

SYNTHESIS, CHARACTERIZATION AND 3D MOLECULAR MODELING OF SOME NEW 8-COORDINATE *Cis*-DIOXOMOLYBDENUM (VI) CHELATES INVOLVING (O, N, O)-DONOR COORDINATION MATRIX OF SCHIFF BASES DERIVED FROM 4-AMINO-2,3-DIMETHYL-1-PHENYL-2-PYRAZOLIN-5-ONE AND SOME β -DIKETOENOLATES

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ABSTRACT

This paper reports the synthesis of five new mononuclear dioxomolybdenum(VI) complexes of the composition $[MoO_2(L)_2] \cdot H_2O$ where $LH = N$ -(*o*-acetoacetotoluidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*o*-aatd-admphpH), *N*-(*o*-acetoacet-anisidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*o*-aans-admphpH), *N*-(acetoacetanilidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*aaa*-admphpH), *N*-(methylacetoacetidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*meacac*-admphpH) or *N*-(ethylacetoacetidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*etacac*-admphpH). These complexes were obtained by the interaction of bis(acetylacetonato)dioxomolybdenum(VI) with the said ligands in 1:2 metal-ligand ratio in ethanol. All these complexes have been characterized by elemental analyses, molar conductance, decomposition temperature and magnetic measurements, thermogravimetry, ¹H-NMR, IR and electronic spectral studies. Based on these studies, an 8-coordinate structure has been proposed for these complexes. The 3D molecular modeling and analysis for bond lengths and bond angles have also been carried for one of the representative compounds, $[MoO_2(aaa-admphp)_2] \cdot H_2O$ (**3**) to substantiate the proposed structure.

KeyWords: Dioxomolybdenum(VI) chelates; O, N O-Donor organic matrix; Bioinorganic; Medicinal relevance; 3D Molecular modeling.

INTRODUCTION

The Schiff base derivatives¹ of 4-amino-2,3-dimethyl-1-phenyl-2-pyrazolin-5-one received much attention due to their applications including biological, clinical, analytical and pharmacological areas. Even though 4-amino-2,3-dimethyl-1-phenyl-2-pyrazolin-5-one itself exhibits antimicrobial activity², it has reported to be enhanced due to the condensation with aldehydes, ketones, thiosemicarbazides, carbazides, etc.

Molybdenum is of essential importance³ for nearly all-biological systems, as enzymes catalyzing diverse key reactions in the global carbon, sulfur and nitrogen metabolism require it. Although it can form complexes with numerous physiologically important compounds, it was supposed that this trace element is absorbed, transported and excreted in a simple molybdate form. Due to its role in the processes of nitrogen fixation and nitrate reduction, molybdenum is essential for

normal growth and development of plants and sometimes it is necessary to enrich the substrate with some molybdenum compounds.

Metal complexes of Schiff bases have been of considerable interest and as such they have occupied a central role in the development of inorganic chemistry of chelate systems^{4,5}. The coordination chemistry of molybdenum(VI) has attracted considerable interest due to its biochemical significance⁶⁻⁹. For example, dioxomolybdenum(VI) complexes are studied as models for oxidized form of molybdoenzymes, such as, aldehyde oxidase and sulfite oxidase, which are supposed to contain *cis*-MoX₂ units (X = O, S) coordinated to sulfur, nitrogen and oxygen donor atoms of the protein structure¹⁰⁻¹². The present view of these enzymes indicates that the formal oxidation state of molybdenum cycles between +IV and +VI in reaction with substrate and oxidant. The two-electron oxygen atom transfer seems to be the relevant mechanism in understanding chemical role of enzymatic reactions.

High-valent molybdenum complexes have attracted considerable interest due to their application as catalysts in various oxidations reactions^{13,14}, such as, epoxidation and hydroxylation of olefins¹⁵, oxidation of alcohols¹⁶, and as catalysts of oxygen atom transfer reactions^{17,18}. Moreover, molybdate can catalyze the oxidation of bromide¹⁹ and some peroxo complexes of molybdenum(VI) have been found to oxidize bromide in a stoichiometric reaction²⁰. At this point it should be mentioned that molybdate as a functional mimic for vanadium-haloperoxidase enzymes shows a higher catalytic activity as compared to vanadate¹⁹. Nevertheless, the rich coordination chemistry of functional haloperoxidase models based on vanadium is not complemented by molybdenum-based coordination compounds²¹. A second very interesting catalytic reaction performed by vanadiumhaloperoxidase enzymes is the oxidation of sulfides by hydrogen peroxide²², yielding to sulfoxides, an important class of compounds widely utilized in the pharmaceutical industry and academia^{13,23}. However, the number of reports on molybdenum-based catalysts performing the oxidation of sulfides still remains very limited²⁴.

