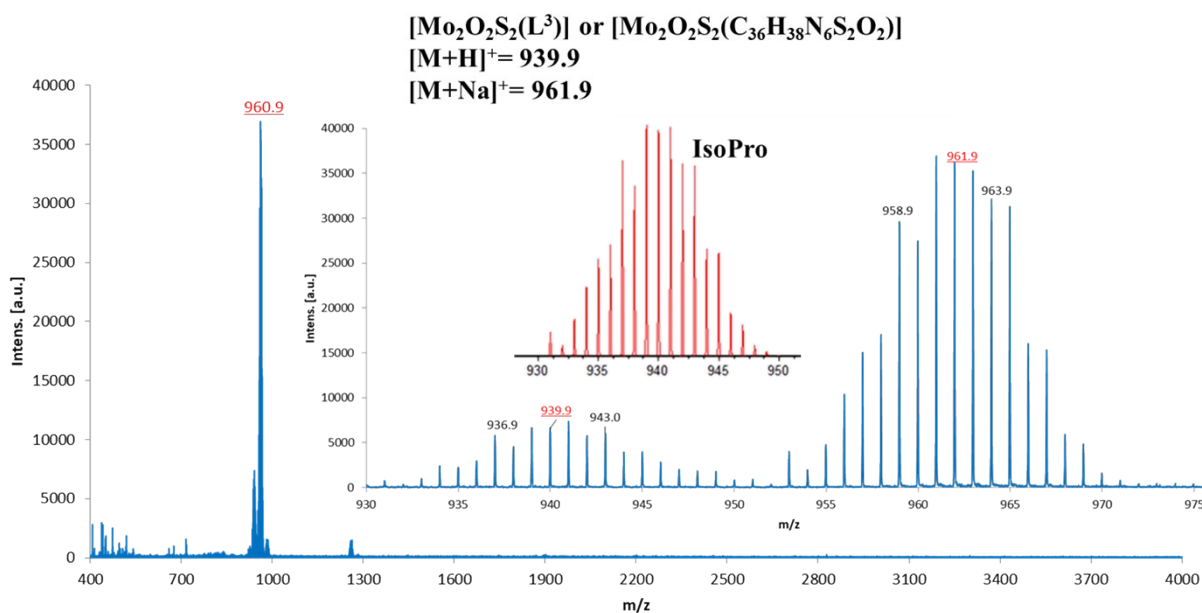


Figure S2 MALDI-TOF spectrum for $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^3)]$ complex

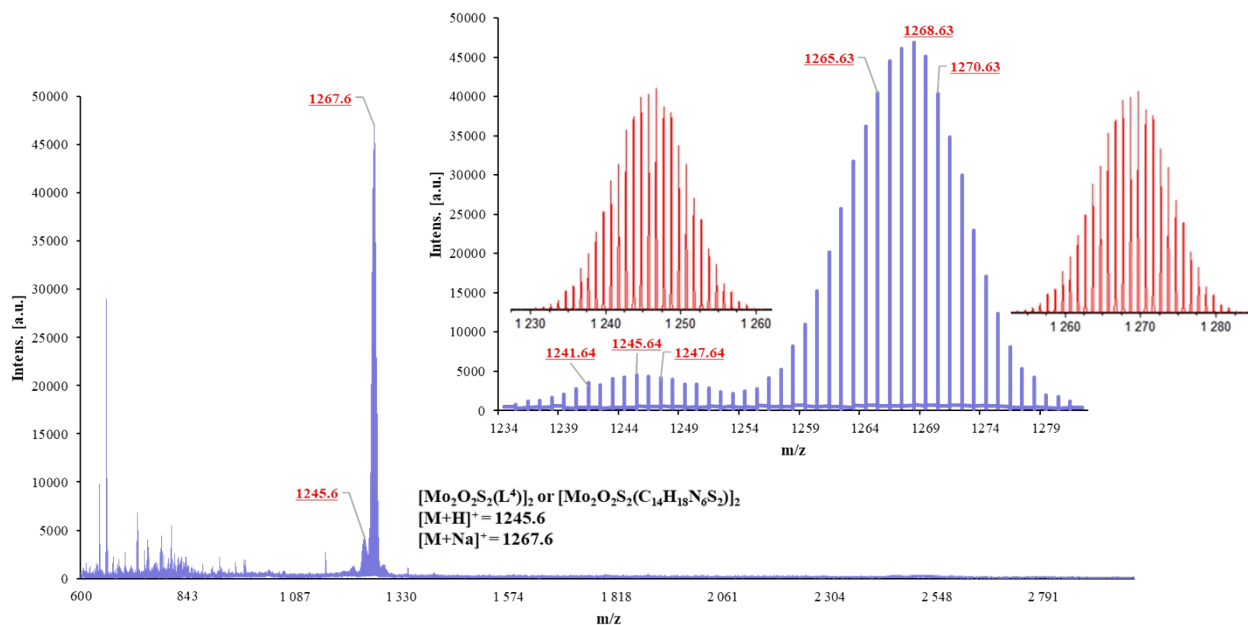


Figure S3 MALDI-TOF spectrum for $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)]_2$ complex

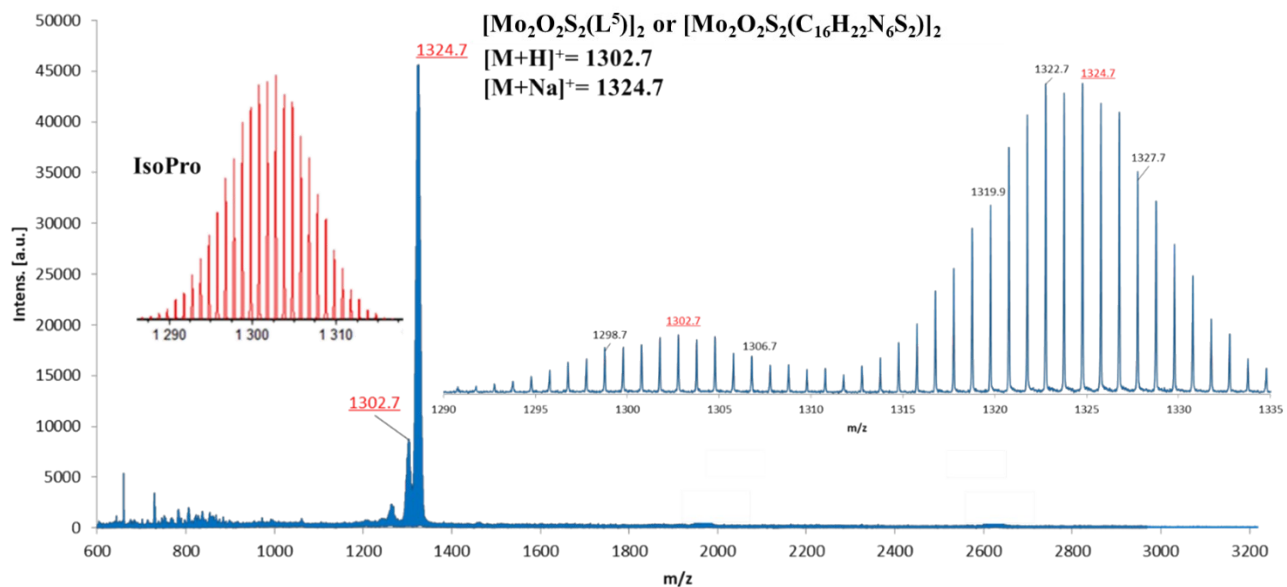


Figure S4 MALDI-TOF spectrum for $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)]_2$ complex

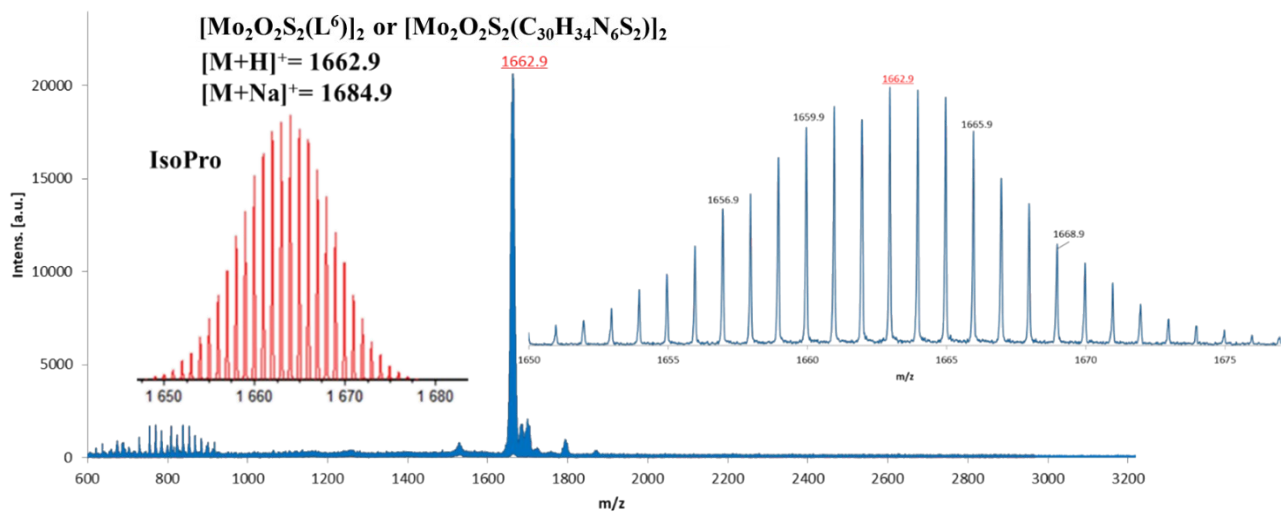


Figure S5 MALDI-TOF spectrum for $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$ complex

Part 2 : X-Ray Diffraction

Table S1. Crystallographic data for complexes [Mo₂O₂S₂(L¹)], [Mo₂O₂S₂(L²)] and [Mo₂O₂S₂(L³)]

Complex	[Mo ₂ O ₂ S ₂ (L ¹)]	[Mo ₂ O ₂ S ₂ (L ²)]	[Mo ₂ O ₂ S ₂ (L ³)]
Formula	C ₂₆ H ₃₆ Mo ₂ N ₈ O ₆ S ₄	C ₃₅ H ₅₁ Mo ₂ N ₉ O ₇ S ₄	C ₃₉ H ₄₇ Mo ₂ N ₆ O ₆ S ₄
M (g mol ⁻¹)	876.75	1029.97	1015.94
Temperature	210	150	210
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pbca</i>	<i>P</i> -1	<i>P</i> 1
<i>a</i> (Å)	14.4020(4)	9.8604(4)	11.2201(6)
<i>b</i> (Å)	18.8426(5)	11.8441(5)	12.1164(6)
<i>c</i> (Å)	27.1560(8)	21.7263(9)	18.3239(9)
α (°)	90	74.869(2)	76.257(2)
β (°)	90	79.023(2)	87.948(2)
γ (°)	90	65.735(2)	88.316(2)
V (Å ³)	7369.4(4)	2223.01(16)	2417.7(2)
Z	8	2	2
D _{calc}	1.580	1.539	1.396
Crystal size (mm)	0.30 × 0.20 × 0.06	0.31 × 0.17 × 0.14	0.20 × 0.12 × 0.04
F(000)	3552	1056	1038
μ (Mo-K α)/mm ⁻¹	0.71073	0.71073	0.71073
Reflections collected	486382	112483	158731
Independent reflections ($I > 2\sigma(I)$)	10137	17397	11937
Parameters	419	520	563
$\Delta(\rho)$ (e Å ⁻³)	0.48 and -0.46	1.379 and -0.947	1.70 and -0.61
Goodness of fit	1.14	1.212	1.11
R1 ^a	0.0215 (0.024) ^b	0.0289 (0.0363)	0.0333 (0.0434)
wR2 ^a	0.0509 (0.0526)	0.0579 (0.0625)	0.0974 (0.107)

^aR = $\sum||F_o| - |F_c||/\sum|F_o|$, wR₂ = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; [F_o > 4 σ (F_o)]. ^bBased on all data.

