



Cite this: DOI: 10.1039/c4dt01945h

Thiohydrazide complexes of molybdenum and their relevance to reduction of dinitrogen to ammonia†

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Aqueous solution of sodium molybdate reacts with aromatic thiohydrazides like thiobenzhydrazide, 2-hydroxythiobenzhydrazide, furan-2-thiohydrazide and thiophen-2-thiohydrazide to form green, neutral diamagnetic 1 : 3 chelates. They were characterized by elemental analysis and spectroscopic methods. Tris(2-hydroxythiobenzhydrazido)molybdenum(vi) was crystallized from benzene and the crystal structure shows that molybdenum(vi) is hexacoordinated to three sulfur and three nitrogen atoms from three identical ligands in facile trigonal prismatic geometry. The OH group is involved in intramolecular and intermolecular hydrogen bonding. The bound ligands of tris(thiohydrazido)molybdenum(vi) undergo a redox reaction differently depending on the solvents. Two complexes of molybdenum bound to those oxidized ligands were isolated and characterized and their structures were also solved. Of them a binuclear complex, containing two MoO_2^{2+} ions, of the ligand *N*-2-hydroxybenzoyl-*N'*-2-hydroxythiobenzoylhydrazine showed some capability to catalyze the reduction of dinitrogen to ammonia by sodium borohydride.

Received 27th June 2014,
Accepted 5th November 2014

DOI: 10.1039/c4dt01945h

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Introduction

Coordination compounds of high-valent molybdenum(v and vi) with bidentate ligands having nitrogen and sulfur as their donor sites, are of interest because of their relevance to redox active molybdo-enzymes.¹ Of the various enzymes containing molybdenum, nitrogenase probably received a greater attention.² Despite intensive investigations, the mechanism of conversion of nitrogen to ammonia by nitrogenase, especially the role of molybdenum in the Fe–Mo cofactor, has not yet been completely understood. However, recent studies³ have shown that dinitrogen can bind to a sterically protected single molybdenum center forming an end-on monometallic complex and subsequently be reduced to ammonia. Alternatively, dinitrogen can be reduced by a reducing agent at an end-on hydrazine

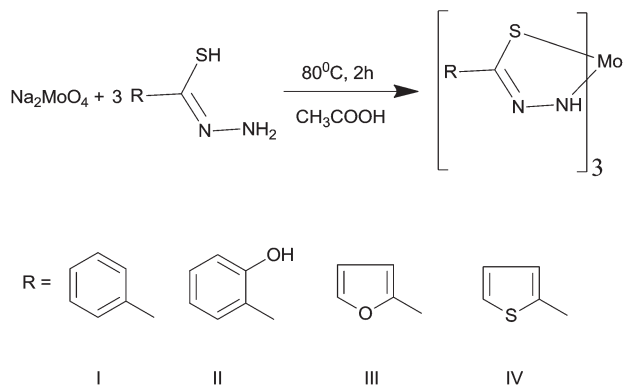
bound to a bimetallic molybdenum center.⁴ Since the model compounds mimicking the Fe–Mo cofactor of nitrogenase have been shown² to contain the cluster core of Fe_7MoS_9 or $\text{Fe}_6\text{Mo}_2\text{S}_9$, the study of the nature of molybdenum complexes of bidentate ligands with nitrogen and sulfur as donor sites, particularly having –S–Mo–N–N– linkage, may be of interest to explore the role of the metal in nitrogen fixation. The pioneering work in this field has revealed some interesting structural types of non-oxomolybdenum⁵ complexes with trigonal prism geometry. Dioxomolybdenum(vi) complexes of similar ligands,⁶ however, behave in a predictable manner. Some hydrazido-bridged binuclear molybdenum complexes of ligands with additional S-donor atoms have also been reported.⁷ In the present paper, synthesis of tris(thiohydrazido)molybdenum(vi) complexes of some aromatic thiohydrazide ligands, namely, thiobenzhydrazide, 2-hydroxythiobenzhydrazide, furan-2-thiohydrazide and thiophen-2-thiohydrazide has been described. The general scheme for the synthesis of the molybdenum complexes are shown in Scheme 1. The spectral properties of all the compounds have been discussed. The behaviour of tris(2-hydroxythiobenzhydrazido)molybdenum(vi) in acetone and DMSO has also been studied. The catalytic properties of the isolated compounds in relation to reduction of dinitrogen to ammonia by a reducing agent, sodium borohydride, have been examined and reported. The structure of the compounds has also been described when single crystals could be isolated.

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†Electronic supplementary information (ESI) available. CCDC 903770–903772. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01945h



Scheme 1 General scheme for synthesis for molybdenum(vi) complexes of thiohydrazides.

Experimental

Materials and methods

Na_2MoO_4 (>98%, Sigma-Aldrich) was used to prepare the molybdenum complexes. The ligands were synthesized as described earlier.⁸ All other chemicals were of reagent grade and used without further purification; solvents were purified and dried according to the standard procedures. Electronic absorption and IR spectra were recorded on a Hitachi (Model U-3210) spectrophotometer and Unicam SP300S (KBr disks and Nujol mulls) respectively. ^1H NMR spectra were recorded on a Bruker 500 MHz instrument in CDCl_3 (99.9%, Cambridge Isotopes Laboratories Inc.) solutions. Continuous wave EPR spectra were recorded on a Bruker X-band EPR instrument in dichloromethane–toluene mixture solution (v/v 1:1) (Sigma-Aldrich) at 70 K temperature using liquid helium. The solutions were degassed by argon flow for 15 min prior to freezing. Magnetic susceptibility was measured with a MAGWAY MFG Mk 1 (Sherwood Scientific Ltd, UK). Cyclic voltammetric measurements were carried out with an EG&G Potentiostat (model 263A) instrument using a platinum working electrode, a platinum wire auxiliary electrode and an Ag/AgCl (saturated KCl) as the reference electrode. All cyclic voltammetric experiments were performed under a nitrogen atmosphere in distilled dichloromethane solution (0.1 M TBAP). Cyclic voltammetric data were collected at 298 K and are uncorrected for junction potential.

Synthesis of tris(thiohydrazido) complexes of molybdenum

Sodium molybdate (20.6 mg, 0.1 mmol) was dissolved in water and diluted to about 100 ml. Acidity of the solution was adjusted between 0.5 and 1 M with respect to acetic acid and it was heated nearly to boiling. A solution of the ligand (0.5 mmol) in ethanol was added with constant stirring and the mixture was allowed to stand at 80 °C for about 2 h. A deep green precipitate, thus formed, was separated by filtration under suction, washed thoroughly with boiling water and dried at 110 °C. Yield of each compound was recorded on the basis of molybdenum.

