Synthesis, structures and solution studies of a new class of \([\text{Mo}_2\text{O}_2\text{S}_2]\)-based thiosemicarbazone coordination complexes

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**Supporting Information**

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Part 1: Experimental section

1°) General methods

**Fourier Transformed Infrared (FT-IR)** spectra were recorded on a 6700 FT-IR Nicolet spectrophotometer, using diamond ATR technique. The spectra were recorded on solid compounds and ATR correction was applied.

**Elemental analyses** (C, H, N, S) were performed by the “service central d’analyses du CNRS”, ICSN, Gif sur Yvette, France.

**XRD analysis.** Yellow-orange crystals were obtained by recrystallization from DMSO solutions. The diffraction data were collected on a Bruker Apex Duo diffractometer with MoKα radiation (λ = 0.71073 Å) by doing φ and ω scans of narrow (0.5°) frames at 200 K. Crystals were glued in paratone oil to prevent any loss of crystallization water. An empirical absorption correction was applied using the SADABS program (G. M. Sheldrick, *Vol. SADABS program for scaling and correction of area detector data* 1997). Structures were solved by direct methods and refined by full-matrix least-squares treatment against |F|^2 in anisotropic approximation with SHELX 2014/7 set (G. M. Sheldrick, *Acta Cryst C* 2015, 71, 3) using ShelXle program (C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J Appl Crystallogr* 2011, 44, 1281). Further details about of the crystal structure determinations may be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif on quoting the depository numbers CCDC- 2072176, CCDC- 2072177, CCDC- 2072178, CCDC- 2072179, CCDC-2072180, CCDC- 2072181, CCDC- 2072820.

**Nuclear magnetic resonance (NMR)** solution spectra were recorded at 298 K. 1H, 13C, and 15N NMR were measured with a Bruker Avance 400 MHz spectrometer equipped with a 5 mm BBI probe head and operated at a magnetic field strength of 9.4 T. DMSO-d₆ was used as deuterated solvent. Typically, 1H spectra were recorded with one pulse sequence at 30° flip angle (pulse duration 2.8 µs), using 2 s recycle delay, 1.6 s acquisition time, and 8 number of scans. 1H-1H COSY, ROESY, NOESY spectra were carried out on some selected samples using standard phase sensitive pulse sequences in States mode. Also 2D 1H{13C} HSQC and 1H{15N} HMBC spectra were carried out on all samples using standard Bruker pulse sequences. The recycle period was shortened to 1 s for all these 2D experiments. Typically, 300 and 500 ms mixing times were used for ROESY and NOESY, while mixing times of 17 ms and 50 ms corresponding to 1/4J_H-C (J_H-C = 145 Hz) and 1/2J_H-N (J_H-N = 10 Hz), were employed for 1H{13C} HSQC and 1H{15N} HMBC experiments, respectively. Such 2D-NMR experiments required at least 16 h of measurement time using a typical concentration on the order of 10 mM based on the ligand. Translational diffusion measurements were performed using Bruker’s “ledbpgs2s” stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform stabilized by maximum entropy. The 13C spectra were obtained with either standard power-gated decoupling or Dept145 pulse sequences, using typically 1 s recycle delay, 1.3 s acquisition time, and number of scans ranging from 2000 to 66000. Chemical shifts are reported relative to 1% Me₄Si in CDCl₃ for both 1H and 13C, and neat MeNO₂ for 15N, according to conventional standards.
MALDI-TOF mass Spectrometry. MALDI-TOF MS analyses were performed on powders of complexes by using an UltrafleXtreme mass spectrometer (Bruker Daltonics, Bremen). Acquisitions were performed in reflector or linear positive ion mode. The laser intensity was set just above the ion generation threshold to obtain peaks with the highest possible signal-to-noise (S/N) ratio without significant peak broadening. The mass spectrometer was externally calibrated using PEG1500 and PEG4500. All data were processed using the program FlexAnalysis (Bruker Daltonics, Bremen). As the matrix was used 1,8-Dihydroxy-9(10H)-anthracenone (Dithranol), the highest grade available and used without further purification) was purchased from Sigma Aldrich Co. Samples were prepared at a concentration of 60 µM in tetrahydrofuran. The matrix solution was prepared at a concentration of 6 mM in THF with or without addition of a sodium salt. The samples were prepared by mixing the sample solution with matrix solution at a volume ratio of 1:9. After drying, the residues were analyzed by MALDI-TOF technique.

2°) Syntheses and routine characterizations

Chemicals
The sulfurated precursor $K_{1.5}(NMe_4)_{0.5}[I_2Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_{5}].20H_2O$, denoted hereafter “Mo$_{10}$”, was prepared as described in the literature [Cadot E, Salignac B, Marrot J, et al. Chem Commun; 2000, 261–262] and characterized by routine methods (FT-IR, TGA). All reagents for the synthesis of ligands and other starting chemicals were purchased form Aldrich, Alfa Aesar or Acros companies and used without further purification.

Syntheses of ligands
Thiosemicarbazone ligands were prepared according to literature procedures and were characterized by means of FT-IR and NMR spectroscopy. Thiosemicarbazones are prepared by condensation of aliphatic/aromatic and heterocyclic aldehydes and ketones with thiosemicarbazides. Refluxing the methanolic/ethanolic mixture of the appropriate two reactants in presence of few drops of some acid as catalyst yields the desired thiosemicarbazones as solid products. [A. A. Hassan, A. M. Shawky, H. S. Shehatta, J. Heterocyclic Chem. 2012, 49, 21] The ligands HL$^5$ and HL$^6$ have been obtained by following the synthetic protocols published in Li M-X et al (2010) Inorganic Chemistry Communications 13:1572–1575 and Rusnac R et al (2016) SUM 96:189–194 respectively. The compounds can be easily isolated and further purified if needed by recrystallization in ethanol.

![Scheme S1. Reaction scheme for the preparation of thiosemicarbazones](image)

Inspired by previous works that have reported biological activities of different strengths for various thiosemicarbazones, we have selected a series of substituted aldehydes and thiosemicarbazides to synthesize highly potent thiosemicarbazone ligands for metal complexation ultimately. The series of 14 thiosemicarbazones prepared herein are depicted in the table below, along with corresponding yields and simplified denotations.
| Denotation | Ligand | Yield | Denotation | Ligand | Yield |
|------------|--------|-------|------------|--------|-------|
| HL¹        | ![HL1](image1) | 33 %  | H₂L³      | ![H2L3](image2) | 68 %  |
| HL²        | ![HL2](image3) | 80 %  | H₃L⁹      | ![H3L9](image4) | 58 %  |
| HL³        | ![HL3](image5) | 40 %  | H₃L¹⁰     | ![H3L10](image6) | 37 %  |
| HL⁴        | ![HL4](image7) | 65 %  | H₃L¹¹     | ![H3L11](image8) | 70 %  |
| HL⁵        | ![HL5](image9) | 80 %  | H₂L¹²     | ![H2L12](image10) | 90 %  |
| H₂L⁶       | ![H2L6](image11) | 90 %  | HL¹³      | ![HL13](image12) | 44 %  |
| HL⁷        | ![HL7](image13) | 89 %  | HL¹⁴      | ![HL14](image14) | 77 %  |
Syntheses of complexes

*Note that during the syntheses, the Mo\textsubscript{10} solution must be prepared quickly and immediately mixed with ligands. This solution corresponds in fact to a solution of the neutral precursor [Mo\textsubscript{10}O\textsubscript{10}S\textsubscript{10}(OH)\textsubscript{10}(H\textsubscript{2}O)\textsubscript{3}] in interaction with two iodides anions for giving the anionic soluble supramolecular systems [I\textsubscript{2}Mo\textsubscript{10}O\textsubscript{10}S\textsubscript{10}(OH)\textsubscript{10}(H\textsubscript{2}O)\textsubscript{3}]\textsuperscript{2-} and [Mo\textsubscript{10}O\textsubscript{10}S\textsubscript{10}(OH)\textsubscript{10}(H\textsubscript{2}O)\textsubscript{3}]\textsuperscript{2-}. In some cases, when the reaction does not occur rapidly, the Mo\textsubscript{10} precursor can reorganize to give the neutral insoluble compound [Mo\textsubscript{10}O\textsubscript{12}S\textsubscript{12}(OH)\textsubscript{12}(H\textsubscript{2}O)\textsubscript{6}], which cannot be separated from the target neutral complexes. Despite our efforts, some of these complexes contains some traces of such impurity called Mo\textsubscript{12}.

[Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{1})\textsubscript{2}]\textsubscript{0.1}CH\textsubscript{3}OH\textsubscript{2}2.8H\textsubscript{2}O, Mm = 700.1 g/mol, denoted [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{1})\textsubscript{2}]

The solid thiosemicarbazone ligand (E)-2-(1-(pyridin-2-yl)ethylidene)hydrazinecarbothioamide C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}S\textsubscript{2} (75 mg, 0.416 mmol) is dissolved in 10 mL MeOH at 60 °C. Freshly prepared 5 mL aqueous solution of the polyoxothiomolybdate precursor Mo\textsubscript{10} (100 mg, 0.0417 mmol; 0.208 mmol [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed yellow precipitate is filtered, washed with methanol dried with diethyl ether (103 mg, η = 71 %). FT-IR (ν, cm\textsuperscript{-1}): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}S\textsubscript{2})(CH\textsubscript{3}OH)\textsubscript{0.1}(H\textsubscript{2}O)\textsubscript{2.8} Calc. (found): C 26.71 (26.45) H 3.22 (2.89) N 15.57 (15.29) S 17.83 (18.10); EDX : expected (found) Mo/S 0.50 (0.53); MALDI-TOF : m/z Calc. (found) 675.5 (675.8) for molecular ion [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}S\textsubscript{2}+ H\textsuperscript{+}].

[Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{2})\textsubscript{2}]\textsubscript{2.5}H\textsubscript{2}O, Mm = 719.6 g/mol, denoted [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{2})\textsubscript{2}]

The solid thiosemicarbazone ligand (E)-N-methyl-2-(pyridin-2-ylmethylene)hydrazinecarbothioamide C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}S\textsubscript{2} (449.3 mg, 0.187 mmol; 0.936 mmol [Mo\textsubscript{10}O\textsubscript{10}S\textsubscript{10}(OH)\textsubscript{10}(H\textsubscript{2}O)\textsubscript{3}]\textsuperscript{2-}) is dissolved in 10 mL MeOH at 60 °C. Freshly prepared 5 mL aqueous solution of the polyoxothiomolybdate precursor Mo\textsubscript{10} (100 mg, 0.0417 mmol; 0.208 mmol [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange precipitate is filtered, washed with methanol dried with diethyl ether (103 mg, η = 71 %). FT-IR (ν, cm\textsuperscript{-1}): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}S\textsubscript{2})(CH\textsubscript{3}OH)\textsubscript{0.1}(H\textsubscript{2}O)\textsubscript{2.8} Calc. (found): C 24.19 (24.49) H 2.88 (2.60) N 16.01 (15.72) S 18.32 (18.61); EDX : expected (found) Mo/S 0.50 (0.53); MALDI-TOF : m/z Calc. (found) 647.5 (647.8) for molecular ion [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}S\textsubscript{2}+ H\textsuperscript{+}].

Single crystals of formula [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{2})\textsubscript{2}]\textsubscript{2.5}H\textsubscript{2}O were obtained by diffusion of water into a solution of [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{2})\textsubscript{2}]\textsubscript{0.5}DMF in DMSO.

[Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{3})\textsubscript{2}]\textsubscript{0.5}H\textsubscript{2}O, Mm = 683.5 g/mol, denoted [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{3})\textsubscript{2}]

The solid thiosemicarbazone ligand (E)-2-(1-(pyridin-2-yl)ethylidene)hydrazinecarbothioamide C\textsubscript{8}H\textsubscript{10}N\textsubscript{4}S\textsubscript{2} (202.4 mg, 1.042 mmol) is dissolved in 40 mL MeOH at 60 °C. Freshly prepared 20 mL aqueous solution of the polyoxothiomolybdate precursor Mo\textsubscript{10} (250 mg, 0.104 mmol; 0.521 mmol [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}) is transferred to the hot solution of
ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange precipitate is filtered, washed with water and let dry completely (233 mg, η = 53 %). FT-IR (ν, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for (Mo₂O₅S₂)(C₈H₄N₄S)₂(H₂O)₀.₅ +0.08Mo₁₂ Calc. (found): C 22.70 (22.39) H 2.49 (2.37) N 13.25 (13.06) S 18.32 (18.44); EDX : expected (found) Mo/S 0.50 (0.47); MALDI-TOF : m/z Calc. (found) 839.8 (839.9) for molecular ion [Mo₂O₅S₂(C₈H₄O₄N₂S)₂+H⁺].

[Mo₂O₅S₂(L⁴)₂], Mm = 702.6 g/mol, denoted [Mo₂O₅S₂(L⁴)₂]
The solid thiosemicarbazone ligand C₃₀H₁₂₅N₄S (238.7 mg, 1.146 mmol) is dissolved in 40 mL MeOH at 60 °C. Freshly prepared 20 mL aqueous solution of the polyoxothiomolybdate precursor Mo₁₀ (250 mg, 0.104 mmol; 0.521 mmol [Mo₂O₅S₂(H₂O)₆]²⁺) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange precipitate is filtered, washed with methanol and dried with diethyl ether (375 mg, η = 92 %). FT-IR (ν, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for Mo₂O₅S₂(C₆H₁₁N₄S)₂ +0.04Mo₁₂ Calc. (found): C 27.57 (27.54) H 2.95 (2.89) N 14.29 (14.18) S 18.32 (18.44); EDX : expected (found) Mo/S 0.50 (0.53); MALDI-TOF : m/z Calc. (found) 703.6 (703.9) for molecular ion [Mo₂O₅S₂(C₆H₁₁N₄S)₂+H⁺].

[Mo₂O₅S₂(L⁵)₂]₁.₅H₂O, Mm = 865.8 g/mol, denoted [Mo₂O₅S₂(L⁵)₂]
The solid thiosemicarbazone ligand C₁₄H₂₀N₄S (316.7 mg, 1.146 mmol) is dissolved in 40 mL MeOH at 60 °C. Freshly prepared 20 mL aqueous solution of the polyoxothiomolybdate precursor Mo₁₀ (250 mg, 0.104 mmol; 0.521 mmol [Mo₂O₅S₂(H₂O)₆]²⁺) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed yellow precipitate is filtered, washed with methanol and dried with diethyl ether (245 mg, η = 92 %). FT-IR (ν, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for Mo₂O₅S₂(C₁₄H₁₉N₄S)₂(H₂O)₁.₅ Calc. (found): C 38.84 (38.49) H 4.77 (4.42) N 12.94 (12.80) S 14.81 (15.36); EDX : expected (found) Mo/S 0.50 (0.47); MALDI-TOF : m/z Calc. (found) 839.8 (839.9) for molecular ion [Mo₂O₅S₂(C₁₄H₁₉N₄S)₂+H⁺].

[Mo₂O₅S₂(HL⁶)₂]₁.₅CH₃OH·H₂O, Mm = 990.9 g/mol, denoted [Mo₂O₅S₂(HL⁶)₂]
The solid thiosemicarbazone ligand (E)-N-(4-(2-(1-(pyridin-2-yl)ethylidene)hydrazinecarbothioamido)phenyl)acetamide C₁₉H₁₇N₅SO (107 mg, 0.327 mmol) is dissolved in 40 mL MeOH at 60 °C. Freshly prepared 20 mL aqueous solution of the polyoxothiomolybdate precursor Mo₁₀ (150 mg, 0.0625 mmol; 0.3125 mmol [Mo₂O₅S₂(H₂O)₆]²⁺) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange precipitate is filtered, washed with methanol and dried with diethyl ether (187 mg, η = 46 %). FT-IR (ν, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for (Mo₂O₅S₂)(C₁₉H₁₆N₄SO)₂(CH₃OH)(H₂O)+0.15Mo₁₂ Calc. (found): C 30.56 (30.55) H 3.23 (3.26) N 10.80 (10.67) S 14.34 (14.44); EDX : expected (found) Mo/S
After cooling down, the orange solution is kept at room temperature for solvent evaporation, by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours.

\[ [\text{MoO}_2\text{S}_2(\text{HL}^8)_2] \_0.1\text{CH}_3\text{OH} \_2\text{.}1\text{H}_2\text{O}, \text{Mm} = 787.6 \text{ g/mol}, \text{denoted [MoO}_2\text{S}_2(\text{L}^7)_2] \]  
The solid thiosemicarbazone ligand (E)-2-(quinolin-2-ylmethylene)hydrazinecarbothioamide \( \text{C}_{11}\text{H}_{10}\text{N}_{3}\text{S} \) (264 mg, 1.146 mmol) is dissolved in 40 mL MeOH at 60 °C. freshly prepared 15 mL aqueous solution of the polyoxothiomolybdate precursor \( \text{MoO}_10 \) (250 mg, 0.104 mmol; 0.521 mmol \( \text{[MoO}_2\text{S}_2(\text{H}_2\text{O})_6]^3^+ \)) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed yellow precipitate is filtered, washed with ethanol and dried with diethyl ether (395 mg, \( \eta = 96 \% \)). FT-IR (\( \nu, \text{cm}^{-1} \)): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for \( \text{MoO}_2\text{S}_2(\text{C}_1\text{H}_9\text{N}_{4}\text{S})_2(\text{CH}_3\text{OH})_{0.1}\text{(H}_2\text{O})_{2.1} \) Calc. (found): C 33.70 (33.73) H 2.65 (2.36) N 12.07 (11.66) S 18.42 (18.80); EDX : expected (found) Mo/S 0.50 (0.53); MALDI-TOF : m/z Calc. (found) 747.6 (747.9) for molecular ion \( \text{[MoO}_2\text{S}_2(\text{C}_1\text{H}_9\text{N}_{4}\text{S})_2 + \text{H}]^+ \).

Single crystals of formula \( \text{[MoO}_2\text{S}_2(\text{L}^7)_2] \_0.1\text{CH}_3\text{OH} \_2\text{.}1\text{H}_2\text{O} \) were obtained by diffusion of water into a solution of \( \text{[MoO}_2\text{S}_2(\text{L}^7)_2] \_0.1\text{CH}_3\text{OH} \_2\text{.}1\text{H}_2\text{O} \) in DMSO.

\[ [\text{MoO}_2\text{S}_2(\text{HL}^8)_2] \_0.1\text{C}_3\text{H}_6\text{OH} \_0.85\text{H}_2\text{O}, \text{Mm} = 696.4 \text{ g/mol}, \text{denoted [MoO}_2\text{S}_2(\text{HL}^8)_2] \]  
The solid thiosemicarbazone ligand (E)-2-(2-hydroxybenzylidene)hydrazinecarbothioamide \( \text{C}_9\text{H}_8\text{N}_2\text{SO} \) (268.5 mg, 0.416 mmol) is dissolved in 30 mL EtOH at 60 °C. freshly prepared 15 mL aqueous solution of the polyoxothiomolybdate precursor \( \text{MoO}_10 \) (300 mg, 0.125 mmol; 0.625 mmol \( \text{[MoO}_2\text{S}_2(\text{H}_2\text{O})_6]^3^+ \)) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed yellow precipitate is filtered, washed with ethanol and dried with diethyl ether (305 mg, \( \eta = 70 \% \)). FT-IR (\( \nu, \text{cm}^{-1} \)): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for \( \text{MoO}_2\text{S}_2(\text{C}_8\text{H}_8\text{N}_3\text{SO})_2(\text{C}_2\text{H}_5\text{OH})_{0.1}\text{(H}_2\text{O})_{0.85} \) Calc. (found): C 27.94 (27.54) H 2.65 (2.36) N 12.07 (11.66) S 18.42 (18.80); EDX : expected (found) Mo/S 0.50 (0.51); MALDI-TOF : m/z Calc. (found) 677.5 (677.8) for molecular ion \( \text{[MoO}_2\text{S}_2(\text{C}_8\text{H}_8\text{N}_3\text{SO})_2 + \text{H}]^+ \).