Table S2 Crystallographic data for complexes $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)_2]$, $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)_2]$ and $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$

Complex	$[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)_2]$	$[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)_2]$	$[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$
Formula	$\text{C}_{40}\text{H}_{64}\text{Mo}_4\text{N}_{16}\text{O}_{9.50}\text{S}$	$\text{C}_{41.50}\text{H}_{67.50}\text{Mo}_4\text{N}_{14.50}\text{O}_{8.25}\text{S}$	$\text{C}_{79}\text{H}_{125}\text{Mo}_4\text{N}_{12}\text{O}_{16.75}\text{S}_{17.5}$
	8	8	0
M (g mol ⁻¹)	1561.31	1541.84	2455.71
Temperature	230	210	220
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
a (Å)	14.458(1)	14.7740(7)	15.1256(5)
b (Å)	15.6676(9)	15.8521(7)	19.0607(6)
c (Å)	16.4741(11)	17.0582(9)	21.7932(11)
α (°)	88.655(3)	66.431(2)	91.701(3)
β (°)	73.617(3)	67.927(2)	95.393(3)
γ (°)	70.679(2)	68.124(2)	108.581(2)
V (Å ³)	3368.5(4)	3275.0(3)	5917.4(4)
Z	2	2	2
D _{calc}	1.539	1.564	1.378
Crystal size (mm)	0.22 × 0.14 × 0.04	0.24 × 0.16 × 0.12	0.30 × 0.06 × 0.04
F(000)	1576	1560	2530
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.71073	0.71073	0.71073
Reflections collected	133440	185221	357366
Independent reflections (I > 2 σ (I))	16036	15880	22742
Parameters	767	721	1214
$\Delta(\rho)$ (e Å ⁻³)	2.20 and -1.10	1.18 and -0.80	1.79 and -1.74
Goodness of fit	1.08	1.10	1.07
R1 ^a	0.0665 (0.0984)	0.0344 (0.0517)	0.0628 (0.077)
wR2 ^a	0.1874 (0.212)	0.0851 (0.0982)	0.1759 (0.1972)

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $[F_o > 4\sigma(F_o)]$. ^bBased on all data.

Table S3: Selected angles ($^{\circ}$) and distances (\AA) in the complexes

complex	phenoxy fragments plans, ($^{\circ}$)	tert-butylphenyl fragments plans, ($^{\circ}$)	Distance between aromatic fragments, (\AA)	4-atom cycle with Mo atoms plans, ($^{\circ}$)
$[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^1)]$	63.35		7.361	80.46
$[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^2)]$	76.83		7.828	70.04
$[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^3)]$	76.19		7.865	67.53
$[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)_2]$		69.02	7.660	Mo1 and Mo2, 82.54 Mo3 and Mo4, 83.84
$[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)_2]$		66.56	7.478	Mo1 and Mo2, 76.77 Mo3 and Mo4, 78.70
$[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$		71.67	7.649	Mo1 and Mo2, 66.16 Mo3 and Mo4, 67.29

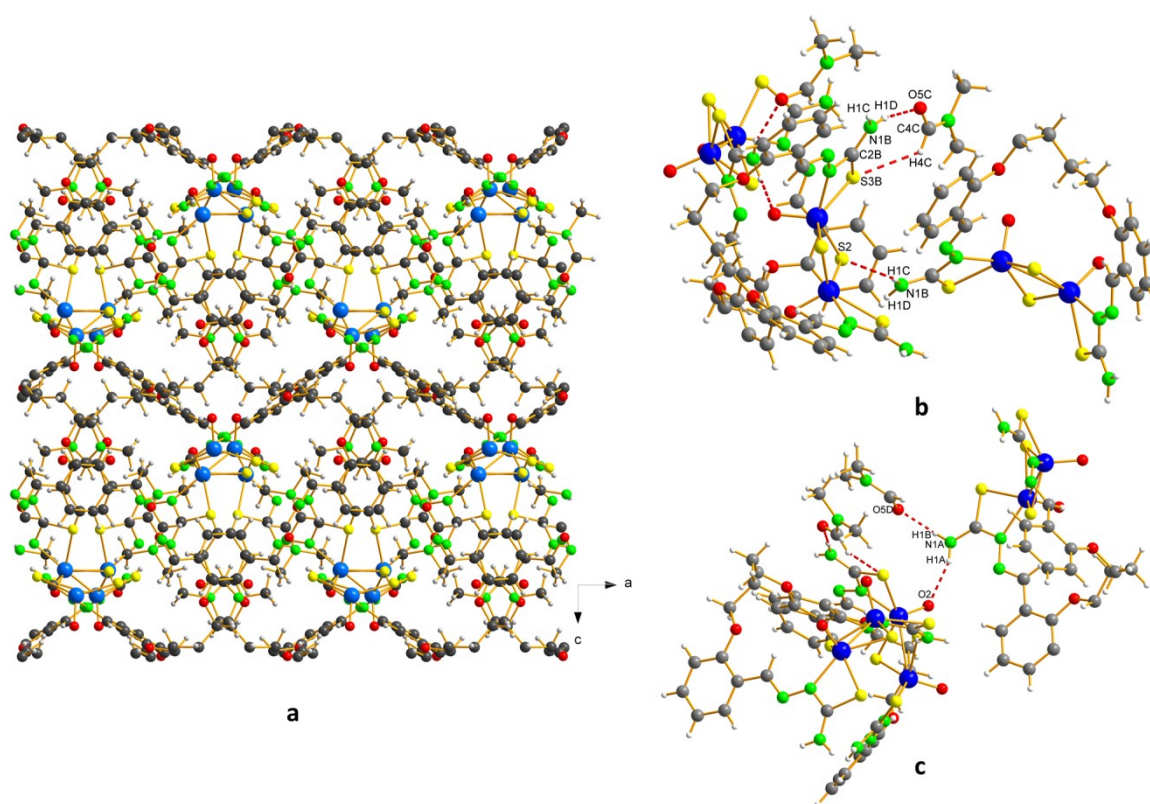


Figure S6. (a) Crystal packing of $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^1)]$ complex viewed along b axis; (b) and (c) intermolecular hydrogen bonding. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

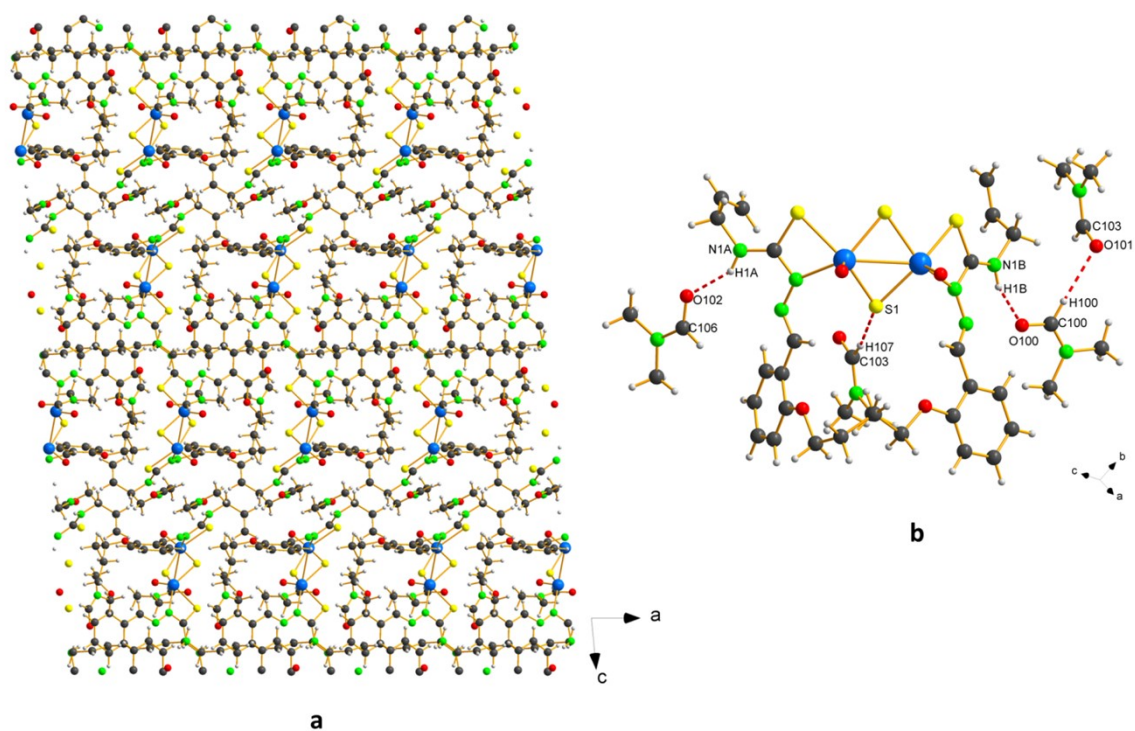


Figure S7 (a) Crystal packing of $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^2)]$ complex viewed along b axis; (b) intermolecular hydrogen bonding. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

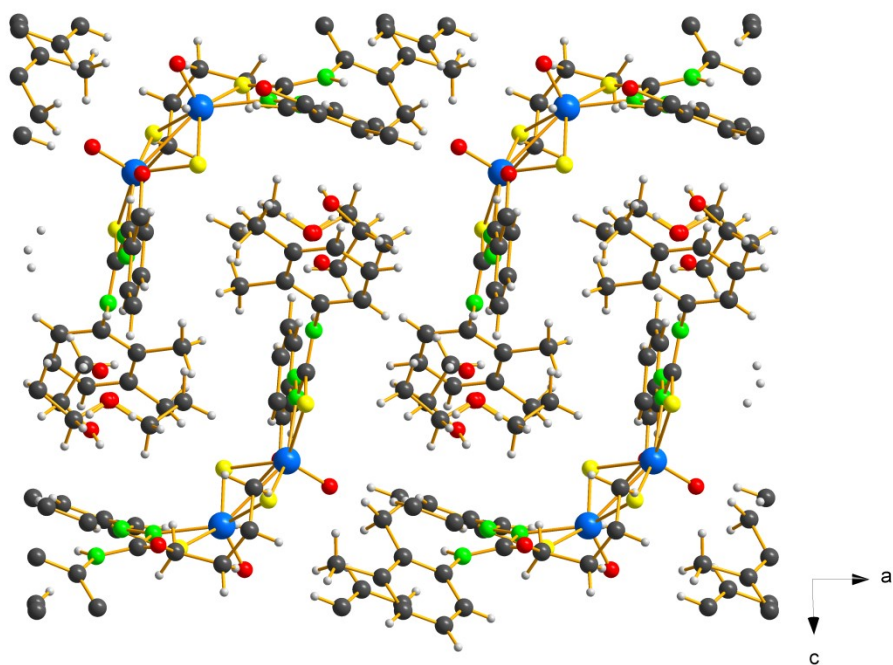


Figure S8 Crystal packing of $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^3)]$ complex viewed along b axis. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