Tris(thiobenzhydrazido)molybdenum(vi) (I). Yield 72%. Anal. Calc. for $[(\text{C}_6\text{H}_5\text{CSNNH})_3\text{Mo}]$: C, 46.15; H, 3.30; N, 15.38; S, 17.58. Found: C, 46.30; H, 3.12; N, 15.31; S, 17.82%. Electronic spectral absorption maxima in benzene solution: 15 710 cm^{-1} (6205 $\text{M}^{-1} \text{cm}^{-1}$), 25 880 cm^{-1} (10 050 $\text{M}^{-1} \text{cm}^{-1}$). IR (cm^{-1}) 3230w ($\nu\text{N-H}$), 1600s (aromatic), 1565m ($\nu\text{C-N}$), 1470s (aromatic), 730m ($\nu\text{C-S}$), 490w ($\nu\text{Mo-N}$), 390w ($\nu\text{Mo-S}$). ^1H NMR: δ (ppm) 6.98–7.26 (m, 2H, 3J 8.6 Hz), 7.45 (t, 1H, 3J 9.2 Hz), 7.54 (d, 2H, 3J 7.7 Hz) 10.22 br. (1H, N-H).

Tris(2-hydroxythiobenzhydrazido)molybdenum(vi) (II). Yield 94%. Anal. Calc. for $[(\text{C}_6\text{H}_4(\text{OH})\text{CSNNH})_3\text{Mo}]$: C, 42.42; H, 3.03; N, 14.14; S, 16.16. Found: C, 42.57; H, 3.10; N, 14.05; S, 16.38%. Electronic spectral absorption maxima in benzene: 14 460 cm^{-1} (11 714 $\text{M}^{-1} \text{cm}^{-1}$), 24 700 cm^{-1} (18 941 $\text{M}^{-1} \text{cm}^{-1}$).

IR (cm^{-1}) 3400–3050 br. ($\nu\text{O-H}$ and $\nu\text{N-H}$), 1600s (aromatic), 1585m ($\nu\text{C-N}$), 1480s (aromatic), 735m ($\nu\text{C-S}$), 485w ($\nu\text{Mo-N}$), 385w ($\nu\text{Mo-S}$). ^1H NMR δ (ppm) 6.96–7.06 (m, 1H, 3J 7.4 Hz), 7.12–7.26 (m, 1H, 3J 6.8 Hz), 7.55 (d, 1H, 3J 7.2 Hz), 7.97 (d, 1H, 3J 7.6 Hz), 10.41br. (N-H), 10.92br. (O-H).

Tris(furan-2-thiohydrazido)molybdenum(vi) (III). Yield 68%. Anal. Calc. for $[(\text{C}_4\text{H}_3\text{OCSNNH})_3\text{Mo}]$: C, 34.88; H, 2.33; N, 16.28; S, 18.60. Found: C, 34.95; H, 2.12; N, 16.31; S, 18.80%. Electronic spectral absorption maxima in benzene solution: 14 440 cm^{-1} (10 987 $\text{M}^{-1} \text{cm}^{-1}$), 24 680 cm^{-1} (15 678 $\text{M}^{-1} \text{cm}^{-1}$).

IR (cm^{-1}) 3290w ($\nu\text{N-H}$), 1590s (aromatic), 1570m ($\nu\text{C-N}$), 820m ($\nu\text{C-S}$), 495w ($\nu\text{Mo-N}$), 390w ($\nu\text{Mo-S}$). ^1H NMR: δ (ppm) 6.41–6.66 (m, 1H, 3J 3.6 Hz), 6.81 (d, 1H, 3J 4.2 Hz), 7.36 (d, 1H, 3J 5.4), 13.57 (N-H).

Tris(thiophen-2-thiohydrazido)molybdenum(vi) (IV). Yield 74%. Anal. Calc. for $[(\text{C}_4\text{H}_3\text{SCSNNH})_3\text{Mo}]$: C, 31.91; H, 2.13; N, 14.89; S, 34.04. Found: C, 31.71; H, 2.10; N, 14.82; S, 34.25%. Electronic spectral absorption maxima in benzene solution: 14 510 cm^{-1} (11 539 $\text{M}^{-1} \text{cm}^{-1}$), 24 780 cm^{-1} (16 330 $\text{M}^{-1} \text{cm}^{-1}$).

IR (cm^{-1}) 3290w ($\nu\text{N-H}$), 1607s (aromatic), 1590m ($\nu\text{C-N}$), 710m ($\nu\text{C-S}$), 495w ($\nu\text{Mo-N}$), 390w ($\nu\text{Mo-S}$). ^1H NMR: δ (ppm) 7.03–7.18 (m, 1H, 3J 4.6 Hz), 7.41 (d, 1H, 3J 5.0 Hz), 7.67 (d, 1H, 3J 5.6 Hz), 13.32 (N-H).

X-ray crystallography

Crystallographic data were collected with MoK_α ($\lambda = 0.71073$) radiation at 150(2) K using the Oxford Diffraction X-Calibur CCD system. The crystal was positioned at 50 mm from the CCD. Frames of 321 were measured with a counting time of 10 s. Data analysis was carried out with the ChrysAlis program.⁹ The structures were solved using direct methods with SHELXS97.¹⁰ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon, nitrogen and oxygen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was carried out using the ABSPACK program.¹¹ The structure was refined on F^2 using SHELXL97.¹⁰

Reduction of dinitrogen to ammonia

A weighed amount of green thiohydrazide complex of molybdenum was dissolved in 5 ml of DMSO and allowed to stand for 2 hours. The solution was then quantitatively transferred to a 3-necked flask fitted to a pressure equalizer dropping funnel, an inlet and an outlet for nitrogen. The outlet leads to an Erlenmeyer flask containing a measured volume of 0.01 M hydrochloric acid to absorb expelled ammonia. About 2 g of sodium borohydride was added and then ethanol was added through the dropping funnel. Nitrogen gas was bubbled through for 2 h. The amount of ammonia that could be expelled was determined either by the spectrophotometric method with Nessler's reagent or by titration of excess acid with the standard sodium hydroxide. The results were expressed as the percentage of ammonia on the basis of nitrogen present in the compound and were calculated using the equations $\frac{n \times 100}{6 \times m}$ for compounds **I–IV** and $\frac{n \times 100}{2m}$ for compound **Ic** where n = number of moles of ammonia purged and m = moles of the compound used. The compounds **I–IV** contain six moles of nitrogen per mole of the complex while compound **Ic** contains two moles of nitrogen per mole of the complex. The experiment was repeated using different passage times of nitrogen.

