

## 丙二酰二脒衍生的二氧化二钼(VI)配合物的合成、表征和晶体结构

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**摘要:** 本文报道了二氧杂钼(VI)配合物 $[\text{MoO}_2(\text{H}_2\text{L})(\text{H}_2\text{O})]$ 的合成、表征和分子结构。该配合物是由马来酰二脒配体双(2-羟基-1-萘醛)丙二酰二脒( $\text{H}_4\text{L}$ )与双(乙酰丙酮)二氧钼(VI)在甲醇中以1:1的物质的量之比反应得到的。通过各种光谱(如IR、MS和NMR)对该配合物进行了表征。通过单晶X射线晶体学确定了配合物的结构。该配合物属于单斜晶系 $P2_1/c$ 空间群。金属中心具有扭曲的八面体配位环境,与 $\text{H}_2\text{L}^{2-}$ 的1个甲亚胺氮原子、2个末端氧基团、 $\text{H}_2\text{L}^{2-}$ 的2个氧原子和配位水分子的1个氧原子相连。

**关键词:** 晶体结构; 金属配合物; 二氧基钼(VI); 八面体配位

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### Dioxidomolybdenum(VI) complex derived from malonoyldihydrazones: Synthesis, characterization, and crystal structure

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**Abstract:** In this paper, we report the synthesis, characterization, and molecular structure of the dioxidomolybdenum(VI) complex  $[\text{MoO}_2(\text{H}_2\text{L})(\text{H}_2\text{O})]$ . The complex was obtained by reaction of malonoyldihydrazones ligand bis(2-hydroxy-1-naphthaldehyde) malonoyldihydrazone ( $\text{H}_4\text{L}$ ) with molybdenum bis(acetylacetonato)dioxomolybdenum(VI) in a 1:1 molar ratio in methanol. The complex was characterized by using various spectroscopic studies, such as IR, MS, and NMR. The structure of the complex was established by single-crystal X-ray crystallography. The complex crystallizes in the monoclinic space group  $P2_1/c$ . The metal center has distorted octahedral coordination environments, connected to one azomethine nitrogen atom of  $\text{H}_4\text{L}$ , two terminal oxido groups, two oxygen atoms of  $\text{H}_4\text{L}$ , and one oxygen atom of a coordinated water molecule. CCDC: 2113523.

**Keywords:** crystal structure; metal complex; dioxidomolybdenum(VI); octahedral coordination

## 0 Introduction

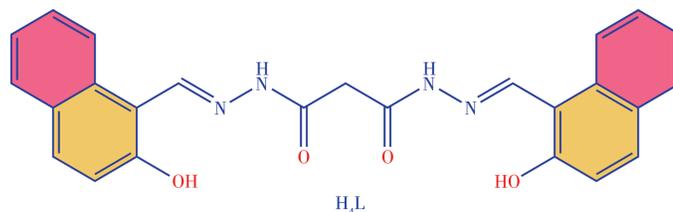
Molybdenum is the only element of the second transition series, being essential for life<sup>[1-2]</sup> and is present in all forms of life, ranging from ancient bacteria to humans and with the exception of nitrogenases, mostly, catalyze oxido transfer reactions<sup>[3-4]</sup>. It is the only bio-metal important for microorganisms, plants, and ani-

mals with a large variety of stable and accessible oxidation states of all the second series of transition metals. Further, the coordination chemistry of molybdenum(VI) assumes special importance due to its relatively harmless nature to the environment<sup>[5]</sup> and is of significant interest and attention due to its biological activity, viz. anticancer, antibacterial, and antitumor properties<sup>[6-8]</sup>. The coordination chemistry of molybdenum gained con-

siderable attention because of its versatile applications in the field of catalysis and biology<sup>[9-10]</sup>, physiology, and industry<sup>[11-13]</sup>. The coordination chemistry of molybdenum attracts more and more attention, due to the chemistry of its variety of oxidation states, coordination number, impact on structure, reactivity, and because of the potential applications of molybdenum compounds<sup>[14-17]</sup>. The dioxomolybdenum complexes have been widely studied, as models for the active sites of oxotransfermolybdoenzymes like xanthine oxidase, xanthine dehydrogenase, nitrate reductase and sulfite and aldehyde oxidase<sup>[18-20]</sup>. In the catalytic activity of molybdoenzymes the oxidation state of molybdenum varies between VI and IV states and Mo(V) coexists along with Mo(VI) and Mo(IV). The study of molybdenum complexes with dianionic tridentate ligands is particularly significant

because the coordination of *cis*-MoO<sub>2</sub><sup>2+</sup> with di-anionic tridentate ligand systems provides an open active site on molybdenum<sup>[21]</sup>. Many reports are available for the studies of dioxomolybdenum complexes with O, N, and S-containing ligands<sup>[22-24]</sup>.