Simple molybdenum compounds, such as Na₂MoO₄ and complex compound, such as, *cis*-MoO₂L₂ [L = (O,O)-donor maltol (3-hydroxy-2-methyl-4-pyrone)] were found to significantly reduce the levels of blood glucose and free fatty acids³. Also, Lord *et al.*²⁵ observed beneficial effects of molybdate treatment on postischaemic cardiac function of diabetic rats. Antitumour activity of molybdenum compounds, especially of Mo₇O₂₄⁶⁻ anion, has been extensively studied and confirmed²⁶. Connected to that, several modes of antineoplastic action were hypothesised²⁷. The polyoxomolybdenum anion has received a lot of interest with their potential applications in catalysis, solid-state technology and medicine including antitumour and anti-virus (HIV) activity^{28,29}.

Recent reports from our laboratory described the synthesis and characterization of some *cis*-dioxomolybdenum(VI) complexes involving (i) Schiff base derivatives of 4-aminoantipyrine³⁰ and some pyrazolone derivatives like 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one, 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (ii) bidentate and tetradentate Schiff bases derived from 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one and certain aromatic amines³¹ and (iii) Schiff base derived from sulpha drugs³² and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, and (iv) chelating ONO donor hydrazones³³.

In view of the diverse and important applications of molybdenum complexes, due to different biological activity of our selected 4-amino-2,3-dimethyl-1-phenyl-2-pyrazolin-5-one Schiff base ligands in the present investigation, and also extending the search for new dioxomolybdenum(VI) complexes in (O,N,O) coordination environment, it was thought of

interest to synthesize and characterize hitherto unknown dioxomolybdenum(VI) complexes of Schiff bases derived from 4-Amino-2,3-Dimethyl-1-Phenyl-2-Pyrazolin-5-One and some β -diketoenolates, viz., N-(*o*-acetoacetotoluidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*o*-aatd-admphpH, I), N-(*o*-acetoacet-anisidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*o*-aans-admphpH, II), N-(acetoacetanilidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (aaa-admphpH, III), N-(methylacetoacetidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (meacac-admphpH, IV), N-(ethylacetoacetidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (etacac-admphpH, V) (Fig.1).

EXPERIMENTAL

Materials used

4-Amino-2,3-dimethyl-1-phenyl-2-pyrazolin-5-one (admphp), acetylacetone, nitric acid, methyl acetoacetate and ethyl acetoacetate were the products of Thomas Baker (Chemicals) Ltd., Mumbai. The other β -diketoenolates, viz., *o*-acetoacetotoluidide and *o*-acetoacetanisidide were products of Aldrich Chemical Company, Inc., U. S. A. Acetoacetanilide was a product of Central Drug House Ltd., Delhi, while ammonium molybdate tetrahydrate was purchased from Sisco Chem. Industries, Mumbai. All other chemicals used were of analytical reagent grade.

Preparation the parent compound

The parent compound bis(acetylacetonato)dioxomolybdenum(VI), $[\text{MoO}_2(\text{acac})_2]$ was prepared by the method of Chen *et al.*¹⁹ as follows:

Ammonium molybdate (30 g.) was dissolved in 100-125 mL. of water and acetylacetone (40 mL.) was added into it drop by drop with stirring in 15-20 min. The pH of the solution was adjusted to 3.5 with 10% HNO_3 solution, with stirring. The mixture was ice-cooled while stirring. After 1.5 h., greenish yellow $[\text{MoO}_2(\text{acac})_2]$ was isolated by filtration and washed with water followed by ether and dried *in vacuo*.