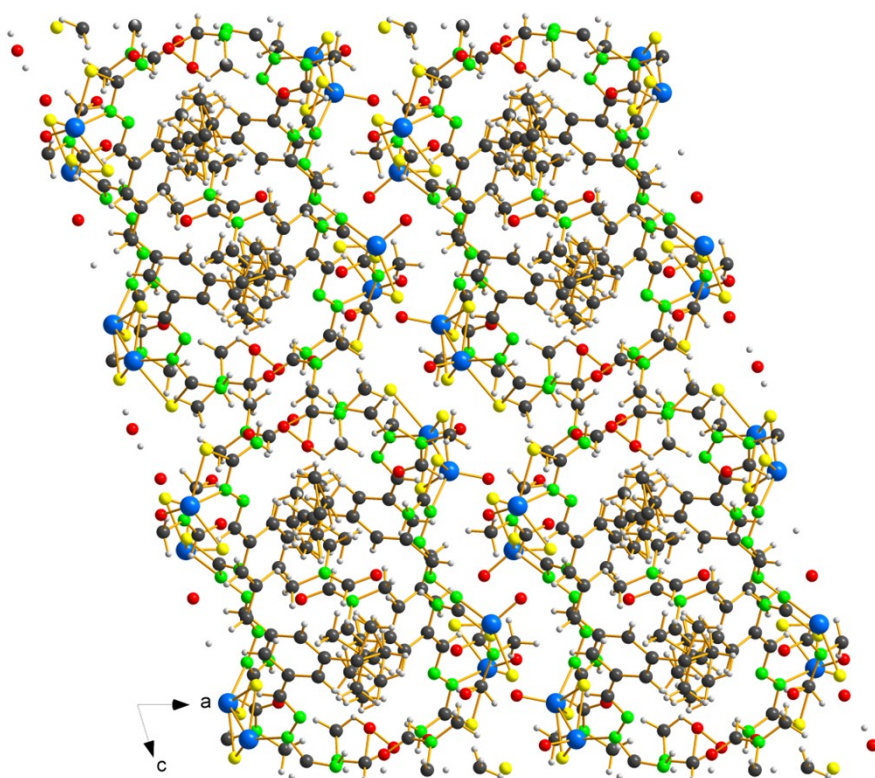


Figure S9 Crystal packing of $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)_2]$ complex viewed along b axis. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

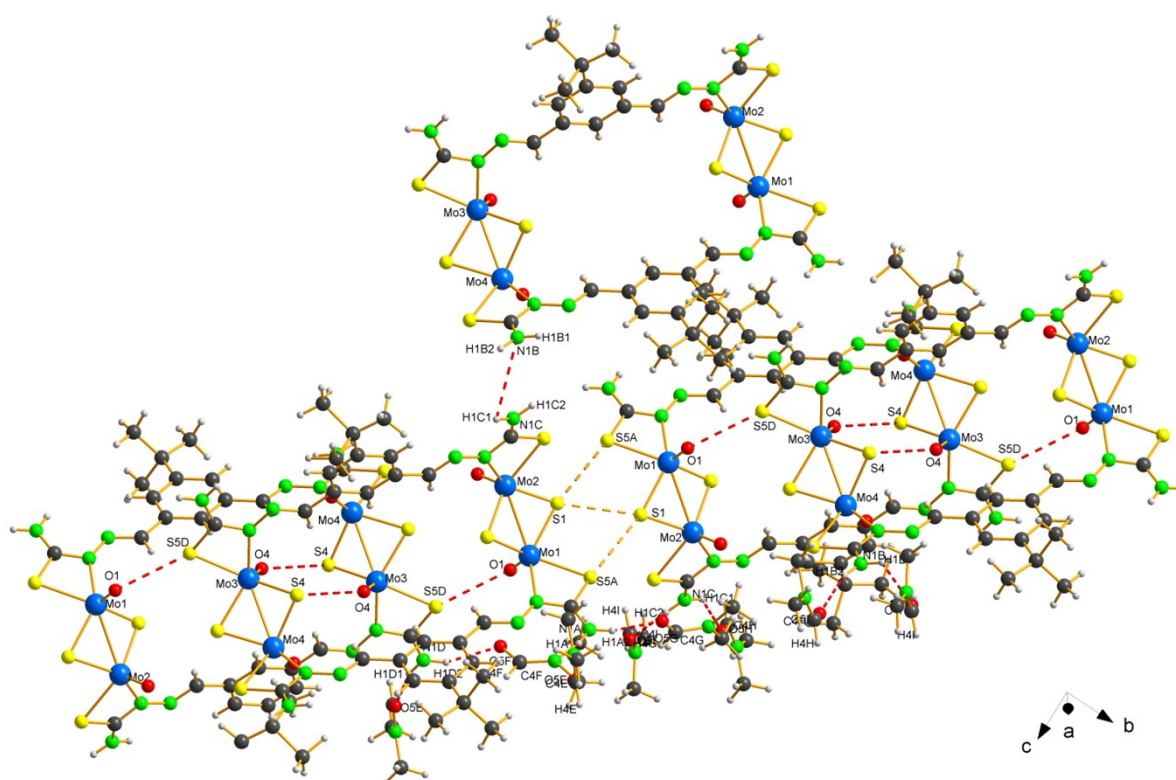


Figure S10 Intermolecular S...O, S...S and N...H interactions in $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)_2]$. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

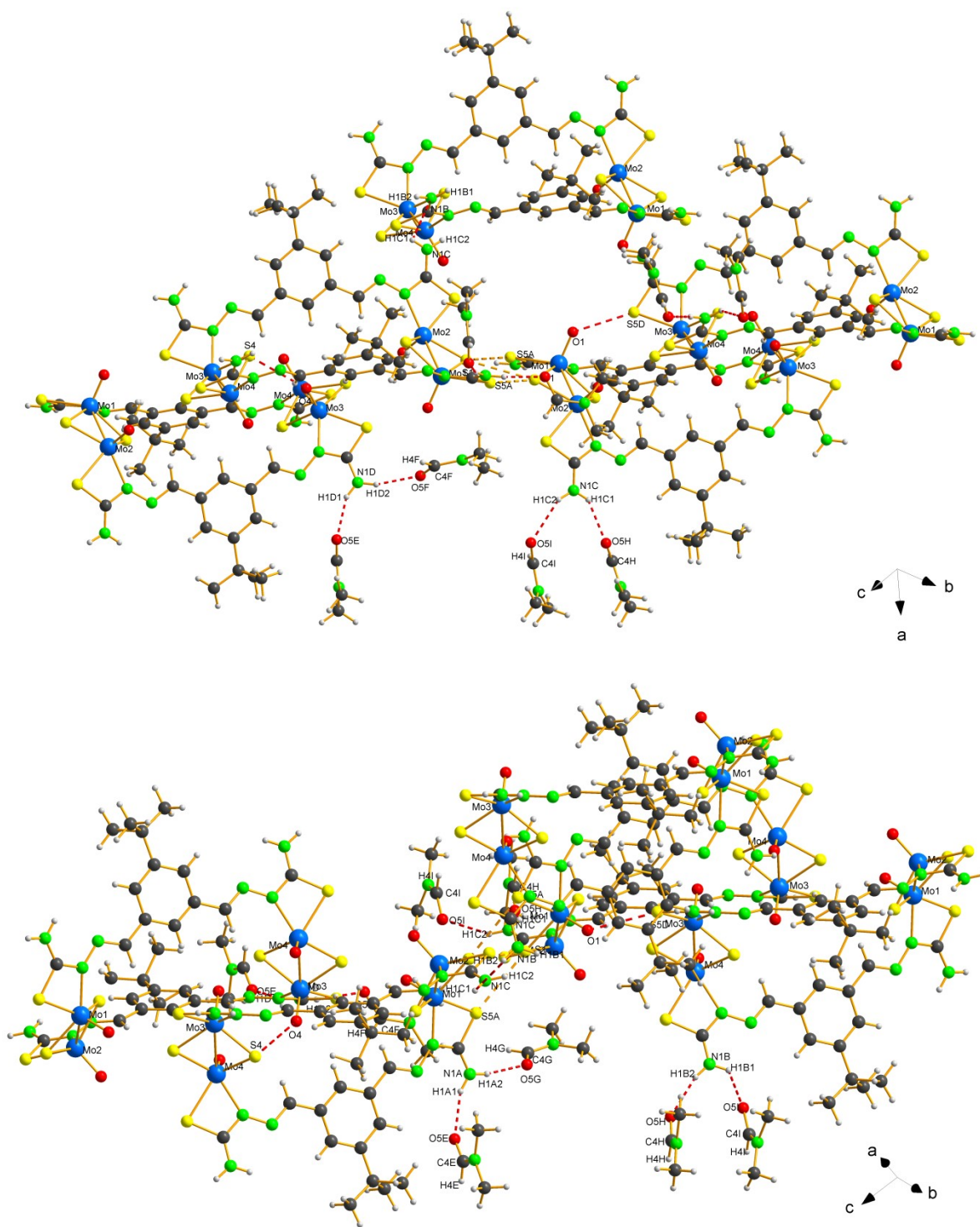


Figure S11 Intermolecular NH...O hydrogen bonding in $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^4)_2]$ involving amino groups and DMF molecules. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