Results and discussion

Behavior of the compounds in different solvents

The green compounds (**I–IV**) retain their color in benzene, toluene, chloroform and dichloromethane solution. While green color persists in benzene and toluene solutions for more than a week, solutions in chloroform and dichloromethane turn red slowly after 24 hours. It is found that in solvents containing oxygen and nitrogen the color of the compounds turned brown quickly. The solvents include acetone, acetonitrile, ethanol, methanol, DMSO and DMF.

Solution of **II** in benzene on slow evaporation formed beautiful green crystals of the molecular formula $[(C_6H_4(OH)CSNNH)_3Mo].3C_6H_6$ (**IIa**) (Anal. Calc. C, 56.53; H, 4.35; N, 10.14; S, 11.59%. Found: C, 56.54; H, 4.32; N, 10.15; S, 11.57%). The compound is diamagnetic.

A black needle shaped crystal obtained from the acetone solution of **II** is found to be paramagnetic ($\mu = 1.58$ BM) and has the molecular formula $[C_{24}H_{21}N_6O_3S_3]Mo \cdot (CH_3)_2CO$ (**IIb**) (Anal. Calc. C, 46.89; H, 3.91; N, 12.16; S, 13.89; Mo, 13.88. Found: C, 46.88; H, 3.92; N, 12.17; S, 13.87; Mo, 13.90%). A brown crystalline diamagnetic compound of the molecular formula $C_{18}H_{20}Mo_2N_2O_9S_3$ (**IIc**) (Anal. Calc. C, 31.03; H, 2.87; N, 4.02; S, 13.79; Mo, 27.57. Found: C, 31.01; H, 2.88; N, 4.04; S, 13.78; Mo, 27.59%) was isolated from the DMSO solution of **II**.

Spectral data

Electronic spectra of three tris(thiohydrazido) complexes of molybdenum(vi), (**II**, **III** and **IV**) in benzene or toluene solution

are dominated by two peaks in the visible region, one in the region of $14\,500\text{ cm}^{-1}$ and the other at around $24\,700\text{ cm}^{-1}$, the energy of separation being about $10\,200\text{ cm}^{-1}$. Compound **I** under similar conditions, however, showed two peaks at slightly higher energy with almost the same difference in energy. The molar absorbance of the compounds at the peaks is of the order of $10^4\text{ dm}^3\text{ mole}^{-1}\text{ cm}^{-1}$ and hence bands may be considered as LMCT bands. Comparing the electronic spectral features of these compounds with those of tris-*cis*-stilbene-dithiolatomolybdenum(vi) the lower energy band may be assigned as $^1A_1 \rightarrow ^1E$ and the higher energy band as $^1A_1 \rightarrow ^1E, ^1A_2$. These bands are characteristics of six coordinate molybdenum(vi) complexes with the trigonal prismatic structure.¹² It has been mentioned earlier that compound **II** in acetone solution gradually turns brown on standing. On following the electronic spectrum with time it was found that the two peaks at $14\,460\text{ cm}^{-1}$ and $24\,700\text{ cm}^{-1}$ lost their intensities gradually and a new peak appeared at $21\,460\text{ cm}^{-1}$ with three isosbestic points at $17\,860\text{ cm}^{-1}$, $22\,730\text{ cm}^{-1}$ and $26\,310\text{ cm}^{-1}$ (ESI Fig. S1†). Compound **IIb** isolated from a concentrated solution of **II** in acetone solution showed only one peak in the visible region at $20\,830\text{ cm}^{-1}$. Compounds isolated from the acetone solution of **I**, **III** and **IV** showed peaks at $22\,025\text{ cm}^{-1}$, $20\,800\text{ cm}^{-1}$ and $20\,877\text{ cm}^{-1}$, respectively, in the visible region of the electronic spectra. Compound **IIc** isolated from the DMSO solution of **II** also showed only one peak in the visible region at $20\,330\text{ cm}^{-1}$.

The infrared spectral data relevant for elucidation of the structure of thiohydrazido complexes are discussed here. None of the tris(thiohydrazido)molybdenum(vi) complexes showed any band in the region of $880\text{--}950\text{ cm}^{-1}$. This suggests the absence of $Mo=O$ in the complexes. The characteristic $\nu(C-S)$ in the complex suffers a change of $\sim 25\text{ cm}^{-1}$ with respect to that of the corresponding ligand and it may be due to the formation of complex through the S-centre. The $\nu(C-N)$ of the complexes are marginally higher than those of ligands showing the increase of double bond character of the C-N bond. The weak bands near $485\text{--}495\text{ cm}^{-1}$ and at $385\text{--}390\text{ cm}^{-1}$ that are not observed in the IR spectra of the ligands may be assigned to the Mo-N and Mo-S stretching frequencies, respectively. The IR spectrum of compound **IIb** showed a medium intensity band at 1695 cm^{-1} in addition to all other characteristic peaks of compound **II**. This peak is assigned to C=O stretching of the acetone molecule linked to the compound through the H-bond. The IR spectrum of compound **IIc** showed characteristic absorption at 921 and 894 cm^{-1} due to ν_{as} and ν_s of the *cis*- MoO_2 group.¹³ The $\nu_{s=O}$ band of the coordinated DMSO molecule in the compound is found at 1003 cm^{-1} ($\nu_{s=O}$ in free DMSO- 1058 cm^{-1}). This indicates coordination of the DMSO molecule through oxygen to the Mo-centre.¹⁴

The 1H NMR spectrum of compound **I** showed two distinct sets of peaks in the region of $6.92\text{--}8.16\text{ ppm}$ and at 10.22 ppm . The signals in the region $6.92\text{--}8.16$ are due to aromatic protons revealing the presence of three sets of aromatic protons and the N-H peak is found at 10.22 ppm . Compound