Single crystals of formula \( \text{[MoO}_2\text{S}_2(\text{HL}^8)_2] \_2.5 \text{ DMSO} \_0.5\text{H}_2\text{O} \) were obtained by diffusion of water into a solution of \( \text{[MoO}_2\text{S}_2(\text{HL}^8)_2] \_2.5 \text{ DMSO} \_0.5\text{H}_2\text{O} \) in DMSO.

\[ [\text{MoO}_2\text{S}_2(\text{H}_2\text{L}^9)_2] \_0\text{H}_2\text{O}, \text{Mm} = 726.5 \text{ g/mol}, \text{denoted [MoO}_2\text{S}_2(\text{H}_2\text{L}^9)_2] \]  
The solid thiosemicarbazone ligand (E)-2-(2,5-dihydroxybenzylidene) hydrazinecarbothioamide \( \text{C}_9\text{H}_8\text{N}_2\text{SO} \) (200 mg, 0.951 mmol) is dissolved in 45 mL EtOH at 60 °C. freshly prepared 15 mL aqueous solution of the polyoxothiomolybdate precursor \( \text{MoO}_10 \) (200 mg, 0.083 mmol; 0.417 mmol \( \text{[MoO}_2\text{S}_2(\text{H}_2\text{O})_6]^2^+ \)) is transferred to the hot suspension of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. After cooling down, the orange solution is kept at room temperature for solvent evaporation,
then the left brown residue is collected (m = 301 mg, η = 99 %). FT-IR (v, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for (MoO₂S₂)(C₉H₆N₅SO₂)₂(H₂O) Calc. (found): C 26.45 (26.43) H 2.50 (2.30) N 11.57 (11.33) S 17.66 (18.00); EDX : expected (found) Mo/S 0.50 (0.48); MALDI-TOF : m/z Calc. (found) 731.5 (731.8) for molecular ion [MoO₂S₂(C₉H₆N₅SO₂)₂ + Na]⁺.

[MoO₂S₂(H₂L¹₀)₂]₂3H₂O, Mm = 790.6 g/mol, denoted [MoO₂S₂(H₂L¹₀)]₂

The solid thiosemicarbazone ligand (E)-2-(2,5-dihydroxybenzylidene)-N-methylhydrazinecarbothioamide C₉H₁₁N₃SO₂ (250 mg, 1.115 mmol) is dissolved in 30 mL MeOH at 60 °C. Freshly prepared 15 mL aqueous solution of the polyoxothiomolybdate precursor Mo₁₀ (242 mg, 0.1008 mmol; 0.504 mmol [MoO₂S₂(H₂O)]²⁺) is transferred to the hot suspension of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed brown precipitate is filtered, washed with methanol and dried with diethyl ether (375 mg, η = 94 %). FT-IR (v, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for MoO₂S₂(C₉H₁₀N₃SO₂)₂(H₂O)₂ Calc. (found): C 36.67 (36.43) H 3.46 (3.28) N 9.87 (9.67); MALDI-TOF : m/z Calc. (found) 759.5 (759.8) for molecular ion [MoO₂S₂(C₉H₁₀N₃SO₂)₂ + Na]⁺.

[MoO₂S₂(H₂L¹¹)₂]₃H₂O, Mm = 784.6 g/mol, denoted [MoO₂S₂(H₂L¹¹)]₂

The solid thiosemicarbazone ligand (E)-2-((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene)hydrazinecarbothioamide C₉H₁₂N₄SO₂ (375.9 mg, 1.564 mmol) is suspended in 100 mL MeOH at 60 °C. Freshly prepared 50 mL aqueous solution of the polyoxothiomolybdate precursor Mo₁₀ (300 mg, 0.125 mmol; 0.625 mmol [MoO₂S₂(H₂O)]²⁺) is transferred to the hot suspension of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for twelve hours. The yellow precipitate is filtered, washed with methanol and dried with diethyl ether to obtain quantitatively the desired complex. FT-IR (v, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for (MoO₂S₂)₂(C₉H₁₁N₃SO₂)₂(H₂O)₂ Calc. (found): C 27.56 (27.64) H 3.08 (3.01) N 14.28 (14.21) S 16.35 (16.51); EDX : expected (found) Mo/S 0.50 (0.48); MALDI-TOF : m/z Calc. (found) 767.6 (767.9) for molecular ion [MoO₂S₂(C₉H₁₁N₃SO₂)₂ + H]⁺.

[MoO₂S₂(HL¹₂)₂]₆C₂H₅OH·1.6H₂O, Mm = 851.5 g/mol, denoted [MoO₂S₂(HL¹₂)]₂

The solid thiosemicarbazone ligand (E)-2-((2-hydroxynaphthalen-1-yl)methylene)hydrazinecarbothioamide C₁₂H₁₁N₃SO (225 mg, 0.917 mmol) is dissolved in 25 mL EtOH at 60 °C. Freshly prepared 10 mL aqueous solution of the polyoxothiomolybdate precursor Mo₁₀ (200 mg, 0.083 mmol; 0.417 mmol [MoO₂S₂(H₂O)]²⁺) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange precipitate is filtered, washed with ethanol and dried with diethyl ether (343 mg, η = 97 %). FT-IR (v, cm⁻¹): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for MoO₂S₂(C₁₂H₁₀N₃SO)₂(C₂H₅OH)(H₂O)₁.₆ Calc. (found): C 36.67 (36.43) H 3.46 (3.28) N 9.87
Single crystals of formula \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{12})]_3\text{DMSO}_3\text{H}_2\text{O}\) were obtained by diffusion of water into a solution of \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{12})]_3\text{C}_2\text{H}_5\text{OH}_3\text{H}_2\text{O}\) in DMSO.

\[\text{[Mo}_2\text{O}_2\text{S}_2(\text{L}^{13})]_2\text{C}_2\text{H}_6\text{O}_2\text{H}_2\text{O}, \text{Mm} = 689.0 \text{ g/mol, denoted [Mo}_2\text{O}_2\text{S}_2(\text{L}^{13})]_2\]

The solid thiosemicarbazone ligand \((E)-2-(\text{thiophen}-2-\text{ylmethylene})\text{hydrazinecarbothioamide}\) \(\text{C}_6\text{H}_7\text{N}_3\text{S}_2\) (382 mg, 2.062 mmol) is dissolved in 50 mL EtOH at 60 °C. Freshly prepared 25 mL aqueous solution of the polyoxothiomolybdate precursor \(\text{Mo}_{10}\) (450 mg, 0.1875 mmol; 0.9375 mmol \(\text{[Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{O})]^{2+}\)) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange precipitate is filtered, washed with ethanol and kept at room temperature to dry (589 mg, \(\eta = 91\%\)). FT-IR (\(\nu, \text{cm}^{-1}\)): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for \(\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_6\text{H}_6\text{N}_3\text{S}_2)\text{(H}_2\text{O})^{1.8}\) Calc. (found): C 20.92 (20.56) H 2.28 (1.97) N 12.2 (11.90) S 27.93 (28.18); EDX : expected (found) Mo/S 0.33 (0.35); MALDI-TOF : m/z Calc. (found) 657.5 (657.8) for molecular ion \([\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_6\text{H}_6\text{N}_3\text{S}_2)]^{+}\).

Single crystals of formula \([\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^{13})]_2\text{C}_2\text{H}_6\text{O}_2\text{H}_2\text{O}\) in DMSO. Solvents were too disordered to be positioned confidently in the crystal structure.

\[\text{[Mo}_2\text{O}_2\text{S}_2(\text{L}^{14})]_2\text{C}_2\text{H}_6\text{OH}_2\text{H}_2\text{O}, \text{Mm} = 666.8 \text{ g/mol, denoted [Mo}_2\text{O}_2\text{S}_2(\text{L}^{14})]_2\]

The solid thiosemicarbazone ligand \((E)-2-(\text{furan}-2-\text{ylmethylene})\text{hydrazinecarbothioamide}\) \(\text{C}_6\text{H}_7\text{SO}\) (155.1 mg, 0.917 mmol) is dissolved in 25 mL EtOH at 60 °C. Freshly prepared 10 mL aqueous solution of the polyoxothiomolybdate precursor \(\text{Mo}_{10}\) (200 mg, 0.083 mmol; 0.417 mmol \(\text{[Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{O})]^{2+}\)) is transferred to the hot solution of ligand by a dropwise addition. The mixture is continuously stirred and heated at 60 °C for two hours. The formed orange solution is filtered and then let dry completely to obtain a solid brown residue (270 mg, \(\eta = 97\%\)). FT-IR (\(\nu, \text{cm}^{-1}\)): 3336 (w), 3179 (w), 3084 (w), 2933 (m), 2854 (w), 1560 (s), 968 (m), 783 (w), 484 (w); Elemental analysis for \(\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_6\text{H}_6\text{N}_3\text{SO})\text{(C}_2\text{H}_5\text{OH})^{0.1}(\text{H}_2\text{O})^{2.1}\) Calc. (found): C 21.97 (21.79) H 2.54 (2.07) N 12.60 (12.40) S 19.23 (18.85); EDX : expected (found) Mo/S 0.50 (0.53); MALDI-TOF : m/z Calc. (found) 625.4 (625.8) for molecular ion \([\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_6\text{H}_6\text{N}_3\text{SO})]^{+}\).
Table S2. Summary of powder analyses data and deduced formulas of the 14 thiosemicarbazonato dimolybdenum complexes. For 2 of them the elemental analyses fill well with the experimental data when a slight amount of the neutral poorly soluble Molybdenum compound [Mo12O12S12(OH)12(H2O)6], denoted Mo12 is considered.