Preparation the Schiff base ligands

4-Amino-2,3-dimethyl-1-phenyl-2-pyrazolin-5-one (0.406 g, 2 mmol.) was weighed and dissolved in 10 mL of ethanol by warming. Then β -diketoenolate [*o*-acetoacetotoluidide, 0.382 g, 2 mmol) *o*-acetoacetanisidide, (0.414 g, 2 mmol) acetoacetanilide (0.354 g, 2 mmol), methyl acetoacetate (0.214 mL, 2 mmol) or ethyl acetoacetate (0.254 mL, 2 mmol) was taken and dissolved in 10 mL ethanol. The above two solutions were mixed and the resulting dark red solution was refluxed over a hot plate having a magnetic stirrer for about 4-5 hrs. The Schiff base ligand started appearing for the first three β -diketoenolates, viz., *o*-acetoacetotoluidide, *o*-acetoacetanisidide and acetoacetanilide. After cooling they were suction filtered and washed several times with 1:1 ethanol: water. For other two β -diketoenolates (methyl acetoacetate and ethyl acetoacetate) after 6 h. of reflux, the solution was kept in china dish which when concentrated gave the respective Schiff base ligand. This was suction filtered and washed with 1:1 ethanol-water solution. The characterization data of the Schiff base ligands are given in Table 1.

Synthesis of complexes

The following general procedure was used in the synthesis of all the complexes. The Schiff base ligand, *o*-aatd-admphpH (0.752 g, 2 mmol), *o*-aans-admphpH (0.784 g, 2 mmol), aaa-admphpH (0.724g, 2 mmol), meacac-admphpH (0.602g, 2 mmol) or etacac-admphpH (0.630g, 2 mmol) was dissolved by heating in 20 mL of ethanol. To this solution, an ethanolic solution (10 mL) of bis(acetylacetonato)dioxomolybdenum(VI) (0.326 g, 1 mmol) was

added. The resulting solution was refluxed for 10-12 h and then concentrated to half of its volume. The precipitate so obtained was suction filtered and washed several times using 1:1 ethanol-water and dried *in vacuo*. The analytical data of the complexes are given in Table 3.

Analyses

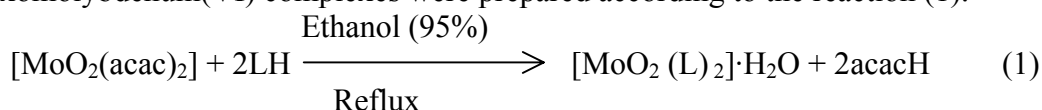
Carbon, hydrogen and nitrogen were determined micro-analytically at Central Drug Research Institute, Lucknow. The molybdenum content in each chelate was determined gravimetrically as MoO_3^{34} as follows. A weighed amount (~200 mg) of the chelate was first decomposed by heating with concentrated nitric acid and then strongly heating the residue over 500 °C for 40 minutes until constant weight was obtained. The residue was weighed as MoO_3 .

Physical methods

Electronic spectra of the complexes were recorded in dimethylformamide on an ATI Unicam UV-2-100 UV/Visible spectrophotometer in our Department. Magnetic measurement was performed by the Vibrating Sample Magnetometer method at SAIF, I. I. T Chennai. ^1H NMR spectra of compounds were recorded in DMSO-d_6 at SAIF, I. I. T Mumbai. The solid-state infrared spectra were recorded in nujol mulls on a Perkin Elmer model 1620 FT-IR Spectrophotometer at SAIF, CDRI, Lucknow. Conductance measurements were performed at room temperature in dimethylformamide using a Toshniwal Conductivity Bridge and dip-type cell with a smooth platinum electrode of a cell constant 1.02. Decomposition temperatures of the Schiff bases and chelates were recorded using an electrothermal apparatus having the capacity to record temperature up to 360°C. Thermogravimetry of the samples was done at SAIF, I. I. T, Mumbai.

RESULTS AND DISCUSSION

The dioxomolybdenum(VI) complexes were prepared according to the reaction (1).



Where LH = *o*-aatd-admphpH (1), *o*-aans-admphpH (2), aaa-admphpH (3), meacac-admphpH (4) or etacac-admphpH (5)

The synthesized complexes are coloured, non-hygroscopic and air-stable solids. They are soluble in dimethylformamide and dimethylsulphoxide, and insoluble in all other common organic solvents. Some physical properties of the complexes are given in Table 3. The resulting complexes were characterized using the following physical studies.

Infrared spectra

The admphp based Schiff base ligands used in the present investigation were synthesized by the scheme as shown in Fig.1.