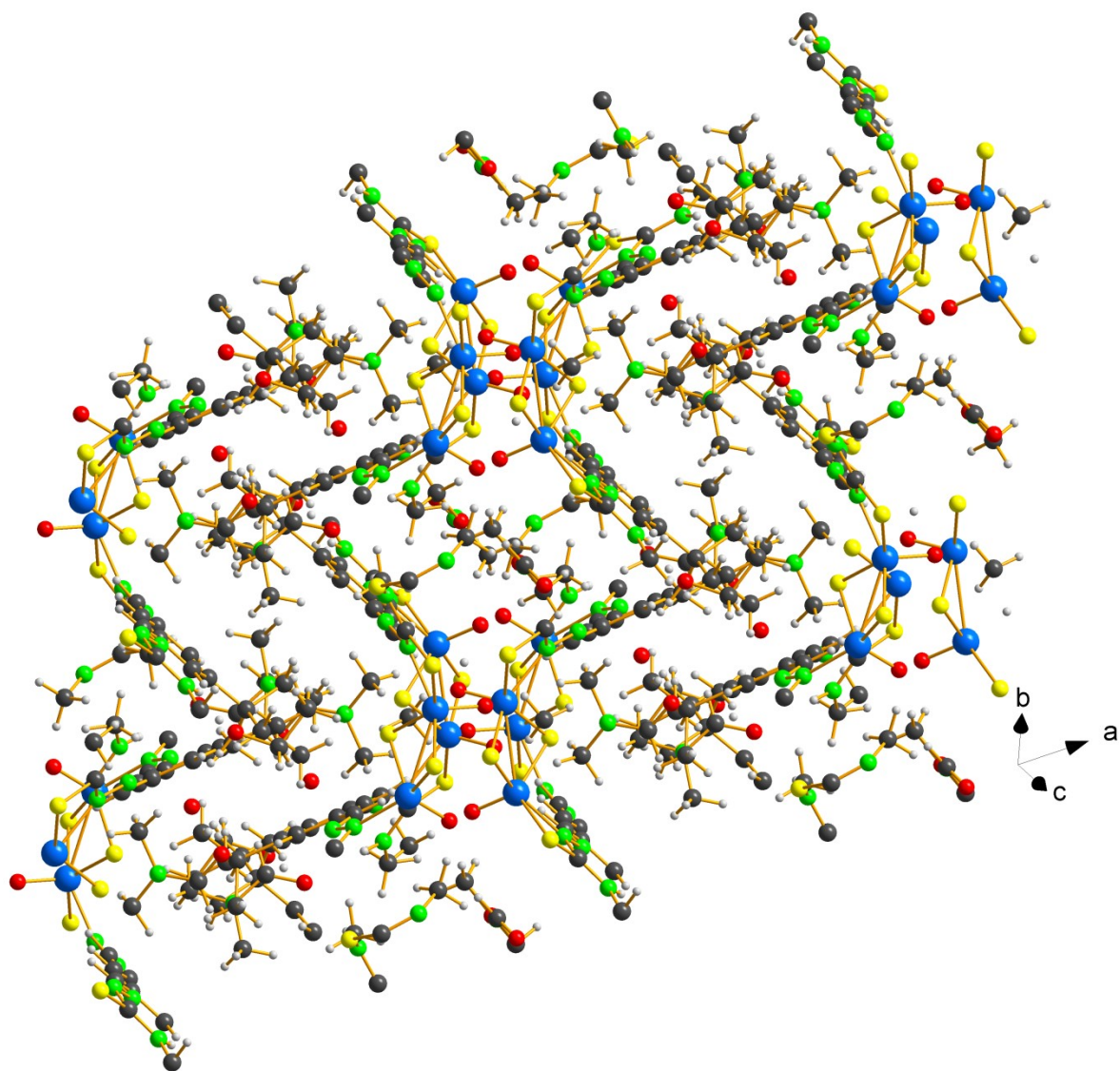


Figure S12 Crystal packing of $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)_2]$ complex. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

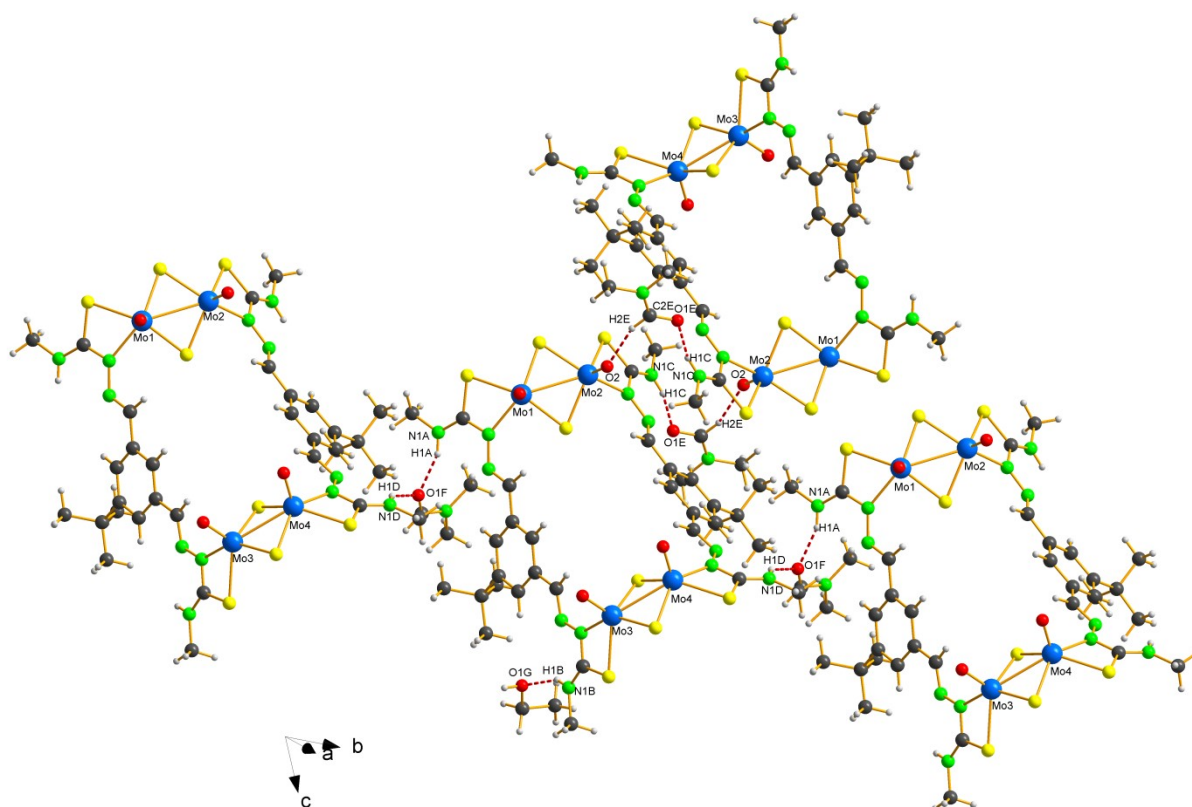


Figure S13 Intermolecular NH...O hydrogen bonding in $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)_2]$ involving amino groups and DMF and EtOH molecules. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

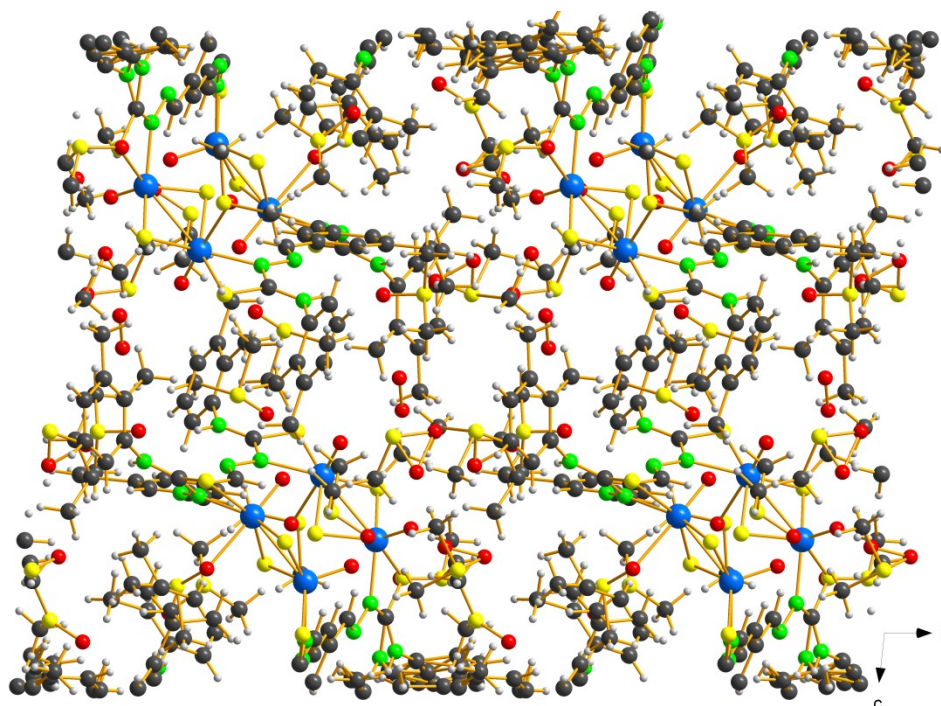


Figure S14 Crystal packing of $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$ complex viewed along b axis. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

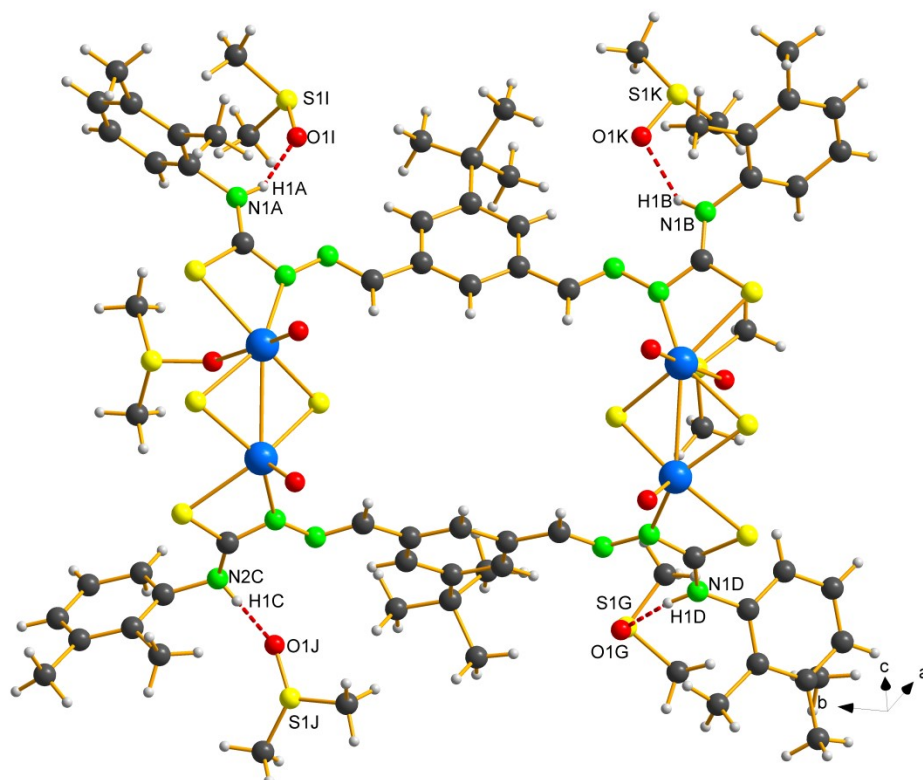


Figure S15 Intermolecular $\text{NH}\cdots\text{O}$ hydrogen bonding in $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$ involving amino groups and DMF molecules. Color code: Mo (blue), C (gray), O (red), N (green), and S (yellow).