In view of the significant role played by molybdenum in biological systems, catalysis, and industry, and only much less work on oxido metal ion complexes of malonyldihydrazones. Therefore, we aimed to synthesize a monometallic complex [MoO<sub>2</sub>(H<sub>2</sub>L)(H<sub>2</sub>O)] of dioxomolybdenum(VI) from bis(2-hydroxy-1-naphthaldehyde) malonyldihydrazone (H<sub>4</sub>L, Scheme 1) and characterized it by using different spectroscopic techniques, such as <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and UV-Vis. The structure of the complex has also been confirmed by single-crystal X-ray crystallography.



Scheme 1 Structural formula of H<sub>4</sub>L

## 1 Experimental

### 1.1 Materials and instrumentation

Solvents were reagent grade and used as received. Other chemicals were E-Merck, Himedia, or equivalent grades, and all reagents were used as received. All operations were performed under aerobic conditions. Infrared spectra in a range of 4 000-200 cm<sup>-1</sup> were recorded as KBr discs by using a BX-III/FTIR Perkin Elmer Spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance II 400 and 100 MHz in DMSO-d<sub>6</sub> solution using TMS as an internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer.

### 1.2 Preparation of H<sub>4</sub>L

To an aqueous methanol solution of malonyldihydrazine (0.66 g, 1 mmol), 2-hydroxy-1-naphthaldehyde (1.72 g, 1 mmol) was added and the reaction mixture was stirred for about half an hour at 40 °C. The yellow precipitate thus obtained was filtered and washed with hot methanol and dried over anhydrous CaCl<sub>2</sub>. Yield:

95%. IR data (cm<sup>-1</sup>, KBr): 3 431, 3 197, 3 042 (vs br, ν<sub>OH+NH</sub>), 1 700(s), 1 666 (vs, ν<sub>C=O</sub>), 1 624, 1 621, 1 540, 1 320, 1 187, 743, 529, 510. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 12.47-11.55 (s, 1H, OH), 9.23, 9.17 (s, 1H, NH), 7.92-7.16 (m, Ar-H), 8.88, 8.23 (s, 2H, C(H)=N), 2.2 (s, 2H, —CH<sub>2</sub>).

### 1.3 Synthetic procedure for the complex

H<sub>4</sub>L (1.00 g, 2.27 mmol) and MoO<sub>2</sub>(acac)<sub>2</sub> (0.81 g, 2.5 mmol) was taken in 50 mL methanol and stirred well at 60 °C to give a homogeneous solution. The yellow precipitate was filtered and washed three times with hot methanol (10 mL each time), and dried under a vacuum. The resulting solution was cooled and filtered. The filtrate was kept for crystallization which yielded blocks of orange crystals within four days. Yield: 92%.

### 1.4 Single crystal X-ray diffraction

Single crystal X-ray data were collected at 298 K, using Xcalibur Eos Gemini diffractometer equipped with a monochromated Mo Kα radiation (λ=0.071 073

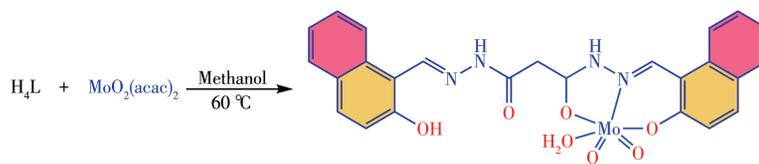
nm). The CrysAlis Pro (Agilent, 2013) software package was used for data collection and reduction. The crystal structure was solved by SHELXT and refined by SHELXL-2014<sup>[25-26]</sup>. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed at a calculated position and refined in the final refinement.

CCDC: 2113523.