| Denotations | Formula | Molar mass g/mol | Yield % | Elemental analysis calculated (found) | EDX expected (found) |
|-------------|---------|------------------|---------|---------------------------------------|---------------------|
| [Mo2O2S2(L1)2] | [Mo2O2S2(C10H26N6S3)2](CH3OH)8(H2O)2.8 | 700.1 | 70 | C 24.19 (24.49) H 2.88 (2.60) N 16.01 (15.72) S 18.32 (18.61) | Mo/S 0.50 (0.53) |
| [Mo2O2S2(L2)2] | [Mo2O2S2(C6H4N6S2)2](H2O)2.5 | 719.6 | 100 | C 26.71 (26.45) H 3.22 (2.89) N 15.57 (15.29) S 17.83 (18.10) | Mo/S 0.50 (0.48) |
| [Mo2O2S2(L3)2] | [Mo2O2S2(C6H4N6S2)2](CH3OH)(H2O) +0.08Mo12 | 683.5 | 53 | C 22.70 (22.39) H 2.49 (2.37) N 13.23 (13.06) S 18.78 (18.98) | Mo/S 0.5 (0.59) |
| [Mo2O2S2(L4)2] | [Mo2O2S2(C6H11N6S2)2] +0.04Mo12 | 702.6 | 92 | C 27.57 (27.54) H 2.95 (2.89) N 14.29 (14.18) S 18.32 (18.44) | Mo/S 0.50 (0.53) |
| [Mo2O2S2(L5)2] | [Mo2O2S2(C10H18N6S2)2](H2O)1.5 | 865.8 | 54 | C 38.84 (38.49) H 4.77 (4.42) N 12.94 (12.80) S 14.81 (15.36) | Mo/S 0.50 (0.47) |
| [Mo2O2S2(2)2] | [Mo2O2S2(C10H16N6S2)2](CH3OH)(H2O) +0.15Mo12 | 990.9 | 46 | C 30.56 (30.55) H 3.23 (3.26) N 10.80 (10.67) S 14.34 (14.44) | Mo/S 0.50 (0.70) |
| [Mo2O2S2(L7)2] | [Mo2O2S2(C6H11N6S2)2](CH3OH)8(H2O)2.1 | 787.6 | 96 | C 33.70 (33.73) H 2.89 (2.68) N 14.23 (13.97) S 16.29 (16.25) | Mo/S 0.50 (0.53) |
| [Mo2O2S2(3)2] | [Mo2O2S2(C6H11N6S2)2](CH3OH)8(H2O)0.85 | 696.4 | 70 | C 27.94 (27.54) H 2.65 (2.36) N 12.07 (11.66) S 18.42 (18.80) | Mo/S 0.50 (0.51) |
| [Mo2O2S2(L9)2] | [Mo2O2S2(C10H18N6S2)2](H2O) | 726.5 | 99 | C 26.45 (26.43) H 2.50 (2.30) N 11.57 (11.33) S 17.66 (18.00) | Mo/S 0.50 (0.51) |
| [Mo2O2S2(H-L10)2] | [Mo2O2S2(C6H10N6S2)2](H2O) | 790.6 | 94 | C 27.35 (27.43) H 3.31 (3.17) N 10.63 (10.37) S 16.22 (16.29) | Mo/S 0.50 (0.67) |
| [Mo2O2S2(H-L11)2] | [Mo2O2S2(C6H11N6S2)2](H2O) | 784.6 | 100 | C 27.56 (27.64) H 3.08 (3.01) N 14.28 (14.21) S 16.35 (16.51) | Mo/S 0.50 (0.48) |
| [Mo2O2S2(12)2] | [Mo2O2S2(C6H10N6S2)2](C2H5OH)8(H2O)1.8 | 851.5 | 97 | C 36.67 (36.43) H 3.46 (3.28) N 9.87 (9.71) S 15.06 (15.30) | Mo/S 0.50 (0.51) |
| [Mo2O2S2(L13)2] | [Mo2O2S2(C6H11N6S2)2](H2O)1.8 | 689.0 | 91 | C 20.92 (20.56) H 2.28 (1.97) N 12.2 (11.90) S 27.93 (28.18) | Mo/S 0.33 (0.35) |
| [Mo2O2S2(L14)2] | [Mo2O2S2(C6H11N6S2)2](C2H5OH)8(H2O)2.1 | 666.9 | 97 | C 21.97 (21.79) H 2.54 (2.07) N 12.60 (12.40) S 19.23 (18.85) | Mo/S 0.50 (0.53) |
Part 2: Characterizations by FT-IR spectroscopy

1°) Example of FT-IR spectra of comparison of IR spectrum of ligand and complex.

In agreement with literature data, the thiosemicarbazone ligands exhibit the same feature: two strong bands in the region 3300-3500 cm\(^{-1}\), which are attributed to asymmetric and symmetric stretches of the terminal NH\(_2\) group; Azomethine group’s \(\nu(C=N)\) absorption frequencies around 1600 cm\(^{-1}\) appearing as very strong bands and medium intensity bands assigned to the thione group \(\nu(C=S)\) stretching in a wide range 800-1100 cm\(^{-1}\) which can be downshifted to wavenumbers as far as 600 cm\(^{-1}\) because of the presence of both thione –NH–C(=S)– and thiol –N=C(–SH)– resonance tautomeric forms (M. Leovac V et al (1995) Journal of Coordination Chemistry 34:357–364; Singh RN et al. (2013) Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 112:182–190). Upon formation of complexes, the deprotonation and the coordination of the ligands are evidenced by the shift of the vibration bands of the ligand, while the presence of the \([\text{Mo}_2\text{O}_2\text{S}_2]^{2+}\) cluster is evidenced by the strong vibration band around 950-960 cm\(^{-1}\).

Figure S1 FT-IR spectra of \(\text{HL}^1\) (red) and \([\text{Mo}_2\text{O}_2\text{S}_2(L^1)]\) (black)
Figure S2 FT-IR spectra of complexes 1–14 corresponding to compounds series \([\text{Mo}_2\text{O}_2\text{S}_2(L^1)_2]\) – \([\text{Mo}_2\text{O}_2\text{S}_2(L^{14})_2]\). The FT-IR spectra of the 14 resulting powders exhibit a strong band around 950 cm\(^{-1}\) typical of terminal Mo\(^{\text{V}}\)O groups within the \{\text{Mo}_2\text{O}_2\text{S}_2\} cluster. Some frequencies due to vibrations within the ligand undergo significant changes associated with complexation, while hydrazinic \(\nu(\text{N-H})\) and thione \(\nu(\text{C=S})\) stretches disappear in the complexes, confirming the loss of the \(\text{C=S}\) double bond character and then S-H deprotonation in agreement with the formation of \(\text{Mo}_2\text{O}_2\text{S}_2\)-based thiosemicarbazonato complexes.
Part 3: MALDI-TOF Experiments

The MALDI-TOF spectra are recorded in positive mode on powders isolated directly by synthesis.

Figure S3 MALDI-TOF spectrum for compound [Mo₂₂S₂(L²)₂]

Figure S4 MALDI-TOF spectrum for compound [Mo₂₂S₂(L³)₂]
Figure S5 MALDI-TOF spectrum for compound \([\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^4)_2]\)

Figure S6 MALDI-TOF spectrum for compound \([\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^5)_2]\)
Figure S7 MALDI-TOF spectrum for compound [MoO$_2$S$_2$(HL)$_2$]

Figure S8 MALDI-TOF spectrum for compound [MoO$_2$S$_2$(L)$_2$]
Figure S9 MALDI-TOF spectrum for compound $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^8)_2]$.

Figure S10 MALDI-TOF spectrum for compound $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^9)_2]$.
Figure S11 MALDI-TOF spectrum for compound \([\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{10})_2]\)

Figure S12 MALDI-TOF spectrum for compound \([\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{11})_2]\)
Figure S13 MALDI-TOF spectrum for compound [Mo₂O₂S₂(HL²)₂]

Figure S14 MALDI-TOF spectrum for compound [Mo₂O₂S₂(L¹³)₂]
Figure S15 MALDI-TOF spectrum for compound [Mo₂O₃S₂(L¹⁴)₂]
Table S3 MALDI-TOF results for [Mo$_2$O$_2$S$_2$(H$_n$L$_x$)$_2$] complexes (n = 0-2; x = 1-14)

| Compounds “M”                  | Experimental m/z | Assignment (calcd m/z) |
|--------------------------------|------------------|------------------------|
| [Mo$_2$O$_2$S$_2$(L$^1$)$_2$]  | 647.8            | [M+H]$^+$ (647.5)     |
| [Mo$_2$O$_2$S$_2$(L$^2$)$_2$]  | 675.8            | [M+H]$^+$ (675.5)     |
|                                | 697.8            | [M+Na]$^+$ (697.5)    |
| [Mo$_2$O$_2$S$_2$(L$^3$)$_2$]  | 675.8            | [M+H]$^+$ (675.5)     |
| [Mo$_2$O$_2$S$_2$(L$^4$)$_2$]  | 703.8            | [M+H]$^+$ (703.6)     |
| [Mo$_2$O$_2$S$_2$(L$^5$)$_2$]  | 839.9            | [M+H]$^+$ (839.8)     |
| [Mo$_2$O$_2$S$_2$(L$^6$)$_2$]  | 941.9            | [M+H]$^+$ (941.8)     |
| [Mo$_2$O$_2$S$_2$(L$^7$)$_2$]  | 747.8            | [M+H]$^+$ (747.6)     |
| [Mo$_2$O$_2$S$_2$(HL$^8$)$_2$] | 677.8            | [M+H]$^+$ (677.5)     |
|                                | 699.8            | [M+Na]$^+$ (699.5)    |
| [Mo$_2$O$_2$S$_2$(H$_2$L$^9$)$_2$] | 731.8        | [M+Na]$^+$ (731.5)    |
| [Mo$_2$O$_2$S$_2$(H$_2$L$^{10}$)$_2$] | 759.8      | [M+Na]$^+$ (759.5)    |
| [Mo$_2$O$_2$S$_2$(H$_2$L$^{11}$)$_2$] | 767.8      | [M+H]$^+$ (767.6)     |
| [Mo$_2$O$_2$S$_2$(HL$^{12}$)$_2$] | 777.8        | [M+H]$^+$ (777.8)     |
|                                | 797.8            | [M+Na]$^+$ (797.9)    |
| [Mo$_2$O$_2$S$_2$(L$^{13}$)$_2$] | 657.7        | [M+H]$^+$ (657.5)     |
| [Mo$_2$O$_2$S$_2$(L$^{14}$)$_2$] | 625.8        | [M+H]$^+$ (625.4)     |
Part 4: Crystallographic data