II showed four peaks in the region for aromatic protons (6.96–8.3 ppm) and two broad peaks at 10.41 and 10.92 ppm. The peaks at 10.41 and 10.92 ppm are due to N–H and O–H, respectively. Compound **III** showed peaks in two distinct regions of 6.41–7.36 ppm and 13.57 ppm. The first set of three peaks is for the furan ring region and the peak at 13.57 is due to N–H. In compound **IV** three peaks for the thiophene ring protons were found in a narrow region of 7.05–7.67 ppm while the peak due to the N–H proton was observed at 13.32 ppm. The large downfield shifts of N–H protons in thiohydrazido complexes may be attributed to coordination of nitrogen to molybdenum in the high oxidation state. In the NMR spectrum of compound **IIb** several peaks were found in the aromatic region of 6.85–8.30 ppm and three sharp peaks at 2.06, 2.44 and 2.64 ppm are due to the methyl protons. The peak at 2.06 ppm is for acetone and the other two peaks are assigned to two non-equivalent methyl groups of the hydrazone. The OH peaks for the three non-equivalent ligands are noticed at 9.15, 11.37 and 13.40 ppm. It may be mentioned that the aromatic protons and the protons in the heterocyclic rings have been identified by comparing them with those found in NMR spectra of the free ligands. The X-band EPR spectrum of compound **IIb** in frozen dichloromethane-toluene (1 : 1) solution is characteristic of molybdenum(v) with $S = 1/2$ and showed g values of 2.0037, 1.9999 and 1.9987. No hyperfine splitting due to ^{14}N ($S = 1$) could be observed because of the large H-strain (anisotropic line broadening). H_x , H_y and H_z values are ~ 50 MHz, 50 MHz and 50 MHz (ESI Fig. S2†). Fine splitting due to ^{95}Mo ($I = 5/2$) could not be observed. No EPR signal could be observed with any of the tris(thiohydrazido) complexes. Absence of the EPR signal and diamagnetism of tris(thiohydrazido) complexes of molybdenum are consistent with the formal oxidation state of +6 (d^0) of the metal. Compound **IIc** also did not exhibit any EPR signal.

Electrochemistry

Two cathodic peak potentials at -0.193 V and -0.821 V were observed in the cyclic voltammogram (Ag/AgCl as the reference electrode) of compound **II**. The corresponding anodic peaks were found at $+0.065$ V and -0.520 V. The large separation of E_{pc} and E_{pa} values (>250 mV) suggests that the electron transfer processes are irreversible or quasi-reversible. The first E_{pc} value corresponds to one electron reduction of Mo(vi) to Mo(v) and the second one to Mo(v)/Mo(IV).⁵ Compound **I** also showed similar peaks only at a slightly shifted position ($E_{\text{pc}} = -0.36$ V and -1.12 V; $E_{\text{pa}} = -0.12$ V and -0.74 V). The E_{pc} value of -1.12 V is close to a cathodic peak at -0.98 V in the cyclic voltammogram of the free ligand and hence it may be due to the ligand based irreversible reduction process. Compounds **III** and **IV** had reduction peaks (E_{pc}) at -0.388 V and -0.459 V, respectively, with their corresponding E_{pa} values at -0.268 V and -0.305 V. All these redox processes are irreversible with high ΔE_{p} (240–305 mV) and it may be due to the ligand based electron transfer process.

Crystal structure of the complexes

The crystal data, together with the data collection and structure refinement parameters of compounds **IIa**, **IIb** and **IIc** are presented in ESI (Table S1†).

The perspective view of the structure of compound **IIa** is shown in Fig. 1.

The selected bond lengths and angles of the compound are listed in Table 1. The crystal structure of compound **IIa** $[(\text{C}_6\text{H}_4(\text{OH})\text{CSNNH})_3\text{Mo}]\cdot 3\text{C}_6\text{H}_6$ contains discrete $[(\text{C}_6\text{H}_4(\text{OH})\text{CSNNH})_3\text{Mo}]$ entities and three C_6H_6 molecules. The compound consists of monomeric molecules and each Mo(vi) is hexacoordinated to three nitrogen and three sulfur atoms from three identical ligands forming a facial structure. The structure shows Mo(vi) in a slightly distorted trigonal prismatic environment being bonded to three bidentate ligands through N and S. One triangular face containing three sulfur atoms is an equilateral triangle of side length 3.295 Å while the other face containing three nitrogen atoms is also another equilateral triangle of side length 2.954 Å. The difference in the side length of two triangular faces arises from the difference in van der Waals radii of S and N and it accounts for the distortion in the trigonal prismatic facial structure. The Mo(1)–N(11) and Mo(1)–S(20) bond lengths are $1.9943(17)$ and $2.4191(5)$ Å, respectively. These bond-lengths are in agreement with those in the tris(thiobenzoyldiazene)molybdenum complex.⁵ The C(13)–S(20) bond length of $1.722(2)$ Å is larger than the

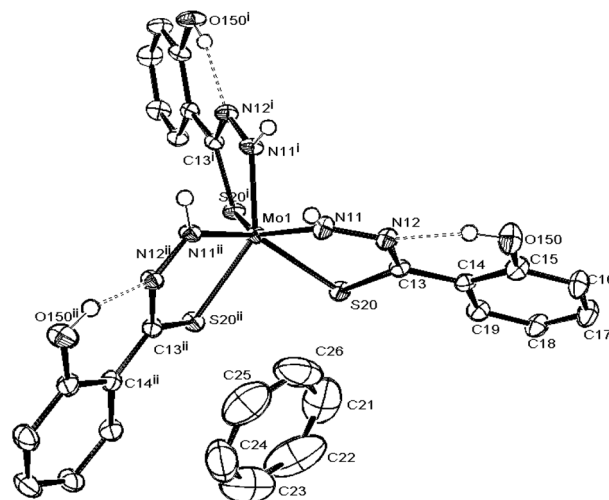


Fig. 1 Molecular structure of compound **IIa** with the numbering scheme adopted. Thermal ellipsoids are shown at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) of compound **IIa**

Mo(1)–N(11)	1.9943(17)	Mo(1)–S(20)	2.4191(5)
C(13)–S(20)	1.722(2)	C(13)–N(12)	1.329(2)
N(11)–N(12)	1.343(2)	C(15)–O(150)	1.362(2)
N(11)–Mo(1)–S(20)	76.18(5)	N(12)–N(11)–Mo(1)	128.22(12)
C(13)–S(20)–Mo(1)	98.40(7)	C(13)–N(12)–(N11)	114.69(17)
N(12)–C(13)–S(20)	119.05(17)		