Part 3: NMR studies

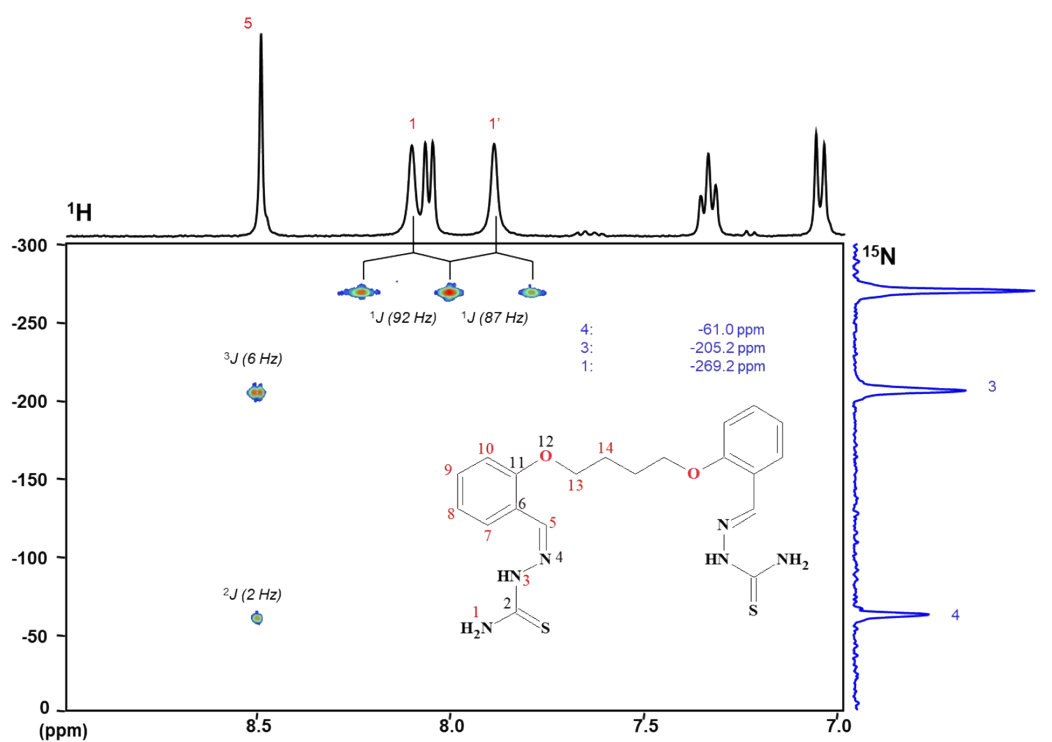


Figure S16 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for H_2L^1 ligand

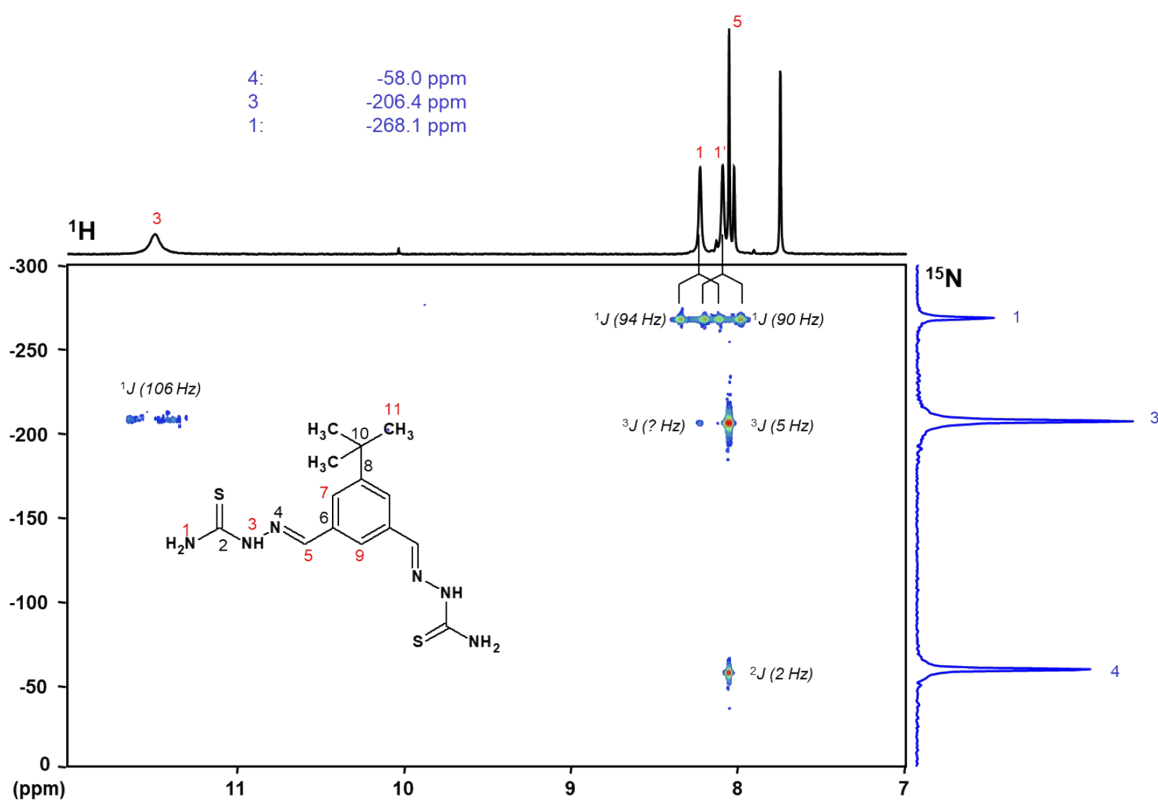


Figure S17 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for H_2L^4 ligand

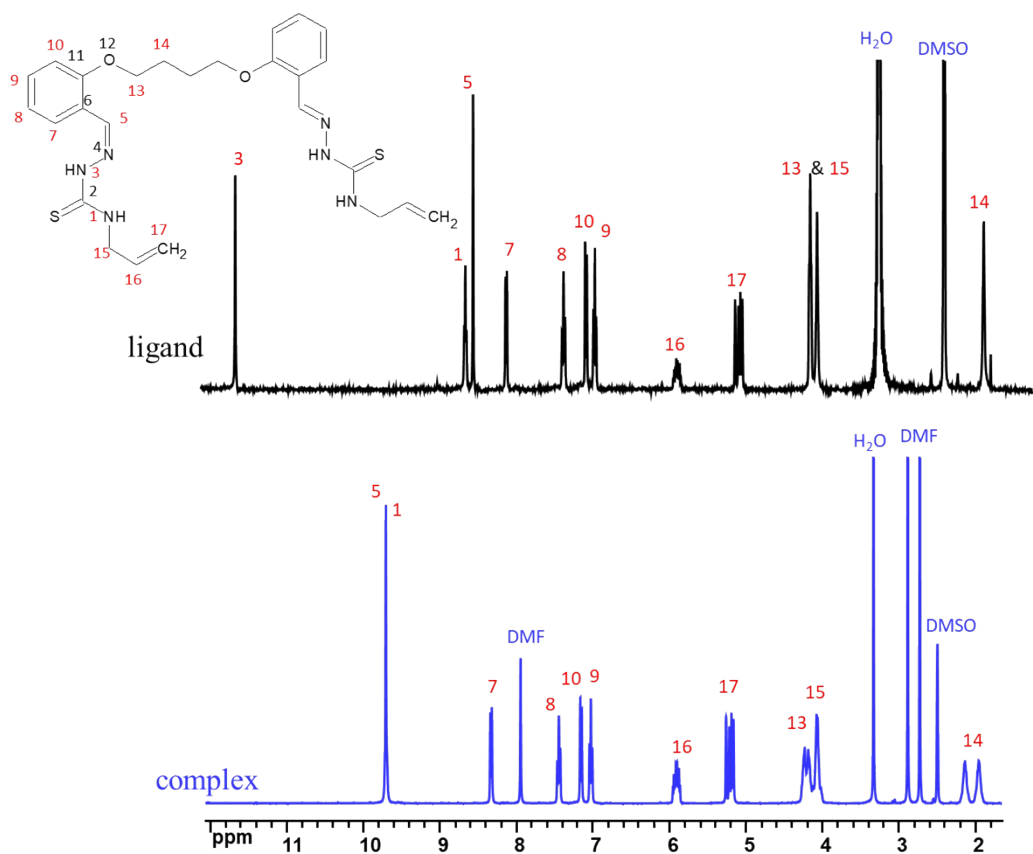


Figure S18 $^1\text{H-NMR}$ spectra of H_2L^2 and $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^2)]$ complex

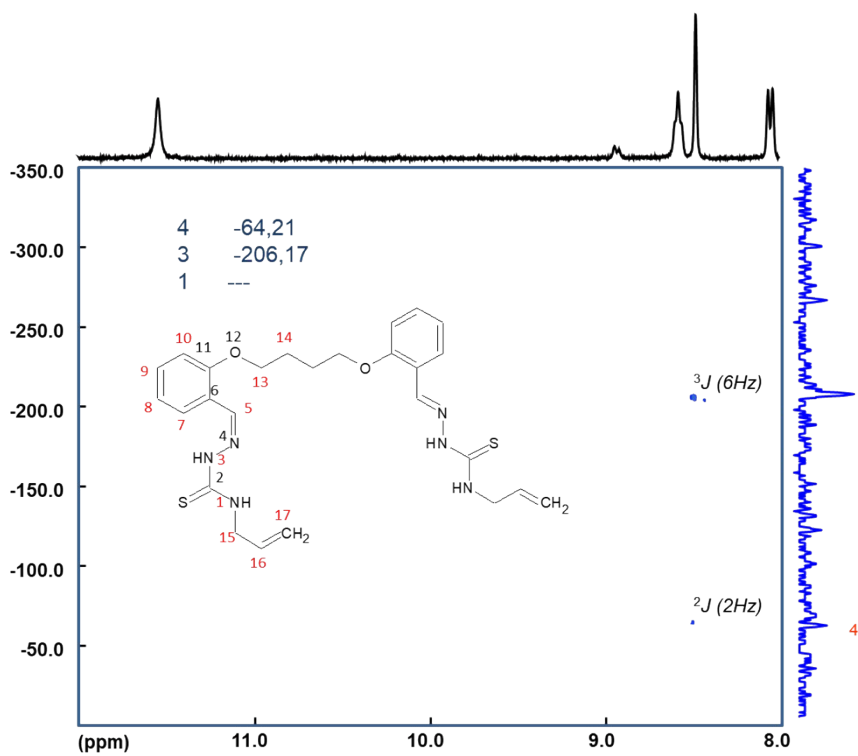


Figure S19 $^1\text{H-NMR}$ DOSY spectrum for H_2L^2 ligand

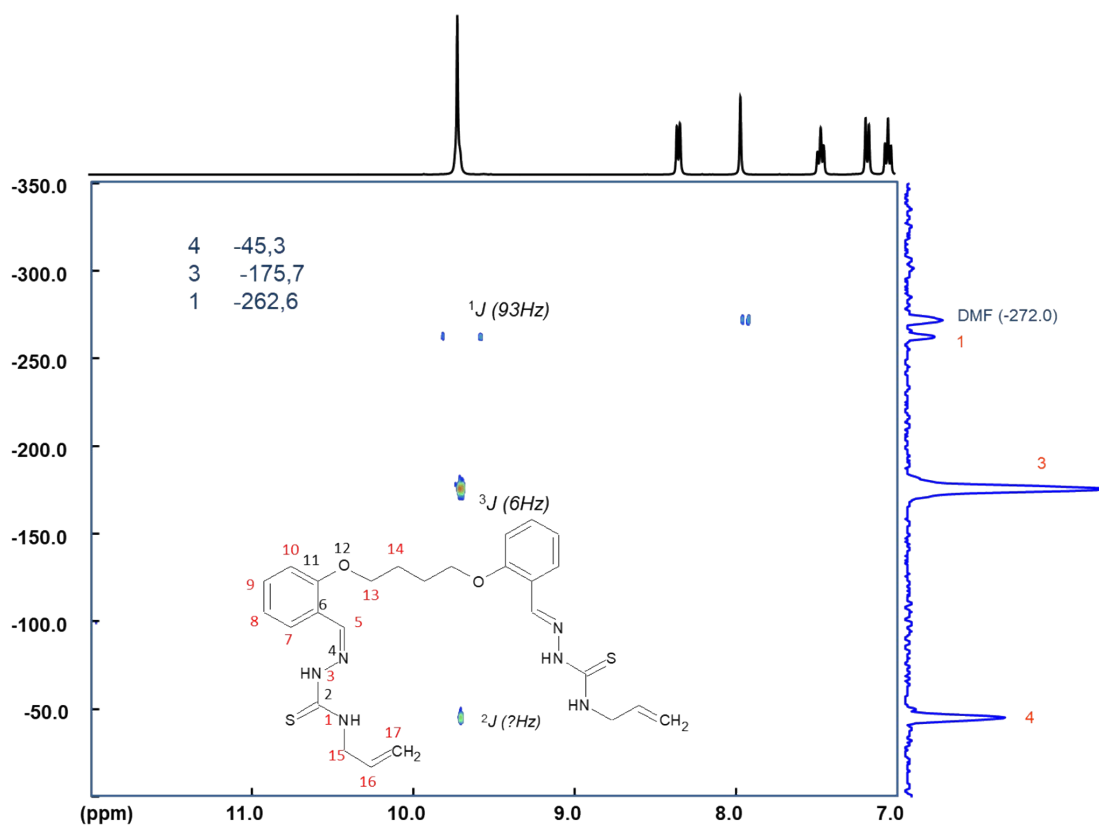


Figure S20 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for H_2L^2 ligand