## 2 Results and discussion

The synthesis of the complex involved the reac-

tion of the stoichiometric amounts of  $\text{MoO}_2(\text{acac})_2$  with the ligand in a 1:1 molar ratio in methanol under stirring conditions (Scheme 2). The complex was insoluble in benzene, hexane, toluene,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , ether, *etc.* The complex was sparingly soluble in acetonitrile, water, methanol, and dichloromethane, and completely soluble in solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide. The molar conductance value for the complex is  $1.8 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  at  $1 \text{ mmol} \cdot \text{L}^{-1}$  dilution in DMSO solution. This value revealed the non-electrolytic nature of the complex in the solution<sup>[27]</sup>.



Scheme 2 Schematic diagram showing the preparation of the complex

### 2.1 Mass spectra

The complex has been studied by ESI mass spectroscopy. Molybdenum had six isotopes of roughly equal abundance, and the peaks were at  $m/z$  values of 694.12, 606.30, 588.29, and 567.14, respectively (Fig. S1, Supporting information). The third prominent peak at  $m/z$  value of 588.29 is assigned to  $[\text{MoO}_2(\text{H}_5\text{L})(\text{H}_2\text{O})]^+$  (587.41), which results from either loss of coordinated methanol molecule followed by coordination of one water molecule or loss of one coordinated water molecule from  $[\text{MoO}_2(\text{H}_5\text{L})(\text{H}_2\text{O})_2]$ . The fourth prominent peak at the  $m/z$  value of 567.14 corresponds to the loss of coordinated methanol molecules from the complex. Recently, we have shown that in the monometallic molybdenum complex in which both the naphthoxido oxygen atoms are bonded to the molybdenum ion center, and the methylene group is further activated leading to its condensation with sulfoxido oxygen atoms<sup>[28]</sup>.

### 2.2 Electronic spectra

The electronic spectrum of the complex in the DMSO solution is shown in Fig.S2. The  $\text{H}_4\text{L}$  ligand (Fig. S3) showed absorption bands at 316 nm ( $\epsilon=8735 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), 365 nm ( $\epsilon=7763 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), and 414 nm ( $\epsilon=2628 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) in the DMSO solution, respectively. The band in the region of 294-316 nm is attributed to the intraligand  $\pi \rightarrow \pi^*$  transition

centered on the phenyl/naphthyl rings. Other absorption bands which were observed in the region of 324-365 nm, owe their origin due to  $n \rightarrow \pi^*$  transitions centered on  $>\text{C}=\text{O}$  and  $>\text{C}=\text{N}$  groups, respectively<sup>[29-30]</sup>. Apart from the intra-ligand band, an additional band was observed at 433 nm ( $\epsilon=1930 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), which was not visible in those of the free dihydrazone. Because of the  $4d^0$  configuration,  $\text{Mo(VI)}$  complex is not expected to show any absorption in the visible region. Therefore, this band may be attributed to the ligand-to-metal charge transfer transition. These results are consistent with the results reported for dioxomolybdenum(VI) complexes<sup>[31]</sup>.

### 2.3 IR spectra

The IR spectra of  $\text{H}_4\text{L}$  and the complex are shown in Fig.S4 and S5. The complex showed the bands at 3396, 3323, 3202, 3176, and 3080  $\text{cm}^{-1}$ , which are attributed to joint contribution from stretching vibrations of secondary  $-\text{NH}$  groups and naphtholic/phenolic  $-\text{OH}$  groups, respectively. The presence of multiple bands in the region of 3396-3080  $\text{cm}^{-1}$  in the complex indicates the presence of both  $-\text{NH}$  and  $-\text{OH}$  groups revealing that all the  $-\text{CONH}-$  and  $-\text{OH}$  groups are not bonded to the molybdenum atom. The carbonyl groups exhibited the bands at 1683 and 1673  $\text{cm}^{-1}$ . This is attributed to the carbonyl stretching