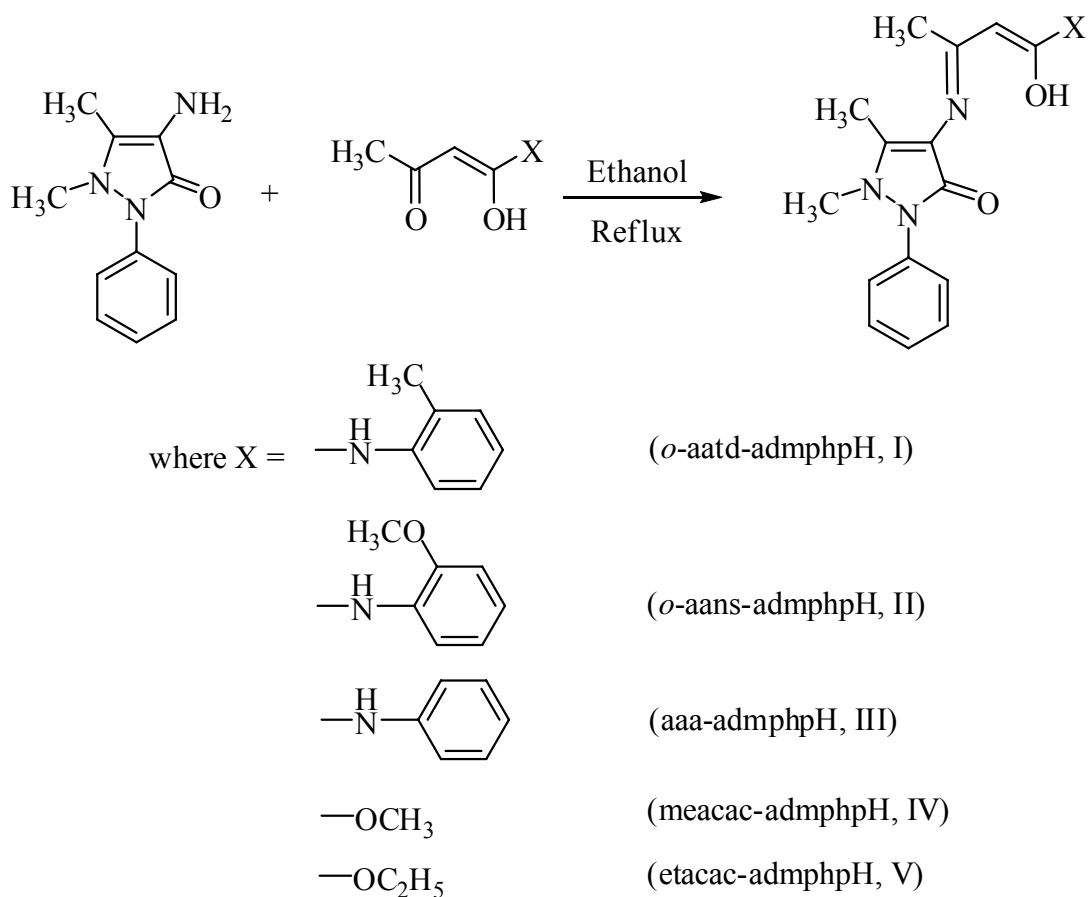
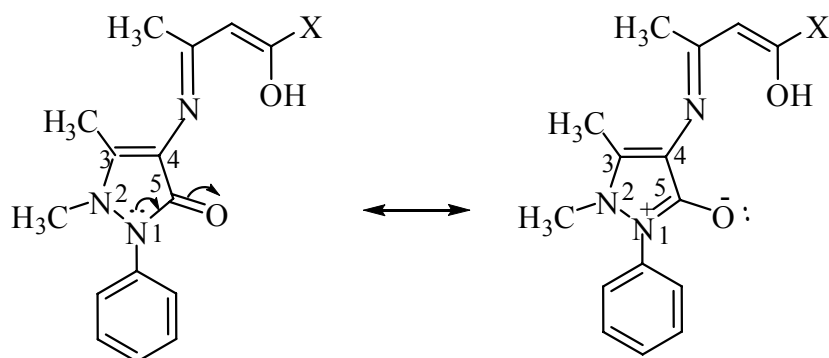


Fig.1. Reaction showing synthesis of Schiff base ligands.