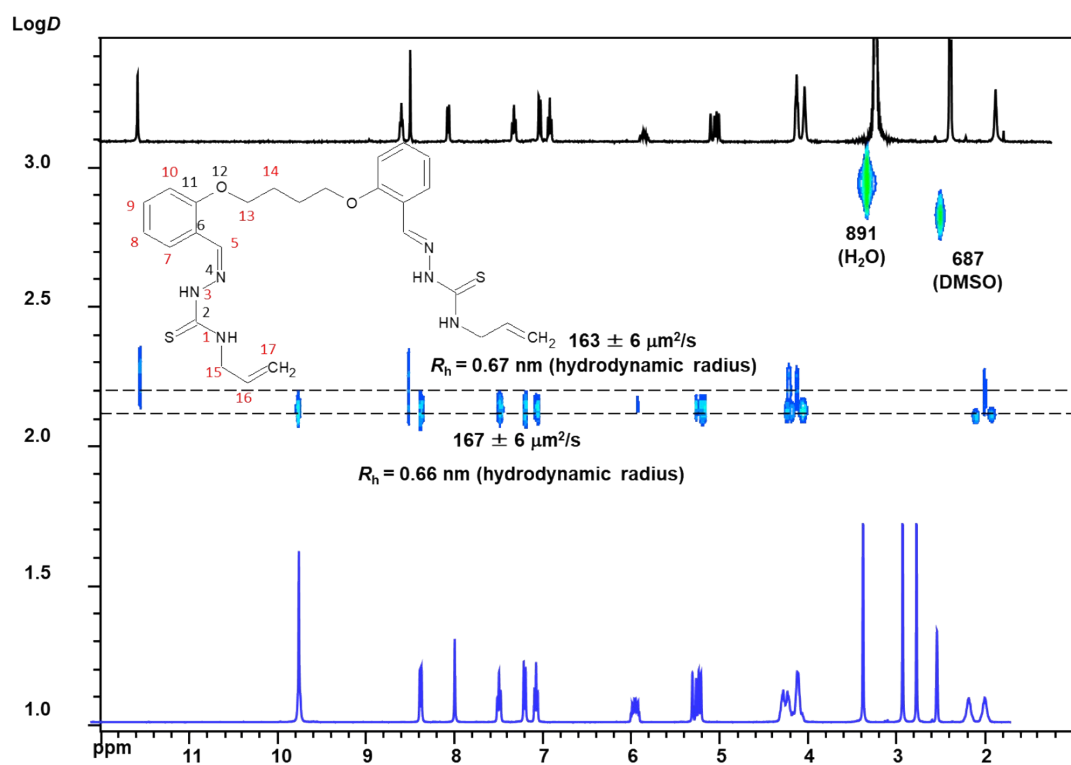


Figure S21 ^1H -NMR DOSY spectra for H_2L^2 (top) and $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^2)]$ complex (bottom)

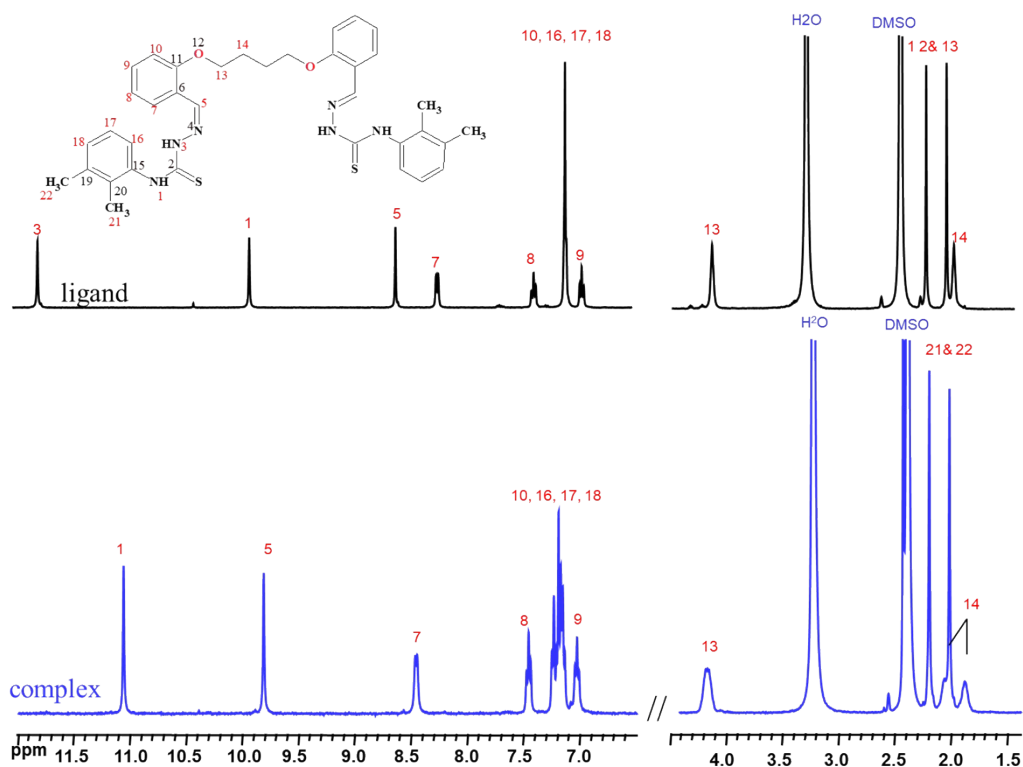


Figure S22 ^1H -NMR spectra of H_2L^3 and $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^3)]$ complex

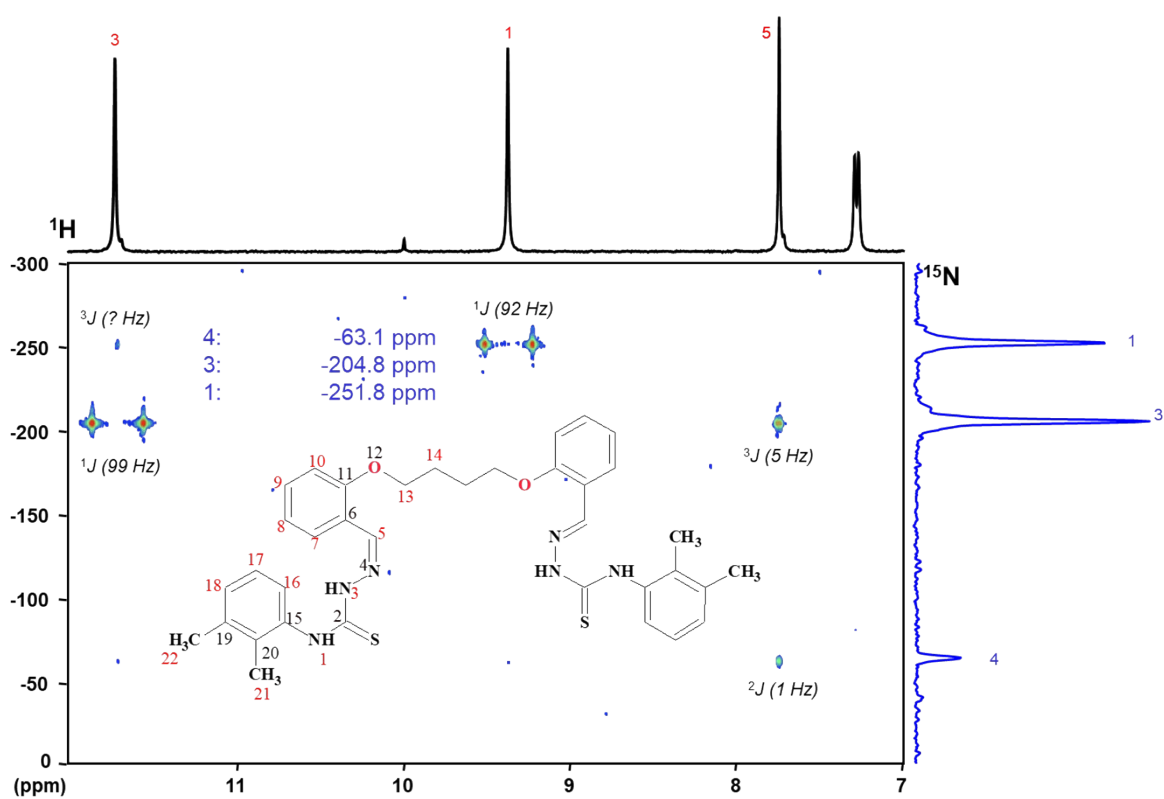


Figure S23 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for H_2L^3 ligand