C=S bond length of 1.61–1.63 Å¹⁵ while the C(12)–N(13) bond length of 1.329(2) Å is shorter than the C–N single bond length of 1.47 Å. From these data it is obvious that the thioenol tautomer of the ligand participates in complex formation.¹⁶ In compound **IIa** the N(11)–N(12) bond length of 1.343(2) Å is shorter than the N–N distance of 1.4187(16) Å as was determined by X-ray crystallography of the free ligand 2-hydroxythiobenzhydrazide monohydrate.¹⁷ The C–N bond length in compound **IIa** remains the same as that of the ligand, while the C–S bond length increases by 0.047 Å from that of the ligand. The shorter N–N distance and constancy in the C–N bond length in the complex in comparison with the ligand may suggest a diazenide formulation but fails to explain the d⁰ electronic configuration of molybdenum(vi). Therefore, it is reasonable to assume that extensive delocalization of π -electrons is responsible for shortening of the N–N bond and constancy of the C–N bond length. This will also explain the diamagnetic nature of compound **IIa** and the absence of any signal in its EPR spectrum. Furthermore, there is an intramolecular hydrogen bond between O(150)–H and N(12). O(150) is also involved in an intermolecular hydrogen bond with N(11)H of another molecule of [(C₆H₄(OH)CSNNH)₃Mo]. These hydrogen bonds may play a vital role in crystal formation. Moreover, the distance between S(20) and H(21) amounting to 3.215 Å is greater than the sum of their van der Waals radii (3.00 Å) and therefore, it may be assumed that there is no direct short contact between benzene molecules of crystallization and the tris(2-hydroxythiobenzhydrazido)molybdenum(vi) entity. Compound **IIa** is related to compound **II** in that it contains three molecules of benzene of crystallization. Benzene molecules may have some role in crystal packing in such a way that the green color is retained.

Fig. 2 represents the view of the structure of compound **IIb** and selected bond lengths and angles are shown in Table 2. The crystal structure of compound **IIb** reveals that the Mo(v) is bonded to three distinct, nonidentical ligand units and one acetone of crystallization. The compound consists of

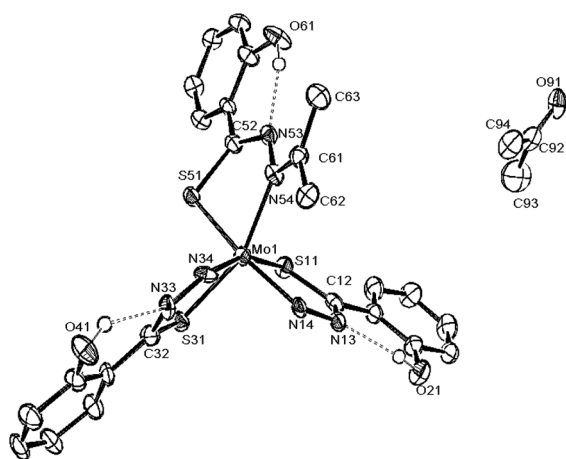


Fig. 2 Molecular structure of compound **IIb** with the numbering scheme adopted. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond lengths (Å) and angles (°) of compound **IIb**

Mo(1)–N(34)	1.783(5)	Mo(1)–N(14)	2.000(5)
Mo(1)–N(54)	2.199(5)	Mo(1)–S(31)	2.4693(17)
Mo(1)–S(11)	2.4682(16)	Mo(1)–S(51)	2.4697(17)
C(32)–S(31)	1.734(7)	C(12)–S(11)	1.738(7)
C(52)–S(51)	1.766(6)	C(32)–N(33)	1.342(8)
C(12)–N(13)	1.325(8)	C(52)–N(53)	1.294(8)
N(33)–N(34)	1.313(7)	N(13)–N(14)	1.356(7)
N(53)–N(54)	1.416(8)	C(40)–O(41)	1.379(9)
C(20)–O(21)	1.359(8)	C(60)–O(61)	1.356(8)
N(34)–Mo(1)–S(31)	73.57(16)	N(14)–Mo(1)–S(11)	76.16(15)
N(54)–Mo(1)–S(51)	76.57(15)	N(33)–N(34)–Mo(1)	141.9(4)
N(13)–N(14)–Mo(1)	129.4(4)	N(53)–N(54)–Mo(1)	118.7(4)
C(32)–S(31)–Mo(1)	97.1(2)	C(12)–S(11)–Mo(1)	98.3(2)
C(52)–S(51)–Mo(1)	96.6(2)	C(32)–N(33)–N(34)	141.9(4)
C(12)–N(13)–N(14)	115.5(5)	C(52)–N(53)–N(54)	116.6(5)
N(33)–C(32)–S(31)	117.0(5)	N(13)–C(12)–S(11)	119.5(5)
N(53)–C(52)–S(51)	123.1(5)		

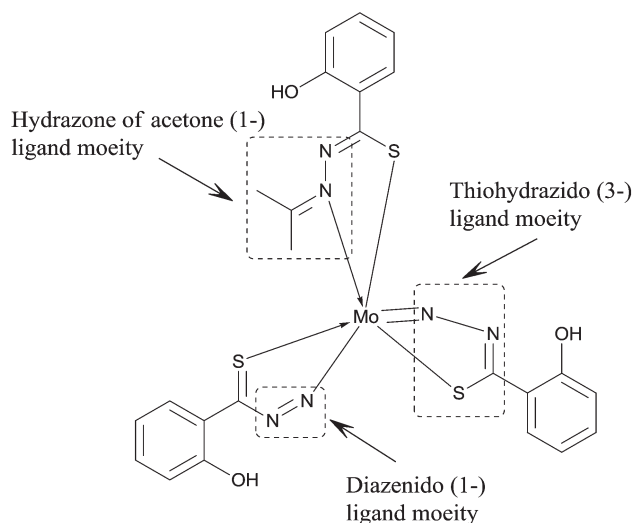


Chart 1 Bonding scheme of three non-equivalent ligands in compound **IIb**.

monomeric units containing Mo(v) ions hexacoordinated to N and S atoms of three different ligands in a distorted trigonal prismatic structure. The bonding scheme in compound **IIb** is presented in Chart 1.