frequency. The disappearance of the narrow band at 1 677 and 1 700  $\text{cm}^{-1}$  in  $\text{H}_4\text{L}$  on complexation and the appearance of either a strong triplet or strong doublet in the region of 1 651-1 683  $\text{cm}^{-1}$  indicates the enolization of the half part of the dihydrazone and the uncoordinated nature of one  $>\text{C}=\text{O}$  group. The complex exhibited two peaks at 454 and 594  $\text{cm}^{-1}$ , respectively. These bands were assigned to  $\text{Mo}-\text{O}$  bands (carbonyl and phenolate/naphtholate), respectively<sup>[32]</sup>. A medium-intensity band was observed at 1 562  $\text{cm}^{-1}$  which is attributed to the mixed contribution of amide  $\text{II} + \nu_{\text{C}=\text{O}}$  (naphtholic). The infrared spectra of the complex exhibited two new strong bands at 938 and 916  $\text{cm}^{-1}$  which are assigned to the symmetric and asymmetric  $\text{Mo}=\text{O}$  stretching vibrations, respectively of the *cis*- $[\text{MoO}_2]^{2+}$  unit<sup>[33]</sup>.

## 2.4 $^1\text{H}$ NMR

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of  $\text{H}_4\text{L}$  and the complex are shown in Fig. S6 and S7. The  $^1\text{H}$  NMR spectra of the complex showed peaks at  $\delta$  12.55, 12.10, and  $\delta$  10.03, 9.70, respectively. While the former signals appearing downfield are attributed to  $-\text{OH}$  proton, the latter peaks displaying upfield are attributed to  $-\text{NH}$  proton. The integration of the signals in the region of  $\delta$  9.62-12.55 corresponds to two protons, one due to the phenolic/naphtholic  $-\text{OH}$  group, while the other one due to the secondary  $-\text{NH}$  group which remains uncoordinated. The azomethine proton signals appear at  $\delta$  9.70. The signal shifted downfield by 0.30 as compared to those in the uncoordinated ligands<sup>[34]</sup>. The phenyl/naphthyl proton signals appeared in the region of  $\delta$  6.73-8.89 in uncoordinated dihydrazones while in the region of  $\delta$  6.92-8.89 in the complex.

## 2.5 Molecular structure

ORTEP plot of the crystal of the complex, with a numbering scheme, is shown in Fig. 1. The complex crystallizes with the solvent (acetonitrile) of crystallization. Crystal data and structure refinement are given in Table 1. Selected bond lengths and bond angles are given in Table 2. The complex crystallizes in the monoclinic space group  $P2_1/c$ . Although dihydrazone is a tetrabasic octa-dentate ligand, it functions as a dibasic tridentate ligand in the complex binding. The metal

center has distorted octahedral coordination environments, connected to one azomethine nitrogen atom of  $\text{H}_2\text{L}^{2-}$ , two terminal oxido groups, two oxygen atoms of  $\text{H}_2\text{L}^{2-}$ , and one oxygen atom of the coordinated water molecule. The  $\text{Mo}=\text{O}$  distances are 0.169 0(6) and 0.169 3(5) nm, respectively, and are within the range of 0.162-0.172 nm observed for dioxidomolybdenum(VI) complexes<sup>[35-36]</sup>. These  $\text{Mo}=\text{O}$  distances are markedly shorter than the  $\text{Mo}-\text{O4}$  distance of the coordinated water molecule which is found to be 0.231 4(5) nm. Additionally, the length of the *trans*- $\text{Mo}-\text{N1}$  and  $\text{Mo}-\text{O4}$  ( $\text{H}_2\text{O}$ ) bonds (0.223 0(5) and 0.231 4(5) nm) are