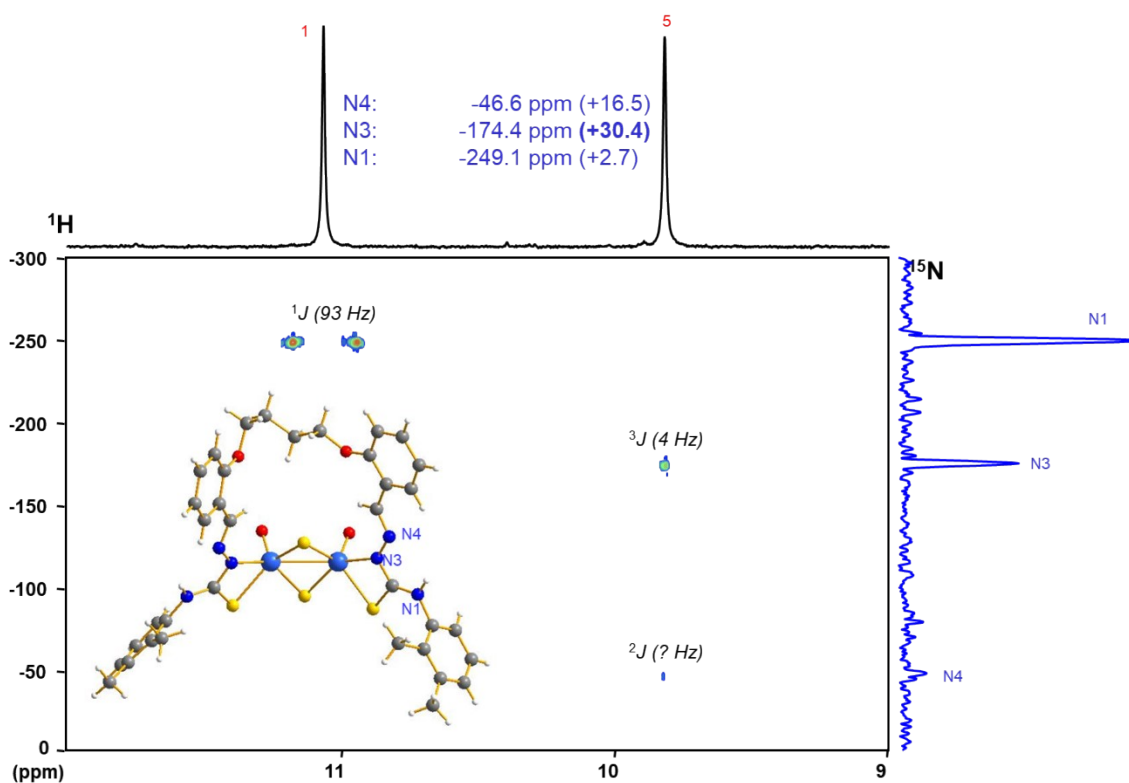


Figure S24 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^3)]$ complex

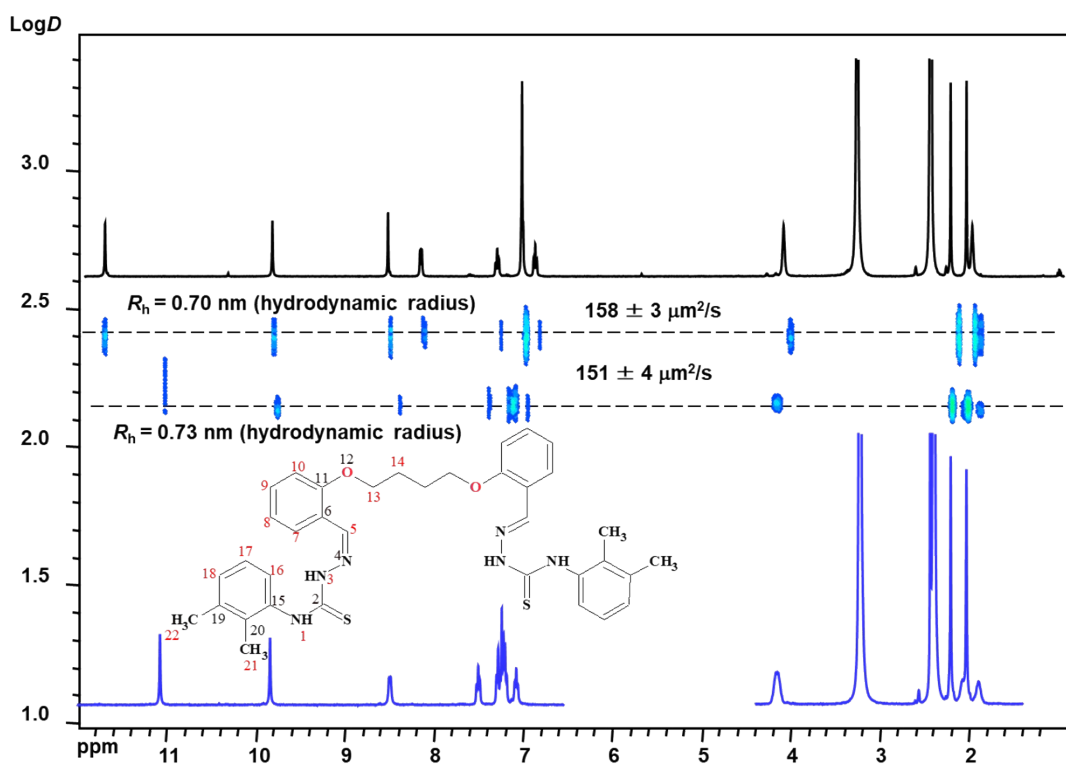


Figure S25 ^1H -NMR DOSY spectra for H_2L^2 (top) and $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^3)]$ complex (bottom)

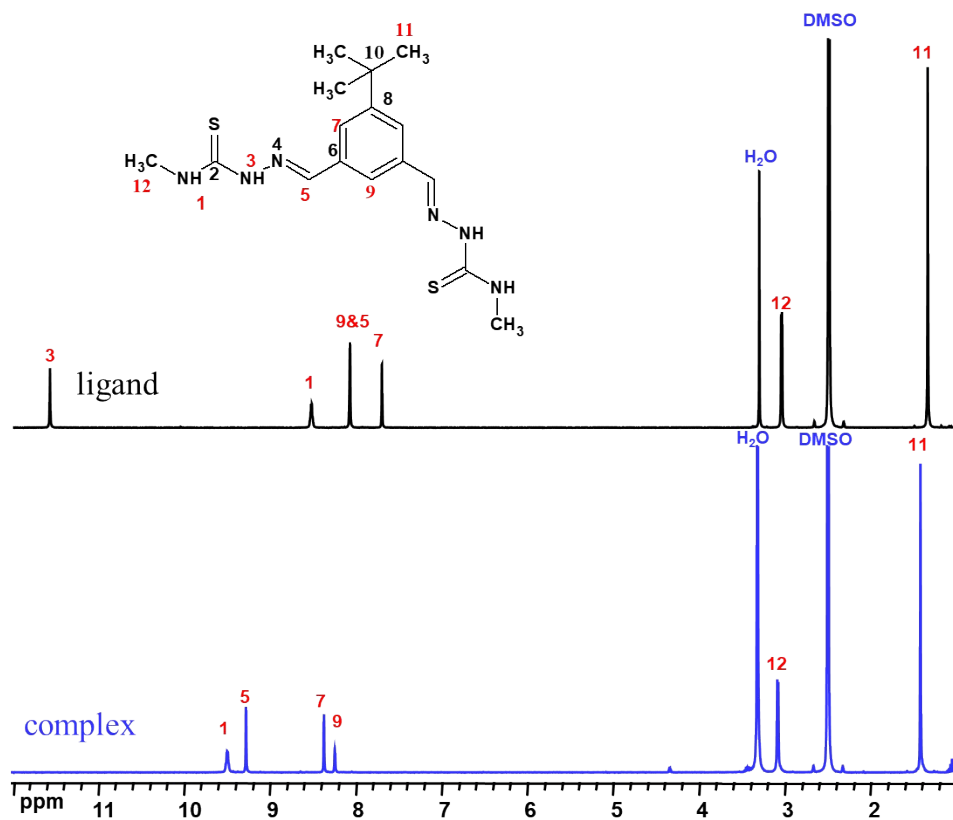


Figure S26 $^1\text{H-NMR}$ spectra of H_2L^5 and $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^5)_2]$ complex

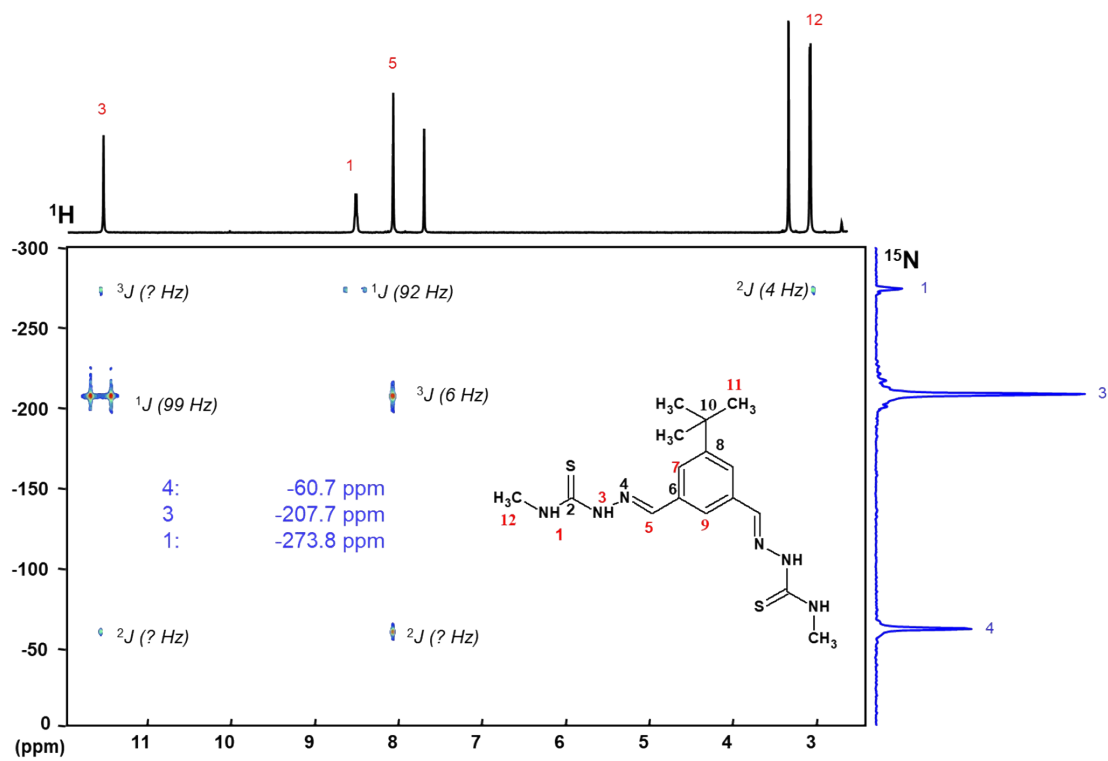
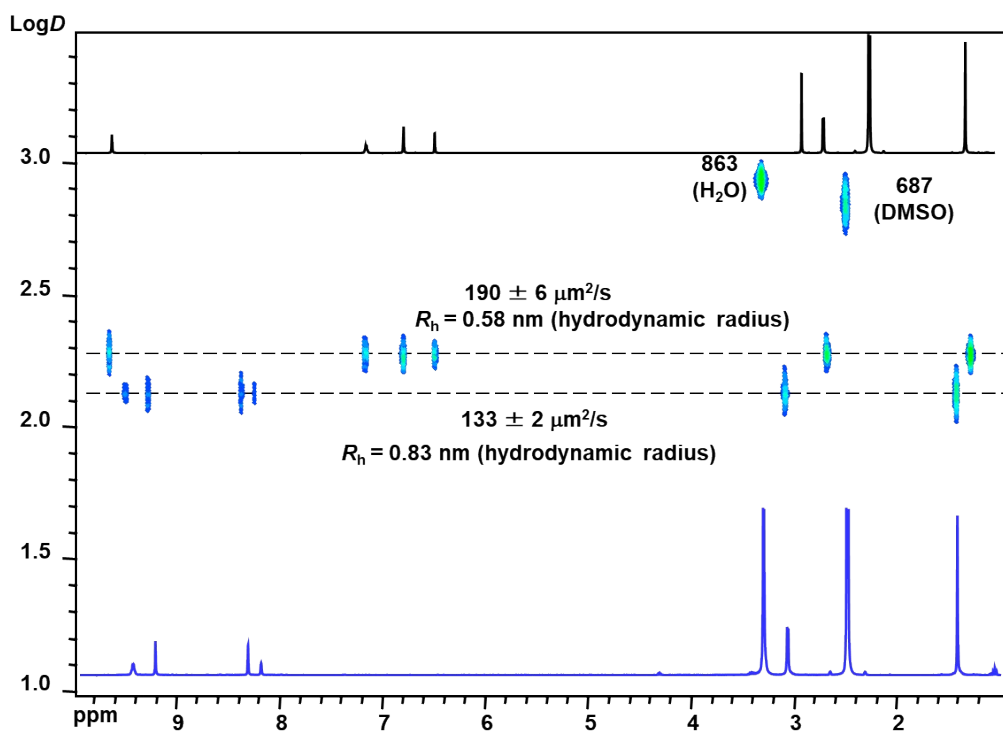
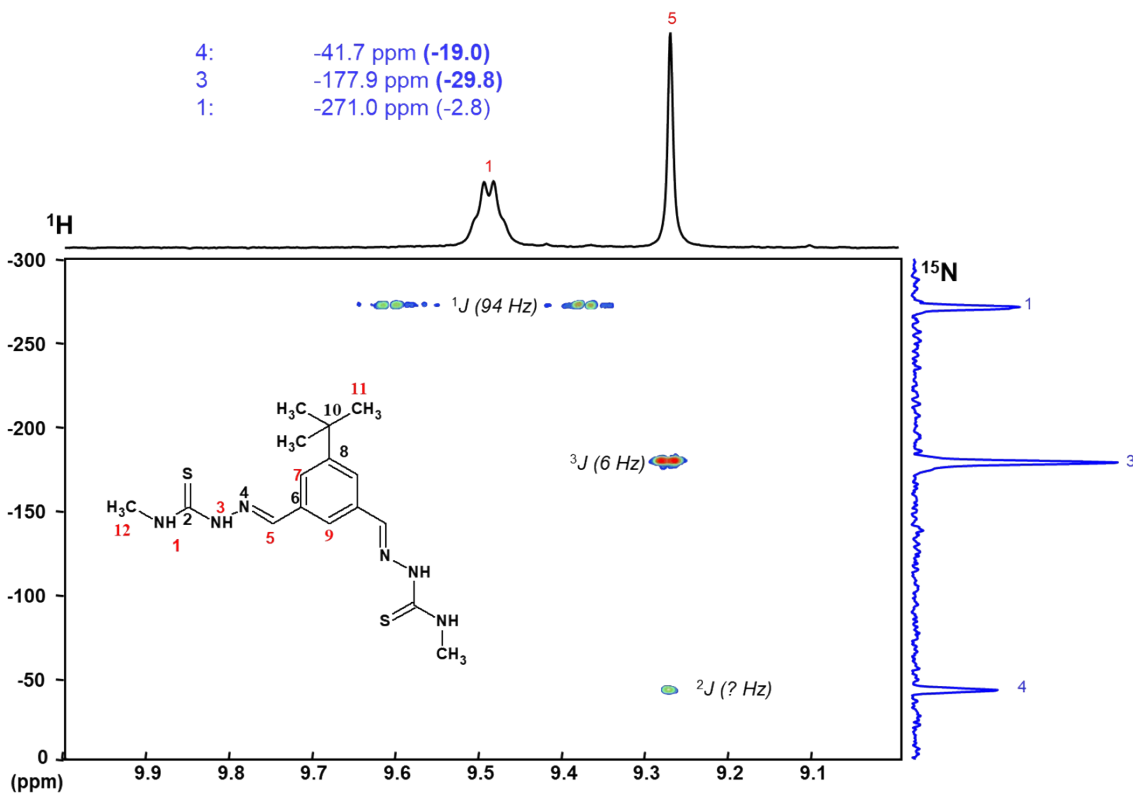