The compound may be represented as [Mo(2-OHC₆H₄CSN₂)-(2-OHC₆H₄C:SN:N)(2-OHC₆H₄CSNNCMe₂)]·(CH₃)₂CO. The internal bond angles of N(14)Mo(1)S(11) [76.1°], N(34)Mo(1)S(31) [73.5°] and N(54)Mo(1)S(51) [76.5°] in the compound are close to those in compound **IIa** which has a trigonal prismatic structure. The only difference is that none of the triangular faces are equilateral.

This may be due to the non-equivalent nature of the ligands. The hydrazido ligand unit bears a charge of 3– due to loss of all the three protons attached to the two nitrogen atoms and the double bonded nature of the Mo–N(34) bond is in conformity with the very short bond distance of 1.783(5) Å.¹⁸ That the ligand is in the thiol form can be predicted from the longer C(32)–S(31) bond length of 1.734(7) Å. Another ligand molecule is modified to a uninegative diazenido unit

Table 3 Hydrogen bond lengths (Å) and angles (°)

Compound	Donor (D)	Acceptor (A)	H...A	D-H...A	D...A
Compound IIa	O(150)H	N(12)	1.813	152.02	2.585
	N(11)H	O(150#)	2.181	140.24	2.895
Compound IIb	O(21)H	N(13)	1.866	150.32	2.636
	O(41)H	N(33)	1.891	147.66	2.651
	O(61)H	N(53)	1.853	154.27	2.645

where molybdenum is singly bonded to the N-14 atom as found from the relatively longer Mo–N(14) bond length [2.000(5) Å]. The third ligand in its thiol form is converted to a hydrazone of acetone and it binds with Mo(v) through its N(54) and S(51). The hydrazone ligand thus behaves as a uninegative bidentate ligand. The thiol form is confirmed by the long C(52)–S(51) bond distance of 1.766(6) Å and the comparatively shorter C(52)–N(53) bond distance of 1.294(8) Å. The unusually long Mo(1)–N(54) bond length of 2.199(5) Å is due to either the bulky hydrazone group or due to the coordinative nature of bonding. The structure shows that O(21)H, O(41)H and O(61)H are hydrogen bonded to N(13), N(33) and N(53), respectively. This H-bonding may be responsible for the more symmetric orthorhombic unit cell of compound **IIb**. The hydrogen bonding parameters in compounds **IIa** and **IIb** are presented in Table 3.

The distance between N(14) (diazenido nitrogen) and O(91) (acetone oxygen) of another molecule is 2.865 Å which is less than the sum of the van der Waals radii of O and N (3.07 Å). Therefore some short term electrostatic interaction may exist between the acetone and the N(14) moiety of the complex.

The crystal structure of compound **IIc** represented in Fig. 3 shows a centrosymmetric dimeric structure which can be represented as [(MoO₂)₂(C₆H₄(O)–C(=O)–N–N–C(=S)(O)C₆H₄)–(DMSO)₂].

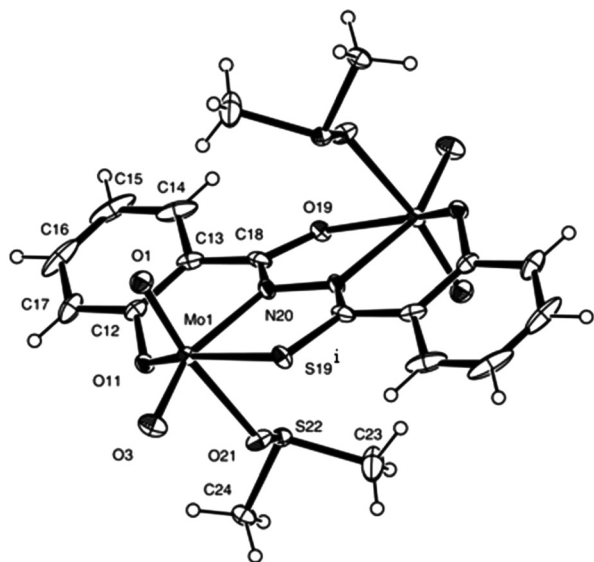


Fig. 3 Molecular structure of compound **IIc** with the numbering scheme adopted. Thermal ellipsoids are shown at the 30% probability level.

Table 4 Selected bond lengths (Å) and angles (°) of compound **IIc**

Mo(1)–O(11)	9415(19)	Mo(1)–O(19)	2.076(4)
Mo(1)–S(19) ⁱ	2.4027(16)	Mo(1)–N(20)	2.248(2)
Mo(1)–O(1)	1.701(2)	Mo(1)–O(3)	1.713(2)
C(18)–N(20)	1.318(4)	C(18)–O(19)	1.334(5)
C(18)–S(19) ⁱ	1.736(3)	N(20)–N(20)*	1.400(5)
C(12)–O(11)	1.359(3)	O(11)–Mo(1)–N(20)	81.93(8)
O(1)–Mo(1)–O(3)	105.90(11)	O(1)–Mo(1)–O(11)	97.35(10)
O(3)–Mo(1)–O(11)	106.26(9)	O(1)–Mo(1)–O(21)	168.23(9)
O(3)–Mo(1)–O(21)	85.86(10)	O(11)–Mo(1)–O(19)*	143.66(14)
O(11)–Mo(1)–S(19) ⁱ *	155.61(7)		

Selected bond lengths and bond angles are shown in Table 4. Each Mo atom is in a distorted octahedral environment being hexacoordinated to two mutually *cis* terminal oxygen atoms, nitrogen, sulfur/oxygen, oxygen atoms of the deprotonated OH group of the ligand *N*-2-hydroxybenzoyl*N*-2-hydroxythiobenzoylhydrazine and the oxygen atom of one DMSO molecule. The structure is disordered with regard to O(19) and S(19)ⁱ atoms which were refined with 50% occupancy. The crystallographic results do not distinguish between the occurrence of asymmetric molecules containing O and S. The structure is disordered over the centre of symmetry or symmetric dimer, 50% containing O(19) and 50% containing S(19)ⁱ as shown in Fig. 3.