1- Crystallographic data

Table S4 XRD experimental details with figures showing the labels of the complexes and solvates around and figures showing the crystalline packing.
Crystal data
Formula: C_{22}H_{32}Mo_{2}N_{10}O_{4}S_{4}
Mr = 820.69
Orthorhombic, Pnca21
\(a = 14.8536 (4) \, \text{Å}\)
\(b = 22.0647 (5) \, \text{Å}\)
\(c = 10.1415 (3) \, \text{Å}\)
\(V = 3323.78 (15) \, \text{Å}^3\)
\(Z = 4\)
\(F(000) = 1656\)
\(D_x = 1.640 \, \text{Mg m}^{-3}\)
Mo K\(\alpha\) radiation, \(\lambda = 0.71073 \, \text{Å}\)
Cell parameters from 9980 reflections
\(\theta = 2.2–29.9^\circ\)
\(\mu = 1.05 \, \text{mm}^{-1}\)
\(T = 220 \, \text{K}\)
Parallelepiped, yellow
0.30 × 0.20 × 0.12 mm

Data collection
Bruker D8 VENTURE diffractometer
Radiation source: microsource
\(\varphi\) and \(\omega\) scans
Absorption correction: multi-scan SADABS (Sheldrick, V2014/5)
128231 measured reflections
9735 independent reflections
8706 reflections with \(I > 2\sigma(I)\)
\(R_{int} = 0.039\)
\(\theta_{\text{max}} = 30.1^\circ, \theta_{\text{min}} = 1.7^\circ\)
\(h = -20\rightarrow20\)
\(k = -31\rightarrow31\)
\(l = -14\rightarrow14\)

Refinement
Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.022\)
\(wR(F^2) = 0.052\)
\(S = 1.08\)
9735 reflections
385 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\(w = 1/\left[\sigma^2(Fo^2) + (0.0241P)^2 + 0.6505P\right]\)
where \(P = (Fo^2 + 2Fc^2)/3\)
(Δ/σ)_{max} = 0.002  
Δρ_{max} = 0.35 \text{ e Å}^{-3}  
Δρ_{min} = -0.23 \text{ e Å}^{-3}  
Absolute structure: Flack x determined using 3858 quotients \([(I^+)-(I^-)]/[(I^+)+(I^-)]\) (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).  
Absolute structure parameter: -0.017 (8)  

BVS Calculation for Mo atoms  
Mo(1) : 5.08  
Mo(2) : 5.12  

Figure S18. Labels of atoms of the complex and solvates around in  
\[\text{[(Mo}_2\text{O}_2\text{S}_2(\text{L}^6)(\text{DMSO}))_2]_2\text{DMSO.2H}_2\text{O (AF119)}}\]
Figure S19. View of the crystalline packing in 

\[ ([\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^4)(\text{DMSO})]_2).2\text{DMSO}.2\text{H}_2\text{O} \]

**Crystal data**

Formula $\text{C}_{42}\text{H}_{60}\text{Mo}_4\text{N}_{10}\text{O}_{14}\text{S}_{11}$

$M_r = 1665.42$

Triclinic, $P1$

$a = 10.947$ (2) Å

$b = 11.639$ (2) Å

$c = 13.130$ (3) Å

$\alpha = 79.111$ (9)$^\circ$

$\beta = 86.279$ (10)$^\circ$

$\gamma = 85.63$ (1)$^\circ$

$V = 1636.0$ (6) Å$^3$

$Z = 1$

$F(000) = 838$

$D_\chi = 1.691$ Mg m$^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9009 reflections

$\theta = 2.4$–30.1$^\circ$

$\mu = 1.13$ mm$^{-1}$

$T = 200$ K
Parallelepiped, red
0.05 × 0.04 × 0.02 mm

**Data collection**
Bruker D8 VENTURE diffractometer
Radiation source: microsource
φ and ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, V2016/2)
91002 measured reflections
9583 independent reflections
7760 reflections with $I > 2\sigma(I)$
$R_{int} = 0.101$
$\theta_{max} = 30.1^\circ$, $\theta_{min} = 2.2^\circ$
$h = -15→15$
$k = -16→16$
$l = -18→18$

**Refinement**
Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.0425$
$wR(F^2) = 0.1072$
$S = 1.106$
9577 reflections
414 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/\left[\sigma^2(F_o^2) + 4.5278P\right]$
where $P = (F_o^2 + 2F_c^2)/3$

BVS Calculation for Mo
Mo(1) : 5.09
Mo(2) : 5.03

$[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^7)_2].2\text{DMF. H}_2\text{O}$
(AF110)
Figure S20. Labels of atoms of the complex and solvates around in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^7)_2].2\text{DMF. H}_2\text{O}$

Figure S21. View of the crystalline packing in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^7)_2].2\text{DMF. H}_2\text{O}$

Crystal data
Formula $\text{C}_{28}\text{H}_{34}\text{Mo}_{2}\text{N}_{10}\text{O}_{5}\text{S}_{4}$  
$Mr = 910.77$

Monoclinic, $P2_1/c$

$a = 13.9986 (4) \text{ Å}$

$b = 13.9460 (3) \text{ Å}$

$c = 19.4729 (5) \text{ Å}$

$\beta = 96.675 (1)^\circ$

$V = 3775.82 (17) \text{ Å}^3$

$Z = 4$

$F(000) = 1840$

$D_x = 1.602 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$

Cell parameters from 9350 reflections

$\theta = 2.4–30.1^\circ$

$\mu = 0.94 \text{ mm}^{-1}$

$T = 219 \text{ K}$

Parallelepiped, yellow

$0.30 \times 0.30 \times 0.14 \text{ mm}$

**Data collection**

Bruker D8 VENTURE diffractometer

Radiation source: microsource

$\phi$ and $\omega$ scans

Absorption correction: multi-scan

$SADABS$ (Sheldrick, V2014/5)

143108 measured reflections

11114 independent reflections

9751 reflections with $I > 2\sigma(I)$

$R_{int} = 0.027$

$\theta_{max} = 30.1^\circ$, $\theta_{min} = 1.8^\circ$

$h = -19 \rightarrow 19$

$k = -19 \rightarrow 19$

$l = -27 \rightarrow 27$

**Refinement**

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.061$

$S = 1.06$

11114 reflections

454 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(Fo^2) + (0.027P)^2 + 2.2518P]$

where $P = (Fo^2 + 2Fc^2)/3$
$\Delta / \sigma_{\text{max}} = 0.002$
$\Delta \rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.47 \text{ e } \text{Å}^{-3}$

BVS Calculation for Mo
Mo(1) : 5.10
Mo(2) : 5.08

$[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}_8)_2] \cdot 2.5 \text{DMSO} \cdot 0.5\text{H}_2\text{O}$
Figure S22. Labels of atoms of the complex and solvates around in $[\text{Mo}_2\text{O}_2\text{S}_2\text{(HL}^8\text{)}_2] \cdot 2.5 \text{DMSO} \cdot 0.5\text{H}_2\text{O}$

Figure S23. View of the crystalline packing in $[\text{Mo}_2\text{O}_2\text{S}_2\text{(HL}^8\text{)}_2] \cdot 2.5 \text{DMSO} \cdot 0.5\text{H}_2\text{O}$
Figure S24. View of the crystalline packing in \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL})_2]\). 2.5 DMSO. 0.5H_2O

**Crystal data**

Formula C_{21}H_{32}Mo_{2}N_{6}O_{7}S_{6.50}

\(M_r = 880.79\)

Triclinic, \(P_1\)

\(a = 10.2877\) (3) Å

\(b = 11.6707\) (3) Å

\(c = 16.6422\) (5) Å

\(\alpha = 89.708\) (1)°

\(\beta = 80.546\) (1)°

\(\gamma = 71.310\) (1)°

\(V = 1864.65\) (9) Å³

\(Z = 2\)

\(F(000) = 888\)

\(D_x = 1.569\) Mg m⁻³

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 9731 reflections

\(\theta = 2.3–30.0°\)

\(\mu = 1.08\) mm⁻¹

\(T = 296\) K

Parallelepiped, yellow

0.30 × 0.24 × 0.08 mm

**Data collection**

Bruker APEX-II CCD diffractometer

Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan SADABS (Sheldrick, 2014/5)
62089 measured reflections
10949 independent reflections
9036 reflections with I > 2σ(I)
\( R_{\text{int}} = 0.029 \)
\( \theta_{\text{max}} = 30.1°, \theta_{\text{min}} = 1.2° \)
\( h = -14 \rightarrow 14 \)
\( k = -16 \rightarrow 16 \)
\( l = -23 \rightarrow 23 \)