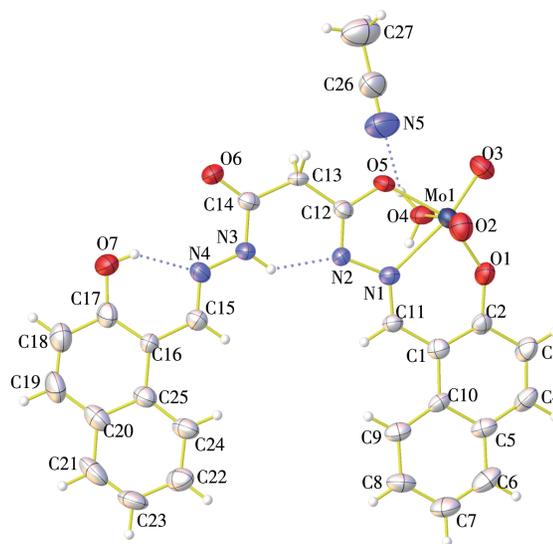


Fig. 1 ORTEP plot of the complex with a 50% probability

**Table 1** Crystal data and details of structure refinement of the complex

Parameter	$[\text{MoO}_2(\text{H}_2\text{L})(\text{H}_2\text{O})]$
Empirical formula	$\text{C}_{25}\text{H}_{22}\text{MoN}_6\text{O}_8$
Formula weight	630.42
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ / nm	1.385 12(7)
$b$ / nm	1.378 27(8)
$c$ / nm	1.402 54(8)
$\beta$ / ( $^\circ$ )	90.771(4)
$Z$	4
Data, restraint, number of parameters	5 202, 0, 364
Goodness-of-fit on $F^2$	1.013
Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1=0.082$ 7, $wR_2=0.186$ 7
Final $R$ indices (all data)	$R_1=0.131$ 3, $wR_2=0.228$ 0
Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	1 340, -880

**Table 2 Bond lengths and bond angles of the complex**

Mo1—O4	0.231 2(5)	Mo1—O3	0.169 6(5)	Mo1—O5	0.199 1(4)
Mo1—N1	0.222 8(5)	Mo1—O1	0.192 7(5)	Mo1—O2	0.168 9(6)
O3—Mo1—O4	83.5(2)	O3—Mo1—O5	97.4(2)	O3—Mo1—N1	160.4(2)
O5—Mo1—O4	80.04(18)	O5—Mo1—N1	72.15(17)	N1—Mo1—O4	78.45(17)
O1—Mo1—O4	80.54(18)	O1—Mo1—O5	148.8(2)	O1—Mo1—N1	80.14(19)
O2—Mo1—O4	171.29(19)	O2—Mo1—O3	105.1(3)	O2—Mo1—O5	97.3(2)
O2—Mo1—N1	92.8(2)	O2—Mo1—O1	98.2(2)		

greater than those of the terminal Mo=O bonds. This is, probably, a direct consequence of the well-known *cis*- and *trans*-internal octahedral (N, O)—Mo—(N, O) bond angles are found in the 72.18(17)° - 104.4(2)° and 148.8(2)° - 171.2(2)° ranges, respectively. A five-membered and another six-membered chelate rings are formed with the angle of 72.18(17)° and 80.16(19)° subtended at molybdenum atom, respectively. This type of hydrazone coordination has a widespread occurrence among complexes with several transition metals<sup>[37-38]</sup>.

## 2.6 Packing diagram

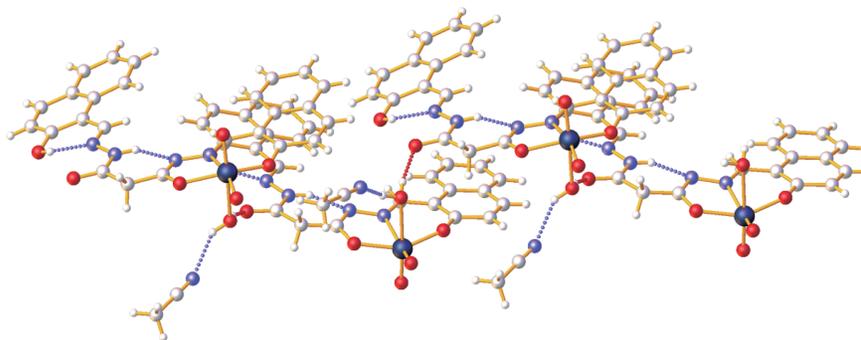
The packing diagram of the crystal of the complex is mediated by weak hydrogen bonds, C—H···O interactions, and N···O interaction of the lattice-held acetonitrile molecule (Table 3). In the crystal structure of

the complex (Fig. 2), the two complex molecules are linked to each other through H-atoms of the coordinated water molecule by one intermolecular O—H···O hydrogen bonds with intermolecular H - bonded distance of 0.266 6 nm. There is a highly directional intramolecular hydrogen bonding in the complex in which the free carbonyl oxygen atom is hydrogen bonded to the free naphtholic —OH oxygen atom of the same ligand molecule with the O—H···O distance being about 0.376 5 nm. The oxygen atom of the free naphtholic —OH group of the first coordinated ligand molecule is H - bonded to the molybdenyl oxygen atom of the third complex molecule with the O—H···O distance being 0.381 6 nm. C—H···O interaction is also partially responsible for crystal packing with the C···O distances falling in the region of 0.313 3-0.339 9 nm. The oxy-