Figure S27 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for H_2L^5



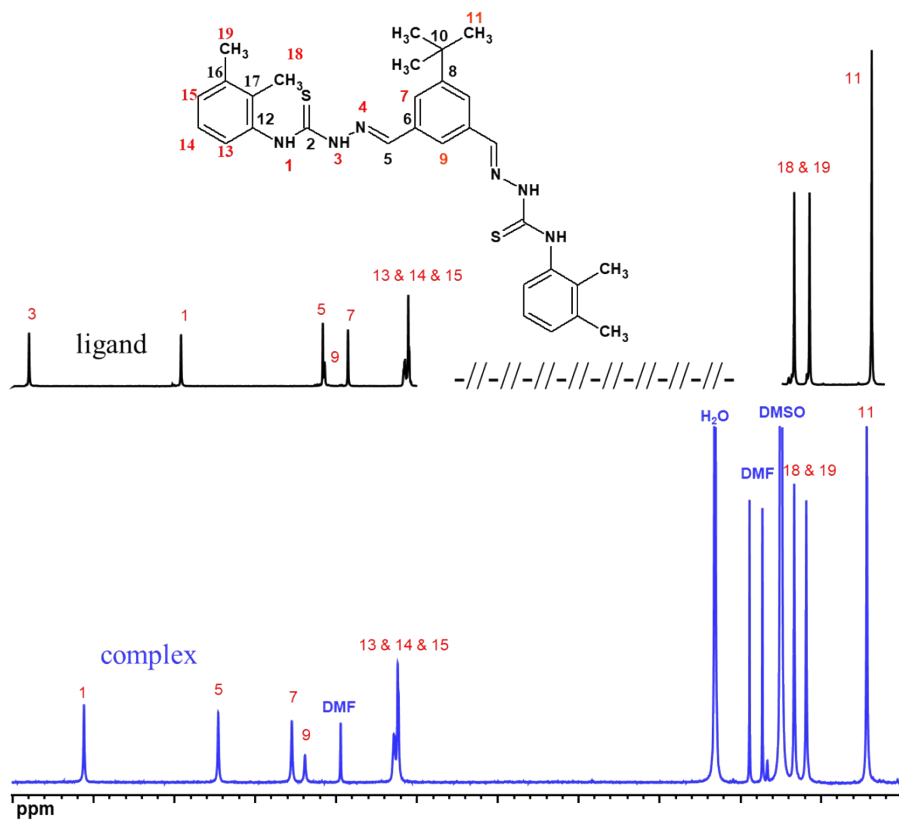


Figure S30 ^1H -NMR spectra of H_2L^6 and $[(\text{Mo}_2\text{O}_2\text{S}_2)_2(\text{L}^6)_2]$ complex

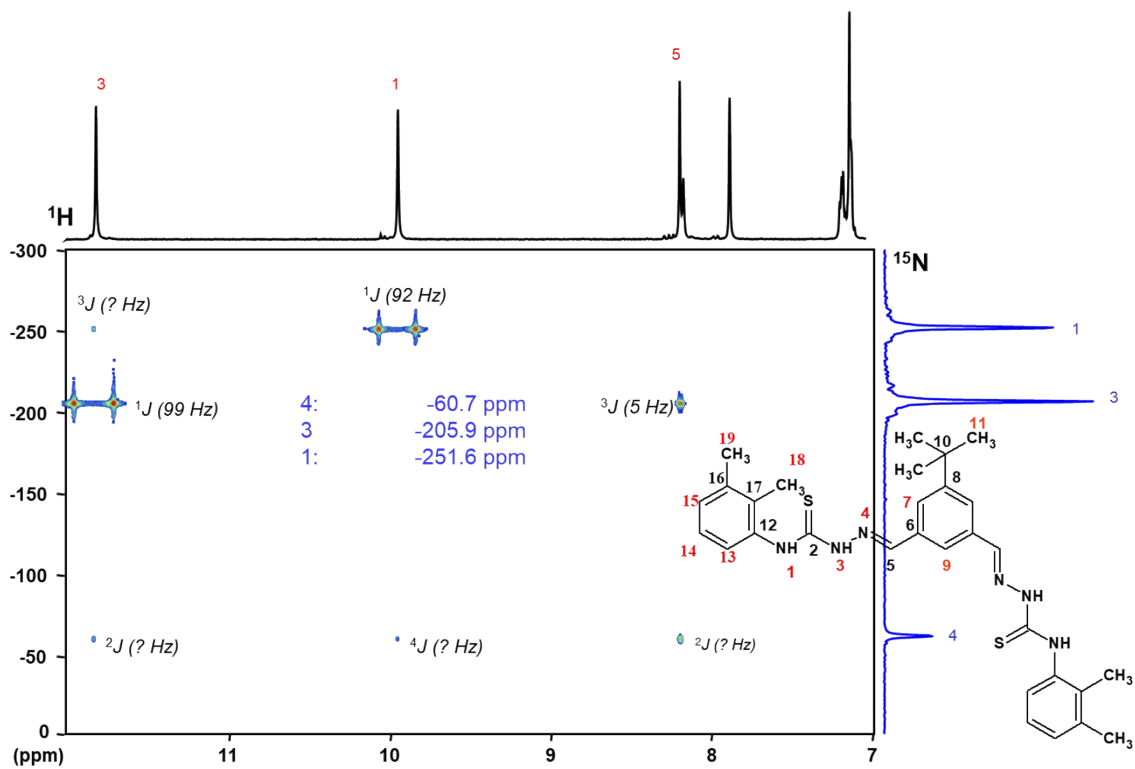


Figure S31 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for H_2L^6 ligand

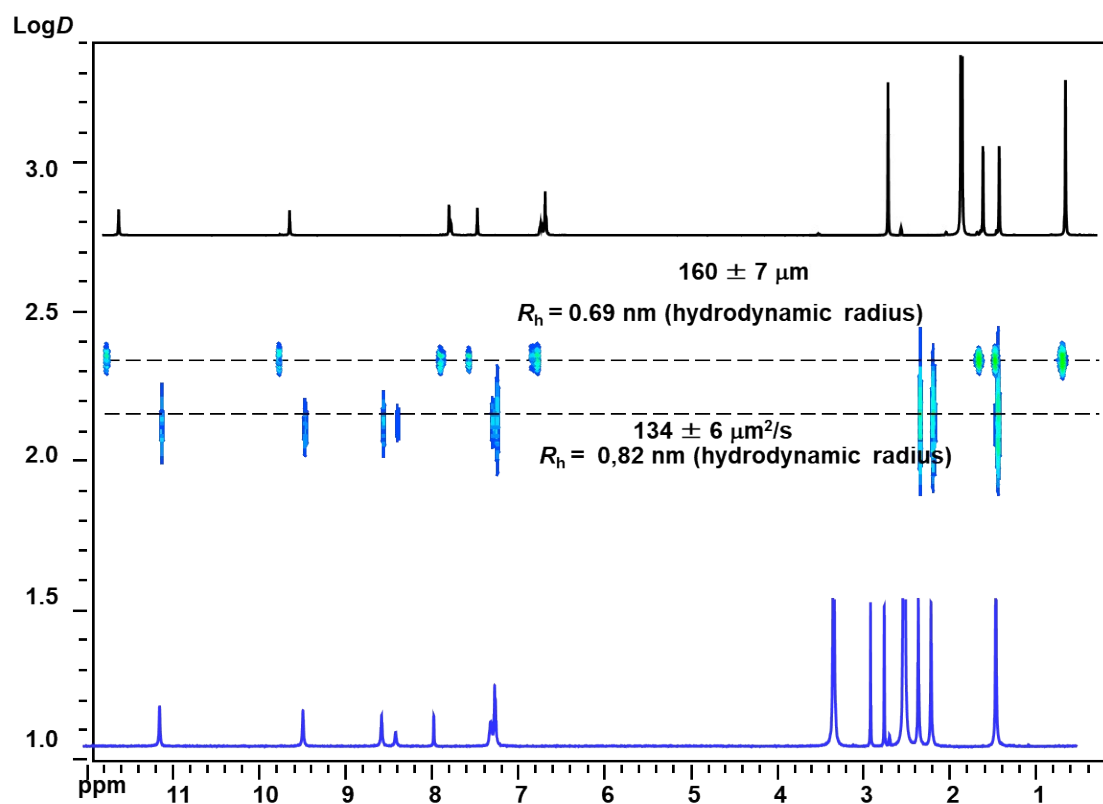


Figure S32 ¹H-NMR DOSY spectra for H₂L⁶ (top) and [(Mo₂O₂S₂)₂(L⁶)₂] complex (bottom)