**Refinement**
Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.043 \)
\( wR(F^2) = 0.135 \)
\( S = 1.07 \)
10949 reflections
414 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = \frac{1}{[\sigma^2(Fo^2) + (0.0682P)^2 + 2.1738P]} \)
where \( P = (Fo^2 + 2Fc^2)/3 \)
\( (\Delta/\sigma)_{\text{max}} = 0.002 \)
\( \Delta \rho_{\text{max}} = 1.98 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.84 \text{ e Å}^{-3} \)

BVS Calculation for Mo
Mo(1) : 5.09
Mo(2) : 5.03

\[ \text{[Mo}_2\text{O}_2\text{S}_2(\text{HL})_2]\_3 \text{DMSO.H}_2\text{O} \]
(AF108)
Figure S25. Labels of atoms of the complex and solvates around in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}_{12})_2] \cdot 3 \text{DMSO.H}_2\text{O}$

Figure S26. View of the crystalline packing in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}_{12})_2] \cdot 3 \text{DMSO.H}_2\text{O}$
Figure S27. View of the crystalline packing in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}_{12})_2] \cdot 3\text{DMSO.H}_2\text{O}$

Crystal data

Formula $\text{C}_{30}\text{H}_{40}\text{Mo}_2\text{N}_6\text{O}_8\text{S}_7$

$M_r = 1028.98$

Monoclinic, $P2_1/n$

$a = 12.3754 (6)$ Å

$b = 18.1139 (9)$ Å

$c = 18.7308 (7)$ Å

$\beta = 96.067 (2)^\circ$

$V = 4175.3 (3)$ Å³

$Z = 4$

$F(000) = 2088$

$D_\lambda = 1.637$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9908 reflections

$\theta = 2.3–23.9$°

$\mu = 1.00$ mm⁻¹

$T = 200$ K

Platelet, yellow

0.24 × 0.18 × 0.08 mm

Data collection

Bruker APEX-II CCD diffractometer

Radiation source: fine-focus sealed tube

$\varphi$ and $\omega$ scans

Absorption correction: multi-scan SADABS (Sheldrick, V2014/5)
93738 measured reflections  
11820 independent reflections  
5766 reflections with $I > 2\sigma(I)$  
$R_{int} = 0.078$  
$\theta_{\text{max}} = 33.3^\circ$, $\theta_{\text{min}} = 1.6^\circ$  
$h = -19\rightarrow16$  
k = $-24\rightarrow24$  
l = $-28\rightarrow24$  

**Refinement**  
Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.059$  
w$R(F^2) = 0.180$  
$S = 1.00$  
11820 reflections  
524 parameters  
0 restraints  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
w = $1/[\sigma^2(Fo2) + (0.0649P)^2 + 12.7651P]$  
where $P = (Fo2 + 2Fc2)/3$  
$(\Delta/\sigma)_{\text{max}} = 0.001$  
$\Delta\rho_{\text{max}} = 1.78$ e Å$^{-3}$  
$\Delta\rho_{\text{min}} = -1.01$ e Å$^{-3}$  

BVS Calculation for Mo  
Mo(1) : 5.04  
Mo(2) : 5.11
Figure S28. Labels of atoms of the complex and solvates around in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^{13})_2]$.

Figure S29. View of the crystalline packing in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^{13})_2]$.

Crystal data

Formula $\text{C}_{12}\text{H}_{12}\text{Mo}_2\text{N}_6\text{O}_2\text{S}_6$

$M_r = 656.52$

Monoclinic, $C2$

$a = 16.5188 (7)$ Å
\( b = 8.2419 (3) \, \text{Å} \)
\( c = 11.6935 (5) \, \text{Å} \)
\( \beta = 125.387 (3) ^\circ \)
\( V = 1297.91 (10) \, \text{Å}^3 \)
\( Z = 2 \)
\( F(000) = 644 \)
\( D_x = 1.680 \, \text{Mg} \, \text{m}^{-3} \)
Mo K\( \alpha \) radiation, \( \lambda = 0.71073 \, \text{Å} \)

Cell parameters from 9893 reflections

\( \theta = 2.5-30.0 ^\circ \)
\( \mu = 1.47 \, \text{mm}^{-1} \)
\( T = 230 \, \text{K} \)
Platelet, yellow
0.15 × 0.10 × 0.03 mm

**Data collection**

Bruker D8 VENTURE diffractometer
Radiation source: microsource
\( \phi \) and \( \omega \) scans
Absorption correction: multi-scan SADABS (Sheldrick, V2016/2)
19807 measured reflections
3780 independent reflections
3416 reflections with \( I > 2\sigma(I) \)

\( R_{int} = 0.149 \)
\( \theta_{\text{max}} = 30.0 ^\circ, \theta_{\text{min}} = 2.5 ^\circ \)
\( h = -23\rightarrow23 \)
\( k = -11\rightarrow11 \)
\( l = -16\rightarrow16 \)

**Refinement**

Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.113 \)
\( wR(F^2) = 0.279 \)
\( S = 1.00 \)
3780 reflections
127 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = 1/[\sigma^2(F_o^2) + (0.1725P)^2 + 54.9894P] \)
where \( P = (F_o^2 + 2F_c^2)/3 \)
Absolute structure: Flack $x$ determined using 1310 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).

Absolute structure parameter: 0.10 (5)

BVS Calculation for Mo
Mo(1) : 5.09

K$_2$[Mo$_2$O$_2$S$_2$(HNTA)$_2$]. 4H$_2$O (AF7)

Figure S30. View of the molecular structure of complex cis-[Mo$_2$O$_2$S$_2$(HNTA)$_2$]$^2^-$ in K$_2$[Mo$_2$O$_2$S$_2$(HNTA)$_2$]. 4H$_2$O

Crystal data
Formula C$_{12}$H$_{12}$K$_2$Mo$_2$N$_2$O$_{18}$S$_2$
$M_r$ = 806.44
Orthorhombic, Pnma
$a$ = 20.8145 (8) Å
$b$ = 18.7730 (8) Å
$c$ = 15.6485 (7) Å
$V$ = 6114.7 (4) Å$^3$
$Z$ = 8
$F(000) = 3168$
$D_x = 1.752$ g cm$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9900 reflections
$\theta = 2.2$–26.4°
$\mu = 1.32$ mm$^{-1}$
$T = 293$ K
**Data collection**

Bruker APEX-II CCD diffractometer  
φ and ω scans  
Absorption correction: multi-scan SADABS2014/5 (Bruker, 2014) was used for absorption correction. wR2(int) was 0.0613 before and 0.0505 after correction. The Ratio of minimum to maximum transmission is 0.9247. The λ/2 correction factor is 0.00150.

\[ T_{\text{min}} = 0.689, \quad T_{\text{max}} = 0.745 \]

45788 measured reflections  
6476 independent reflections  
5129 reflections with \( I > 2\sigma(I) \)

\[ R_{\text{int}} = 0.041 \]

\[ \theta_{\text{max}} = 26.4^\circ, \quad \theta_{\text{min}} = 1.6^\circ \]

\[ h = -26 \rightarrow 16 \]

\[ k = -23 \rightarrow 19 \]

\[ l = -17 \rightarrow 19 \]

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full  
\[ R[F^2 > 2\sigma(F^2)] = 0.0395 \]

\[ wR(F^2) = 0.1195 \]

\[ S = 1.10 \]

6476 reflections  
347 parameters  
0 restraints  

Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  

\[ w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 13.4488P] \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\[ (\Delta/\sigma)_{\text{max}} = 0.003 \]

\[ \Delta\rho_{\text{max}} = 1.48 \text{ e Å}^{-3} \]

\[ \Delta\rho_{\text{min}} = -1.20 \text{ e Å}^{-3} \]

BVS Calculation for Mo

\[ \text{Mo(1)} : 5.11 \]

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**2- Additional figures**
Figure S31 Molecular Structure of trans isomer of [Mo$_2$O$_2$S$_2$(HNTA)$_2$]$^{2-}$ compound (ref. Duval S, Floquet S, Simonnet-Jégat C, et al (2010) Capture of the [Mo$_3$S$_4$]$^{4+}$ Cluster within a {Mo$_{18}$} Macrocycle Yielding a Supramolecular Assembly Stabilized by a Dynamic H-Bond Network. J Am Chem Soc 132:2069–2077.)
Part 5: NMR studies in solution

Thiosemicarbazone ligands HL\(^1\)-HL\(^{14}\) and their complexes were extensively studied by \(^1\)H, \(^{13}\)C, \(^{15}\)N-NMR with various techniques to do precise assignment of peaks and to study the coordination modes in relation to crystal structures when obtained. Ligand HL\(^8\) and its complex are discussed in the main text of this study. The others are given in the figures below. All the spectra have been recorded in DMSO on powder isolated from synthesis.

1\(^{\circ}\) NMR Studies of Ligand HL\(^1\) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^1\))\(_2\)] in DMSO.

Figure S32 \(^1\)H-NMR spectra for HL\(^1\) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^1\))\(_2\)]

Figure S33 \(^1\)H-NMR DOSY spectra for ligand HL\(^1\) (top) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^1\))\(_2\)] (bottom)
Figure S34 $^{13}$C{$^1$H} NMR HSQC spectrum for HL$^1$

Figure S35 $^{13}$C{$^1$H} NMR HSQC spectrum for complex [Mo$_2$O$_2$S$_2$(L$^1$)$_2$]. Arrows indicate the cross-peaks corresponding to coupled carbon number 5 (two peaks) and proton number 5 (two peaks).
Figure S36 $^{15}$N-$^1$H NMR HMBC spectrum for HL$^1$

Figure S37 $^{15}$N-$^1$H NMR HMBC spectrum for complex [Mo$_2$O$_2$S$_2$(L$^1$)$_2$]
2°) NMR Studies of Ligand HL₂ and complex [Mo₂O₂S₂(L²)_₂] in DMSO.