**Table 3 Hydrogen bond parameters of the complex**

D—H···A	$d(\text{D—H}) / \text{nm}$	$d(\text{H···A}) / \text{nm}$	$d(\text{D···A}) / \text{nm}$	$\angle \text{D—H···A} / (^\circ)$
O4—H4A···N5	0.086	0.214	0.287 1(11)	143
O4—H4B···O6#1	0.086	0.182	0.266 6(6)	168
O7—H7A···N4	0.082	0.185	0.254 9(7)	142
C15—H15···O2#2	0.093	0.247	0.330 2(9)	150
C22—H22···O5#3	0.093	0.247	0.339 5(9)	174

Symmetry codes: #1:  $x, 1/2-y, -1/2+z$ ; #2:  $1-x, 1-y, -z$ ; #3:  $1+x, y, z$ .

Fig.2 Packing diagram of the complex showing hydrogen bonding along *b*-axis

gen atom of the coordinated water molecule belonging to the first complex molecule is bonded to the free carbonyl oxygen atom of the second complex molecule with an O—H···O distance being 0.266 6 nm. The acetonitrile nitrogen atom is extensively H-bonded to different H-atoms of coordinated dihydrazone molecule with C—H···N distance being 0.271 0 nm as well as to the oxygen and hydrogen atoms both of coordinated water molecule present in the second complex molecule with N···O and N···H distance being 0.287 1 and 0.214 1 nm, respectively. These are engaged in cooperative water-to-acetonitrile interaction. The discrete type of solvent clusters, *i.e.*, water, in particular, have been reported by different workers. In the literature, there are also some polymeric water clusters which may be chains (1D clusters), layers (2D clusters), and a handful of frameworks (3D clusters)<sup>[39]</sup>.

### 3 Conclusions

In the present study, we have synthesized a monometallic molybdenum (VI) complex obtained from the reaction of MoO<sub>2</sub>(acac)<sub>2</sub> with bis(2-hydroxy-1-naphthaldehyde)malonyldihydrazone. The complex is monomeric in nature. The dihydrazone ligand is present in keto-enol forms and functions as a monobasic tridentate ligand coordinating with the metal center through phenolate/naphtholate oxygen atoms and azomethine nitrogen atoms.

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**Conflict of interest:** The authors declare no conflict of interest.