The ligand thus has two tridentate donor sites each of which coordinates with a MoO₂²⁺ unit in a *mer* configuration forming a six- and a five-membered ring with bite angles O(11)Mo(1)N(20) and N(20)Mo(1)S(19)ⁱ/N(20)Mo(1)O(19) of 81.93°(8), 80.80°(7)/66.33°(14), respectively. It is clear from the structure that the benzoylated N atom and the sulfur atom of the thiobenzoyl group S(19)ⁱ coordinate with one Mo-centre whereas the thiobenzoylated N atom (N') and the oxygen atom of the benzoyl group(O19) coordinate with the other Mo-centre. The ligand is significantly distorted from planarity due to the stereochemical requirement of accommodating two *cis* oxygen atoms in the coordination sphere. Two thiohydrazido ligands in compound **IIa** are oxidized to a hydrazine derivative on exposure to DMSO. It cannot be predicted for certain whether the oxidation is incurred through DMSO oxygen or aerial oxygen. However, smell of dimethylsulfide in the course of the reaction supports the prediction that DMSO is responsible for oxygen transfer. The Mo-centers are also oxygenated in this environment probably through DMSO, which has been previously reported.¹⁹ Finally the structural requirement to accommodate the newly formed diazene ligand and two *cis* dioxo groups around each Mo-centre forced the third ligand out of the coordination sphere. The short Mo(1)–O(1) and Mo(1)–O(3) bond distance [1.701(2) Å and 1.713(2) Å] proves the double bond character of the Mo=O bonds. The electrostatic interaction between O(1) and S(19)ⁱ of another molecule of compound **IIc** is predicted from the shorter distance of separation between the atoms (3.24 Å) than the sum of their van der Waals radii (3.32 Å). The N–N covalent bond distances in compound **IIc** is 1.400(5) Å which is close to the N–N single bond distance. The shortening of the bond length may be explained by extensive delocalization of π -electrons over the entire

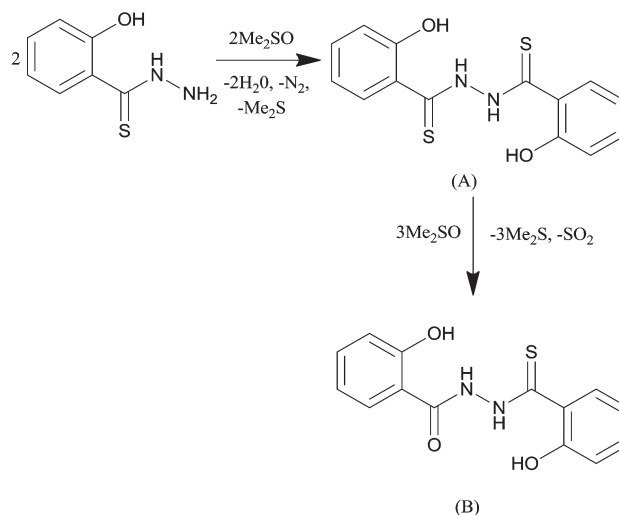
hydrazine moiety. The delocalization is also reflected in the lengthening of the C=N bond length [1.418(4) Å] from the usual C=N bond distances in hydrazones [C(52)–N(53) 1.294(8) Å] in compound **IIb**.

Reduction of dinitrogen to ammonia

The percentage of ammonia that could be expelled is shown in Table 5. It is observed that of all the compounds only compound **II** could liberate more than 120% ammonia in 2 h on the basis of total nitrogen present in the compound. On the other hand compounds **I**, **III** and **IV** could generate only 6 to 23% of ammonia in 6 h. Admittedly, the total amount of ammonia that was formed cannot be purged simply by bubbling nitrogen. In spite of that formation of more than 100% of ammonia clearly indicates that there is some other source of nitrogen that was reduced to ammonia in the presence of compound **II**. Compound **II** differs from the other compounds in this series in that it contains a free –OH group in the 2-position of the phenyl ring. This –OH group is capable of providing an additional donor site.

It was proposed earlier⁴ that an important factor that can strongly influence the catalytic activity of molybdenum in the reduction of dinitrogen to ammonia is the formation of a binuclear complex of the type $\text{Mo} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{array} \text{Mo}$ having a common ligand binding both metal atoms and dinitrogen closing the cycle at coordination. Compound **II** can fulfil this requirement in the presence of DMSO. In order to explain the role of DMSO the following reaction scheme involving the free ligand shown in Scheme 2, in the absence of a reducing agent, may be suggestive.

Both dimethylsulfide and sulfur-dioxide could be detected when compound **II** was dissolved in DMSO. However, when the free ligand is dissolved in DMSO neither dimethylsulfide nor sulfur-dioxide could be detected and hence it is stable in DMSO solution. The presence of a metal ion is necessary to catalyze these reactions. Earlier it was observed¹⁷ that rhodium(III) could catalyze such oxidation by oxo-transfer reaction of DMSO. In the case of the molybdenum complex the coordinated ligands are oxidized, suggesting that the compound is labile and undergoes dissociation at the nitrogen bound



Scheme 2 Probable scheme for oxidation of 2-hydroxy thiobenzhydrazide by DMSO.

end. The formation of a hydrazone of acetone in solution of compound **II** in that the solvent is a clear indication of lability of the thiohydrazido complex of the molybdenum(vi) complex at the nitrogen bound end.

The first part of the reaction scheme shown in a box of Scheme 3 suggests that $\text{Mo}(\text{HO}-\text{C}_6\text{H}_4-\text{CS}-\text{N}-\text{NH})_3$ (compound **II**) may serve as a model for the active site of DMSO reductase.¹⁹ Oxygen of DMSO is not only responsible for the generation of MoO_2^{2+} , but also for the oxidation of coordinated ligand 2-hydroxy thiobenzhydrazide to *N*-2-hydroxybenzoyl-*N'*-2-hydroxythiobenzoyl hydrazine [(B) of Scheme 2]. From the reaction scheme it may be observed that *N*-*N'*-di(2-hydroxythiobenzoyl)-hydrazine [(A) of Scheme 2] is produced. Possibility of its involvement to generate *N*-2-hydroxybenzoyl-*N'*-2-hydroxythiobenzoyl hydrazine [(B) of Scheme 2] cannot be ruled out. Since the oxidation state of molybdenum in the binuclear complex is +6 (d^0) a strong reducing agent like sodium borohydride in the presence of ethanol is necessary to reduce molybdenum(vi) to a lower oxidation state to provide a source of electron in the vicinity of the coordinated nitrogen to produce ammonia.