Figure S38 ¹H-NMR spectra of HL₂ and complex [Mo₂O₂S₂(L²)_₂]

Figure S39 ¹H-NMR DOSY spectra for HL₂ (top) and complex [Mo₂O₂S₂(L²)_₂] (bottom)
Figure S40 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for HL\textsuperscript{2}

Figure S41 $^{15}\text{N}\{^1\text{H}\}$ NMR HMBC spectrum for complex [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{2})\textsubscript{2}]
3°) NMR Studies of Ligand HL\(^3\) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^3\))\(_2\)] in DMSO.

Figure S42 \(^1\)H-NMR spectra of HL\(^3\) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^3\))\(_2\)]. For each proton, 4 signals (a, b, c, d) appear, suggesting that the complex is existing in 4 isomeric forms. Presence of free ligand impurities is also noticed.

Figure S43 \(^1\)H-NMR DOSY spectra for HL\(^3\) (top) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^3\))\(_2\)] (bottom)
Figure S44 COSY $^1$H NMR spectrum for complex [Mo$_2$O$_2$S$_2$(L$_3$)$_2$]

Figure S45 EXSY/NOESY $^1$H NMR spectrum for complex [Mo$_2$O$_2$S$_2$(L$_3$)$_2$]
Figure S46 HMBC $^1$H($^{15}$N) NMR spectrum for ligand HL

Figure S47 HMBC $^1$H($^{15}$N) NMR spectrum for complex [Mo$_2$O$_2$S$_2$(L$^3$)$_2$]
4°) NMR Studies of Ligand H₄L and complex [Mo₂O₂S₂(L⁴)₂] in DMSO.

Figure S48 ¹H-NMR spectra of H₄L and complex [Mo₂O₂S₂(L⁴)₂]. Letters a, b, c, d, e depict the 5 individual peaks obtained for H2 proton due to its 5 different environments, thus suggesting 5 types of complexes (isomers).

Figure S49 ¹H-NMR DOSY spectra of H₄L (top) and complex [Mo₂O₂S₂(L⁴)₂] (bottom)
Figure S50 COSY $^1$H NMR spectrum for complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^4)_2]$.

Since there are 5 isomers, each form of the proton H2 ($a$(25%), $b$(28%), c, d, e) will show spin-spin coupling with neighboring H1 of the methyl group.

Figure S51 COSY $^1$H NMR spectrum for complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^4)_2]$, zoom on H2 – H1 correlation. Since there are 5 isomers, each form of the proton H2 ($a$(25%), $b$(28%), c, d, e) will show spin-spin coupling with neighboring H1 of the methyl group.
Figure S52 $^{15}\text{N}\{^1\text{H}\}$ HMBC spectrum for HL$^4$

Figure S53 $^{15}\text{N}\{^1\text{H}\}$ HMBC spectrum for complex [Mo$_2$O$_2$S$_2$(L$^4$)$_2$]
NMR Studies of Ligand HL\textsuperscript{5} and complex [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{5})\textsubscript{2}] in DMSO.

Figure S54 \textsuperscript{1}H-NMR spectra of HL\textsuperscript{5} and complex [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{5})\textsubscript{2}]

Figure S55 \textsuperscript{1}H-NMR DOSY spectra of HL\textsuperscript{5} (top) and complex [Mo\textsubscript{2}O\textsubscript{2}S\textsubscript{2}(L\textsuperscript{5})\textsubscript{2}] (bottom)
Figure S56 ROESY $^1$H spectrum for HL$^5$
Figure S57 COSY $^1$H NMR spectrum for complex [Mo$_2$O$_2$S$_2$(L$_5$)$_2$]

Figure S58 COSY spectrum for complex [Mo$_2$O$_2$S$_2$(L$_5$)$_2$]. Zoom on the aromatic protons.
Figure S59 $^{15}$N-$^1$H HMBC spectrum for HL$^5$

Figure S60 $^{15}$N-$^1$H HMBC spectra for complex $\left[\text{Mo}_2\text{O}_2\text{S}_2(\text{L}^5)\right]_2$
6°) NMR Studies of Ligand $H_2L^6$ and complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}_6)_2]$ in DMSO.

**Figure S61** $^1\text{H}$-NMR spectrum of $H_2L^6$

- **Free ligand**
  - **Complex**

**Figure S62** $^1\text{H}$-NMR spectra of $H_2L^6$ and complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}_6)_2]$
Figure S63 $^1$H-NMR spectra of H$_2$L$^6$ and complex [Mo$_2$O$_2$S$_2$(HL$^6$)$_2$]

Figure S64 $^1$H-NMR DOSY spectra of H$_2$L$^6$ and complex [Mo$_2$O$_2$S$_2$(HL$^6$)$_2$]
Figure S65 ROESY $^1$H spectrum for H$_2$L$^6$.

Figure S66 NOESY $^1$H spectrum for complex [Mo$_2$O$_2$S$_2$(HL)$_2$].
Figure S67 $^{15}\text{N} \{^1\text{H}\}$ HMBC spectrum for ligand $\text{H}_2\text{L}^6$. 

Figure S68 $^{15}\text{N} \{^1\text{H}\}$ HMBC spectrum for complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^6)_2]$. Correlations shown for main isomers a and b.
7°) NMR Studies of Ligand HL\(^7\) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^7\))\(_2\)] in DMSO.

Figure S69 \(^1\)H-NMR spectra of HL\(^7\) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^7\))\(_2\)]. Again 2 isomers (a – 67\% and b – 33\%) and traces of free ligand (*).

Figure S70 \(^1\)H-NMR DOSY spectra of HL\(^7\) (top) and complex [Mo\(_2\)O\(_2\)S\(_2\)(L\(^7\))\(_2\)] (bottom)
Figure S71 $^{13}\text{C}^{1}\text{H}$ HSQC, spectrum for HL

Figure S72 $^{13}\text{C}^{1}\text{H}$ HSQC spectrum for complex [Mo$_2$O$_2$S$_2$(L)$_2$]
Figure S73 $^{15}$N {$^1$H} HMBC spectrum for HL$^7$

Figure S74 $^{15}$N {$^1$H} HMBC spectrum for HL$^7$ and complex [Mo$_2$O$_2$S$_2$(L$^7$)$_2$]
8°) Additional NMR spectra for complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^8)_2]\) in DMSO

Figure S75 $^1$H-NMR and NOESY spectra for $\text{H}_2\text{L}^8$ thiosemicarbazone in DMSO-$d_6$

Figure S76 400 MHz $^1$H NOESY NMR (DMSO-$d_6$) spectrum of complex $\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^8)_2$
9°) NMR Studies of Ligand H$_3$L$^9$ and complex [Mo$_2$O$_2$S$_2$(H$_2$L$^9$)$_2$] in DMSO.

Figure S77 $^1$H-NMR spectra of H$_3$L$^9$ and complex [Mo$_2$O$_2$S$_2$(H$_2$L$^9$)$_2$]

Figure S78 $^1$H-NMR DOSY spectra of H$_3$L$^9$ (top) and complex [Mo$_2$O$_2$S$_2$(H$_2$L$^9$)$_2$] (bottom)
Figure S79 ROESY $^1$H spectrum for complex $[\text{Mo}_2\text{O}_5\text{S}_2(\text{H}_2\text{L}^\nu)_2]$. 

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Figure S80 $^{15}$N-$^1$H HMBC spectrum for H$_3$L$^9$

Figure S81 $^{15}$N-$^1$H HMBC spectrum for complex [Mo$_2$O$_2$S$_2$(H$_2$L$^9$)$_2$]. Correlations in both isomers a and b.
10°) NMR Studies of Ligand $\text{H}_3\text{L}^{10}$ and complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{10})_2]$ in DMSO.

Figure S82 $^1\text{H}$-NMR spectra of $\text{H}_3\text{L}^{10}$ and complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{10})_2]$

Figure S83 $^1\text{H}$-NMR DOSY spectra of $\text{H}_3\text{L}^{10}$ (top) and complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{10})_2]$ (bottom)
Figure S84 ROESY spectrum for complex \([\text{Mo}_2\text{O}_2\text{S}_2\text{H}_2\text{L}^{10}_2]\)
Figure S85 $^{15}\text{N}\{^1\text{H}\}$ HMBC spectrum for $\text{H}_3\text{L}^{10}$

Figure S86 $^{15}\text{N}\{^1\text{H}\}$ HMBC spectrum for complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{10})_2]$
11°) NMR Studies of Ligand $H_3L^{11}$ and complex $[Mo_2O_2S_2(H_2L^{11})_2]$ in DMSO.

Figure S87 $^1H$-NMR spectra of $H_3L^{11}$ and complex $[Mo_2O_2S_2(H_2L^{11})_2]$

Figure S88 $^1H$-NMR DOSY spectra of $H_3L^{11}$ (top) and complex $[Mo_2O_2S_2(H_2L^{11})_2]$ (bottom)
Figure S89 Simulated spectra for $\text{H}_3\text{L}^{11}$ (black) and complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{11})_2]$ forms a and b (green and red).

Figure S90 ROESY $^1\text{H}$ spectrum for complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{L}^{11})_2]$. Two isomers (a and b).
Figure S91 \[^{15}N\{^1H\}\) HMBC spectrum for H\(_3\)L\(_{11}\)

Figure S92 \[^{15}N\{^1H\}\) HMBC spectrum for complex [Mo_2O_2S_2(H_2L_{11})_2]
NMR Studies of Ligand \( H_2L^{12} \) and complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{12})_2] \) in DMSO.