Supporting information is available at <http://www.wjhxzb.cn>

### References:

- [1]Kurbah S D, Kumar A, Syiemlieh I, Asthana M, Lal R A. Bimetallic *cis*-dioxomolybdenum(VI) complex containing hydrazine ligand: Syntheses, crystal structure and catalytic studies. *Inorg. Chem. Commun.*, **2017**,**86**:39-43
- [2]Amini M, Haghdoost M M, Bagherzadeh M. Oxido-peroxido molybdenum(VI) complexes in catalytic and stoichiometric oxidations. *Coord. Chem. Rev.*, **2013**,**257**:1093-1121
- [3]Hille R. The molybdenum oxotransferases and related enzymes. *Dalton Trans.*, **2013**,**42**:3029-3042
- [4]Khatua S, Naskar T, Nandi C, Majumdar A. Mononuclear bis(dithiolene) Mo(IV) and W(IV) complexes with P,P; S,S; O,S and O,O donor ligands: A comparative reactivity study. *New J. Chem.*, **2017**,**41**:9769-9783
- [5]Kurbah S D, Kumar A, Shangpung S, Syiemlieh I, Khongjoh I, Lal R A. Synthesis, characterization, and fluorescence chemosensor properties of a *cis*-dioxomolybdenum(VI) complex containing multidentate hydrazone ligands. *Z. Anorg. Allg. Chem.*, **2017**,**643**:794-801
- [6]Majumdar A. Structural and functional models in molybdenum and tungsten bioinorganic chemistry: Description of selected model complexes, present scenario and possible future scopes. *Dalton Trans.*, **2014**,**43**:8990-9003
- [7]Cherak S J, Turner R J. Assembly pathway of a bacterial complex iron sulfur molybdoenzyme. *BioMolecular Concepts*, **2017**,**8**:155-167
- [8]Rakshit S, Palit D, Hazari S K S, Rabi S, Roy T G, Olbrich F, Rehder D. Synthesis, characterization and biomedical activities of molybdenum complexes of tridentate Schiff base ligands. Crystal and molecular structure of [MoO<sub>2</sub>(L<sub>10</sub>)(DMSO)] and [MoO<sub>2</sub>(L<sub>11</sub>)(DMSO)]. *Polyhedron*, **2016**,**117**:224-230
- [9]Sarkheil M, Lashanizadegan M. New magnetic supported hydrazone Schiff base dioxomolybdenum(VI) complex: An efficient nanocatalyst for epoxidation of cyclooctene and norbornene. *Appl. Organomet. Chem.*, **2018**,**32**:e4459
- [10]Maia L B, Moura J J G, Moura I. Molybdenum and tungsten-dependent formate dehydrogenases. *J. Biol. Inorg. Chem.*, **2015**,**20**:287-309
- [11]Heinze K. Bioinspired functional analogs of the active site of molybdenum enzymes: Intermediates and mechanisms. *Coord. Chem. Rev.*, **2015**,**300**:121-141
- [12]Li F, Talipov M R, Dong C, Bali S, Ding K. Acid-facilitated product release from a Mo(IV) center: Relevance to oxygen atom transfer reactivity of molybdenum oxotransferases. *J. Biol. Inorg. Chem.*, **2018**,**23**:193-207
- [13]Nishino T, Okamoto K. Mechanistic insights into xanthine oxidoreductase from development studies of candidate drugs to treat hyperuricemia and gout. *J. Biol. Inorg. Chem.*, **2015**,**20**:195-207
- [14]Tamm M, Dre Bel B, Urban V, Lugger T. Coordinatively unsaturated molybdenum complexes with chelating cycloheptatrienyl-phosphane ligands and their use in transition metal catalysis. *Inorg. Chem. Commun.*, **2002**,**5**:837-840
- [15]Ahamed A S, Saadia A A, Orabi A. Spectral and thermal studies of some chromium and molybdenum complexes with ONO donor Schiff bases. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, **2006**,**65**:841-845
- [16]Salonen P, Peuronen A, Lehtonen A. Bioinspired Mo, W and V complexes bearing a highly hydroxyl-functionalized Schiff base ligand. *Inorg. Chim. Acta*, **2020**,**503**:119414
- [17]Maurya M R, Mengesha B, Maurya S K, Avecilla F. Synthesis, char-