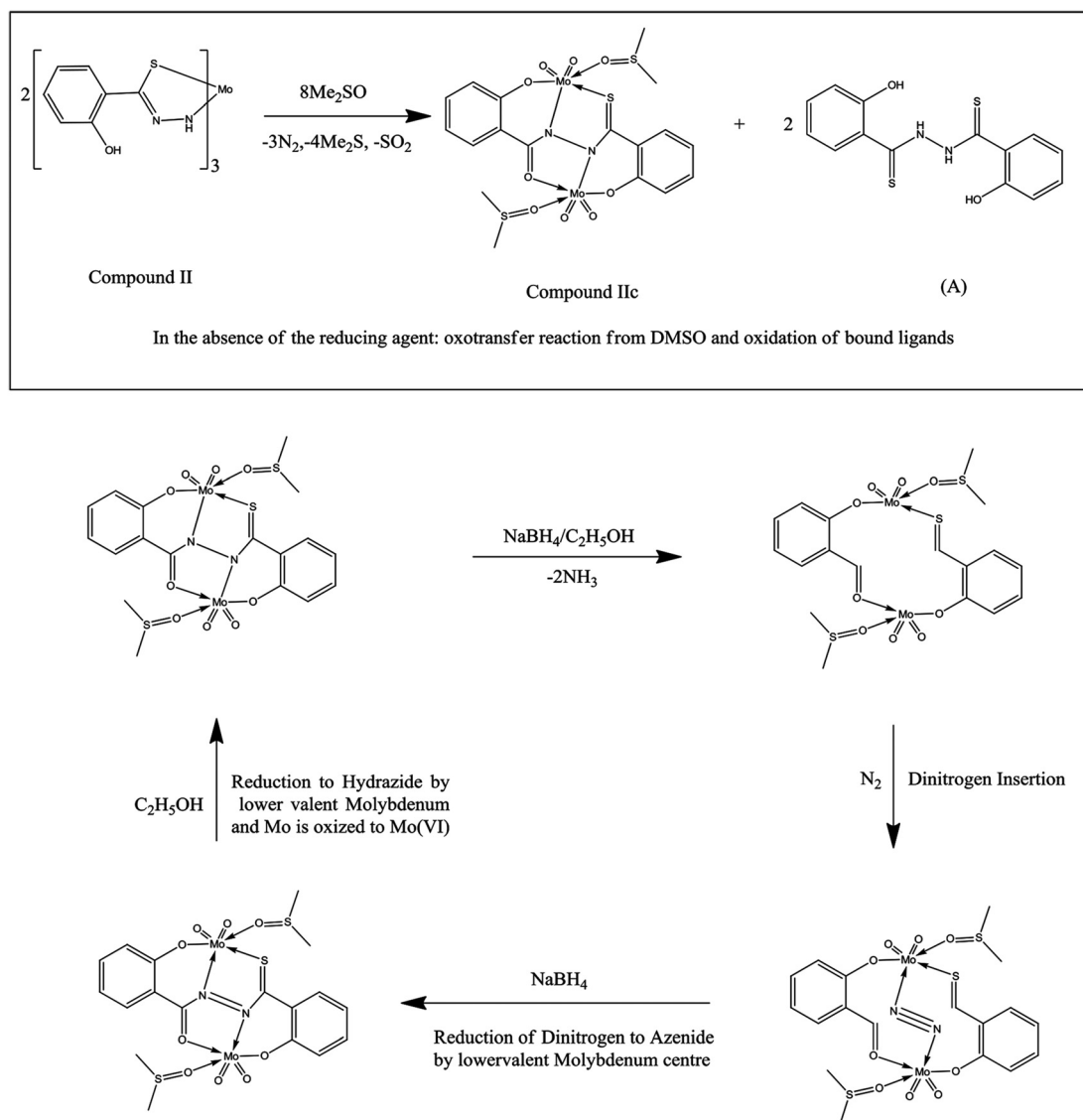
Therefore, as a mechanism for reduction of dinitrogen to ammonia, it is proposed that molybdenum reduced by sodium borohydride acts as a source electron for the bridged nitrogen atoms of hydrazine in **IIc** to ammonia, opening up the link between two molybdenum atoms. After that dinitrogen is inserted in that position leading to the formation of a bridged dinitrogen complex which is successively reduced to azenide and hydrazide and the reaction continues. The proposed reactions in the presence of sodium borohydride are shown in Scheme 3 (outside the box).

We could not isolate all the intermediates that we proposed. It is definite that compound **IIc** was isolated and fully characterized. In addition compound **II** could produce more than 100% ammonia on the basis of nitrogen present in the compound. The above facts are sufficient indication in favour of our proposed mechanism.

Table 5 Percentage of ammonia produced on the basis of nitrogen present in the compound

Compound	Time for passing N_2	% NH_3 formed ^a
I	2 h	16
	6 h	18
II	2 h	120
	6 h	125
IIc	1 h	180
	2 h	200
	6 h	210
III	2 h	6
	6 h	6
IV	2 h	20
	6 h	23

^a Percentages have been presented as the nearest integer.



Scheme 3 Probable scheme representing the formation of compound IIc from compound II and the catalytic activity of IIc in the presence of sodium borohydride.

It has been observed that compounds **I**, **III** and **IV** could liberate only a small amount of ammonia due to the reduction of the hydrazido part of the ligand in the complexes by sodium borohydride and ethanol. In those compounds the additional coordination sites, like the $-OH$ group in compound **II** are not available. As a result none of them could be converted to a binuclear complex having similarity with compound **IIc**. Therefore the reduction process could not be sustained.

Conclusions

The present study shows that molybdenum(vi) in a weakly acidic medium forms green, diamagnetic, 1 : 3 inner metallic chelates with thiohydrazide ligands where the charge on the ligands is 2 – due to the loss of two protons. The compounds are stable in the solid state and also in non-polar solvent solu-

tion. In a polar solvent like acetone molybdenum(vi) is even reduced to molybdenum(v) at the expense of one ligand being oxidized to diazenide. The most interesting feature of this work is that the complex of the ligand 2-hydroxythiobenzhydrazide is involved in oxo-transfer with DMSO to form a binuclear complex of O_2Mo^{2+} of a newly generated ligand *N*2-hydroxybenzoyl*N*'2-hydroxythiobenzoylhydrazine and the compound has the capability to catalyze the reduction of dinitrogen to ammonia by a strong reducing agent sodium borohydride at room temperature.

Acknowledgements

The authors thank EPSRC (UK), and the University of Reading for funds for the diffractometer. Financial assistance received

from the University Grants Commission, New Delhi and the Higher Education Department, Government of West Bengal is gratefully acknowledged.

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