Figure S93 \(^1\)H-NMR spectra of \( H_2L^{12} \) and complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{12})_2] \)

Figure S94 \(^1\)H-NMR DOSY spectra of \( H_2L^{12} \) (top) and complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{12})_2] \) (bottom)
Figure S95 $^1$H NOESY spectrum for H$_2$L$^{12}$

Figure S96 $^1$H NOESY spectrum for complex [Mo$_2$O$_2$S$_2$(HL$^{12}$)$_2$]. Two isomers are present, so the protons and their 2 forms a (56%) and b (44%) are identified by NOESY experiment, e.g. H5a will correlate through space with H8a and H5b with H8b accordingly.
Figure S97 $^{15}\text{N}\{^1\text{H}\}$ HMBC spectrum for $\text{H}_2\text{L}^{12}$

Figure S98 $^{15}\text{N}\{^1\text{H}\}$ HMBC spectrum for complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{HL}^{12})_2]$
13°) NMR Studies of Ligand HL$^{13}$ and complex [Mo$_2$O$_2$S$_2$(L$^{13}$)$_2$] in DMSO.

Figure S99 $^1$H-NMR spectra of HL$^{13}$ and complex [Mo$_2$O$_2$S$_2$(L$^{13}$)$_2$]

Figure S100 $^1$H-NMR DOSY spectra of HL$^{13}$ (top) and complex [Mo$_2$O$_2$S$_2$(L$^{13}$)$_2$] (bottom)
Figure S101 NOESY $^1$H spectrum for HL$^{13}$

Figure S102 ROESY $^1$H spectrum for complex [Mo$_2$O$_2$S$_2$(L$^{13}$)$_2$]. Multiple isomers belonging to the 2 sets of isomers, denoted I and II.
Figure S103 $^{15}$N-$^{1}$H HMBC spectrum for HL$^{13}$

Figure S104 $^{15}$N-$^{1}$H HMBC spectrum for complex [Mo$_2$O$_2$S$_2$(L$^{13}$)$_2$]. Correlations in isomers from both sets I and II.

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14°) NMR Studies of Ligand HL$^{14}$ and complex [Mo$_2$O$_2$S$_2$(L$_{14}$)$_2$] in DMSO.

Figure S105 $^1$H-NMR spectra of HL$^{14}$ and complex [Mo$_2$O$_2$S$_2$(L$_{14}$)$_2$]. Two main isomers (a and b) are seen on the spectrum and traces of other possible isomers.

Figure S106 $^1$H-NMR DOSY spectra of HL$^{14}$ (top) and complex [Mo$_2$O$_2$S$_2$(L$_{14}$)$_2$] (bottom)
Figure S107 NOESY $^1$H spectrum for complex [Mo$_2$O$_2$S$_2$(L$_{14}$)$_2$]. Evolution in time of isomer proportions – now 5 isomers detected. Free ligand impurities also detected.
Figure S108 $^{15}$N-$^1$H} HMBC spectrum for HL$^{14}$

Figure S109 $^{15}$N-$^1$H} HMBC spectrum for complex [Mo$_2$O$_2$S$_2$(L$^{14}$)$_2$]. Crowded peaks in the region 8.7 ppm – 9.7 ppm and weak HMBC signals makes assignment difficult for each isomer of H1 and H5.
### Summary of NMR data

The table S5 gathers the chemical shifts obtained for ligands and complexes in DMSO. Only the two major isomers are considered in this table.

**Table S5.**

| Scheme of the ligands | Ligand | Complex (main isomers) |
|-----------------------|--------|------------------------|
|                       | $^1$H, ppm | $^{13}$C, ppm | $^{15}$N, ppm | $^1$H, ppm | $^{13}$C, ppm | $^{15}$N, ppm |
|                       | isomer a | isomer b | isomer a | isomer b | isomer a | isomer b |
| HL$^1$                | 1: 8.16, 8.34 | 2: 179.9 | 5: 144.1 | 6: 154.9 | 7: 121.8 | 11: -62.4 | 1: -267.2 | 3: -205.7 | 4: -50.5 |
|                       | 3: 11.63 | 4: 147.2 | 5: 154.6 | 6: 123.1 | 7: 8.50 | 8: 7.95 | 9: 7.52 | 10: 8.75 | 11: -60.5 |
|                       | 5: 8.01 | 6: 144.1 | 7: 154.6 | 8: 123.1 | 9: 8.01 | 10: 154.6 | 11: -62.4 | 1: -267.2 | 3: -205.7 | 4: -50.5 |
|                       | 7: 8.27 | 8: 147.2 | 9: 154.6 | 10: 123.1 | 11: 8.01 | 12: 154.6 | 13: -62.4 | 1: -267.2 | 3: -205.7 | 4: -50.5 |
|                       | 8: 7.82 | 9: 147.2 | 10: 154.6 | 11: 123.1 | 12: 8.01 | 13: 154.6 | 14: -62.4 | 1: -267.2 | 3: -205.7 | 4: -50.5 |
|                       | 9: 7.37 | 10: 147.2 | 11: 154.6 | 12: 123.1 | 13: 8.01 | 14: 154.6 | 15: -62.4 | 1: -267.2 | 3: -205.7 | 4: -50.5 |
|                       | 10: 8.56 | 11: 147.2 | 12: 154.6 | 13: 123.1 | 14: 8.01 | 15: 154.6 | 16: -62.4 | 1: -267.2 | 3: -205.7 | 4: -50.5 |
| HL$^2$                | 1: 3.02 | 2: 8.65 | 4: 11.68 | 6: 8.08 | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 3: 11.63 | 5: 144.1 | 6: 154.9 | 7: 121.8 | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 2: 8.65 | 4: 11.68 | 6: 8.08 | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 5: 144.1 | 6: 154.9 | 7: 121.8 | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 6: 154.9 | 7: 121.8 | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 7: 121.8 | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 8: 8.25 | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 9: 7.84 | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 10: 7.36 | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |
|                       | 11: 8.56 | Not recorded | 1: -272.0 | 2: 9.73 | 4: 120.6 | 6: 8.48 | 8: 9.75 | 9: 7.52 | 10: 8.75 | 11: 8.74 | 12: -60.5 |

**Not recorded** indicates that the data was not recorded.
|   | 13: 7.87 | 14: 7.19 | 16: 10.47 | 14: 7.33 | 16: 11.15 | 14: 7.24 | 16: 11.20 |
|---|----------|----------|------------|----------|------------|----------|------------|
| HL\textsuperscript{13} | 1: 8.19  
3: 11.43  
5: 8.24  
7: 7.45  
8: 7.12  
9: 7.65  | Not recorded | 1: -271.0  
3: -207.6  
4: -66.3  | isomer b  
1: 9.16  
5: 9.41  
7: 7.86  
8: 7.28  
9: 9.02  | isomer c  
1: 9.19  
5: 9.39  
7: 7.85  
8: 7.26  
9: 9.09  | Not recorded | isomer b  
1: -264.3  
3: -178.6  
4: -47.2  | isomer c  
1: -264.3  
3: -178.6  
4: -47.2  |
| HL\textsuperscript{14} | 1: 8.19  
3: 11.41  
5: 7.96  
7: 6.96  
8: 6.61  
9: 7.80  | Not recorded | 1: -269.9  
3: -206.5  
4: -64.9  | 1: 9.19  
5: 9.18  
7: 7.27  
8: 6.74  
9: 7.94  | 1: 9.17  
5: 9.09  
7: 7.30  
8: 6.77  
9: 7.98  | Not recorded | 1: -262.7  
3: -176.7  
4: -45.7  | 1: -261.9  
3: -176.9  
4: -45.5  |
**16°) Discussion about the possible isomers**

Considering that all ligands are bidentate are coordinated by Sulfur atom as thiolate and one nitrogen atom, which can vary as a function of the ligand.

Considering also that for each ligand the isomers formed involve the same N atom, i.e. azomethinic N atom for instance, 12 positional isomers can be formed as a function of the coordination sites occupied on each Mo, 3 positions being available (2 equatorial and one axial) on each.

- **Case 1:** the equatorial positions are clearly favored, in agreement with X-Ray diffraction data. **2 isomers, cis and trans are considered.** This is in full agreement with the NMR data for the major part of the complexes of this study. The free position remaining on the Mo can be free or occupied by a solvent molecule.

- **Case 2:** One ligand occupies two equatorial position and the second ligand occupies one equatorial and one axial position. The free position remaining on the Mo atoms can be free or occupied by a solvent molecule (in case of free equatorial position, the latter is necessarily occupied by a solvent molecule). This kind of complex is rarely observed in literature but such a configuration could be supported by the structure of complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{IDA})_2]^{2-}\) (IDA\(^2-\) = iminodiacetate ligand) [Fuior et al. *J. Inorg. Biochem.* 2022, 226]. In this hypothesis, **4 isomers can be formed.**

![Figure S110. Molecular structure of the complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{IDA})_2]^{2-}\)](image)

- **Case 3:** The two ligands occupy one equatorial and one axial position as do oxalate ligands in complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{Ox})_2]^{2-}\). The free position remaining on the Mo atoms are occupied by a solvent molecule. In this hypothesis, **6 isomers can be formed.**

![Figure S111. Molecular structure of the complex \([\text{Mo}_2\text{O}_2\text{S}_2(\text{Ox})_2(\text{H}_2\text{O})_2]^{2-}\)](image)

Considering these 3 hypotheses, 12 isomers are possible. The latter are depicted in the figure S96 below. This number can dramatically increase if the coordination modes of ligands can vary. For example, if we consider also that coordination of the N imino group is possible, at least 12 additional isomers are expected and much more if we suppose that the coordination mode of both ligands can differ.
Figure S112. Schematic representation of isomers envisioned by coordination of two bidentate ligands on the cluster \([\text{Mo}_2\text{O}_2\text{S}_2]^{2+}\).