- acterization and catalytic activity of dioxouranium(VI) complexes of ONNO tetradentate Mannich bases. *Inorg. Chim. Acta*, **2019**,**493**:118-126
- [18]Bray R C. The inorganic biochemistry of molybdoenzymes. *Q. Rev. Biophys.*, **1988**,**21**:299-329
- [19]Malthouse J P G, Bray R C. Coupling of [<sup>33</sup>S]sulphur to molybdenum(V) in different reduced forms of xanthine oxidase. *Biochem. J.*, **1980**, **191**:629-637
- [20]Holm R H. Metal-centered oxygen atom transfer reactions. *Chem. Rev.*, **1987**,**87**:1401-1449
- [21]Gupta S, Barik A K, Pal S, Hazra A, Roy Butcher R J, Kar S K. Oxomolybdenum(VI) and (V) complexes of pyrazole derived ONO donor ligands — Synthesis, crystal structure studies and spectroelectrochemical correlation. *Polyhedron*, **2007**,**26**:133-141
- [22]Vrdoljak V, Pisk J, Prugoveki B, Calogovi D M. Novel dioxomolybdenum(VI) and oxomolybdenum(V) complexes with pyridoxal thiosemicarbazone ligands: Synthesis and structural characterization. *Inorg. Chim. Acta*, **2009**,**362**:4059-4064
- [23]Cindri M, Vrdoljak V, Strukan N, Kamenar B. Synthesis and characterization of some mono- and dinuclear molybdenum(VI) thiosemicarbazonato complexes. *Polyhedron*, **2005**,**24**:369-376
- [24]Rao S N, Munshi K N, Rao N N, Bhadbhade M M, Suresh E. Synthesis, spectral and X-ray structural characterization of [*cis*-MoO<sub>2</sub>(L)(solv)] (L=salicylidene salicyloyl hydrazine) and its use as catalytic oxidant. *Polyhedron*, **1999**,**18**:2491-2497
- [25]Sheldrick G M. *SADABS, Program for empirical absorption correction of area detector data*. University of Göttingen, Germany, **1996**.
- [26]Sheldrick G M. *SHELXL-14, Program for crystal structure refinements*. University of Göttingen, Germany, **1996**.
- [27]Geary W J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.*, **1971**,**7**:81-122
- [28]Ahmed A, Lal R A. Synthesis and electrochemical characterization (the original text is characterisation) of molybdenum(VI) complexes of disalicylaldehyde malonoyl-dihydrazone. *J. Mol. Struct.*, **2013**,**1048**:321-330
- [29]Lal R A, Chanu O B, Borthakur R, Asthana M, Kumar A, De A K. Synthesis and characterization of molybdenum(V, VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone. *J. Coord. Chem.*, **2011**,**64**:1393-1410
- [30]Zhi F, Shao N, Wang Q, Zhang Y, Wang R, Yang Y. Crystal structures and antibacterial activity of hydrazone derivatives from 1*H*-indol-3-acetohydrazide. *J. Struct. Chem.*, **2013**,**54**:148-154
- [31]Lal R A, Choudhury S, Ahmed A, Borthakur R, Asthana M, Kumar A. Synthesis of homobimetallic molybdenum(VI) complex of bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone and its reaction with electron and proton bases. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, **2010**,**75**:212-224
- [32]Percy G C. Infrared spectra of nickel(II) and cobalt(II) N-salicylidene-glycinates. *J. Inorg. Nucl. Chem.*, **1975**,**37**:2071-2073
- [33]Kumar A, Koch A, Borthakur R, Chakraborty R, De A K, Phukan A, Bez G, Lal R A. Synthesis and spectroscopic characterization of monometallic molybdenum(VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone. *J. Mol. Struct.*, **2014**,**1063**:92-101
- [34]Lal R A, Chakravorty M, Choudhury S, Ahmed A, Borthakur R, Kumar A. Synthesis and spectral characterization of homobimetallic molybdenum(VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone. *J. Coord. Chem.*, **2009**,**62**:1-13
- [35]Gupta S, Kirillova M V, Guedes da Silva C, Pombeiro A J L, Kirillov A M. Alkali metal directed assembly of heterometallic V<sup>V</sup>/M (M=Na, K, Cs) coordination polymers: Structures, topological analysis, and oxidation catalytic properties. *Inorg. Chem.*, **2013**,**52**:8601-8611
- [36]Hossini Monfared H, Asghari Lalami N, Pazio A, Wozniak K, Janiak C. Dinuclear vanadium, copper, manganese and titanium complexes containing O,O,N-dichelating ligands: Synthesis, crystal structure and catalytic activity. *Inorg. Chim. Acta*, **2013**,**406**:241-250
- [37]Adams H, Fenton D E, Minardi G, Mura E, Soliras C P. A coordination polymer derived from the copper(II) complex of a bis-(salicylhydrazone) derived from iminodiacetic acid diethyl ester. *Inorg. Chem. Commun.*, **2000**,**3**:24-28
- [38]Maurya M R, Haldar C, Kumar A, Kuznetsov M L, Avecilla F, Pessoa J C. Vanadium complexes having [VO]<sup>2+</sup>, [VO]<sup>3+</sup> and [VO<sub>2</sub>]<sup>+</sup> cores with hydrazones of 2,6-diformyl-4-methylphenol: Synthesis, characterization, reactivity, and catalytic potential. *Dalton Trans.*, **2013**,**42**:11941-11962
- [39]Shi F N, Cunha-Silva L, Lal R A, Ferreira S, Mafra L, Trindade T, Carlos L D, Paz F A A, Rocha J. Interconvertible modular framework and layered lanthanide(III)-etidronic acid coordination polymers. *J. Am. Chem. Soc.*, **2008**,**130**:150-167