The formation of the Schiff base ligands is consistent with the microanalytical data of the ligands. The C, H and N data, decomposition temperatures, colors, % yield and important infrared spectral bands are given in Tables 1 and 2. The formation of the Schiff base ligands is supported by the appearance of a strong band at $1613\text{-}1625\text{ cm}^{-1}$ due to $\nu(\text{C}=\text{N})$ (azomethine) in the IR spectra of these ligands. The presence of a strong band at $1650\text{-}1675\text{ cm}^{-1}$ is assigned to $\nu(\text{CO})$ (cyclic) of the admphp moiety in these ligands. The appearance of a fine structured broad band due to νOH centered at $3453\text{-}3485\text{ cm}^{-1}$ suggests that these ligands exist in enol form in the solid state. This is further supported by the appearance of a medium band at $1136\text{-}1160\text{ cm}^{-1}$ assignable to $\nu(\text{C}-\text{O})$ (enolic)³⁵.

The important infrared spectral bands of the complexes along with their tentative assignments are given in Table 4. All the Schiff base ligands used in this investigation exist in enol form as discussed above. Hence, they possess five or six potential donor sites: (i) the ring nitrogen N_1 , (ii) the ring nitrogen N_2 , (iii) the cyclic carbonyl oxygen, (iv) azomethine nitrogen, (v) enolic oxygen of β -diketone moiety, and (vi) the anilide N in case of ligands (I), (II) or (III).

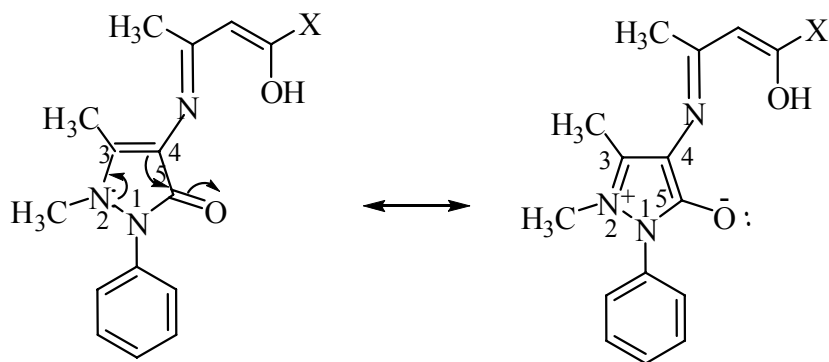
The coordination of the ring nitrogen N_1 is unlikely because of the presence of a bulky phenyl group attached to it. Moreover, the coordination of N_1 is also unfavorable due to the possible Zwitterion formation on account of cyclic amide group³⁶ and thereby lowering the basicity of N_1 and enhancing the basicity of cyclic carbonyl oxygen as shown below in Scheme 1.



Scheme 1. Zwitterion formation due to cyclic amide in 3-pyrazolin-5-one skeleton

Considering the planarity of ligands, the coordination of ring nitrogen N_2 is also unlikely because of being on the backside of the suitable donor sites, (iii), (iv) and (v) with reference to the details of donor sites given above. Moreover, the coordination of the ring nitrogen N_2 is also unfavorable due to the presence of bulky CH_3 group over that and also due to possible Zwitterion formation on account of conjugation³⁶ and thereby lowering the basicity of N_2 , and again enhancing the basicity of cyclic carbonyl oxygen, as shown in Scheme 2.

For the facile synthesis of these complexes along with the elimination of acacH , the driving force³² for the completion of reaction (1) is the better donating capability of the admphp Schiff bases compared to weak³⁷ acetylacetonate ligand. We have already reported such a result in the synthesis of dioxomolybdenum(VI) complexes³⁸ with hydrazones derived from acid hydrazides and furfural or thiophene-2-aldehyde using $[\text{MoO}_2(\text{acac})_2]$ as a precursor.



Scheme 2. Zwitterion formation due to conjugation in 3-pyrazolin-5-one skeleton

The MoO_2^{2+} moiety prefers to form a *cis*-dioxo grouping due to the maximum utilization of the d-orbital for bonding. The dioxo-configuration is characterized by two infrared active modes of $\nu_{\text{as}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{Mo}=\text{O})$ in C_{2v} symmetry. The *trans*- MoO_2^{2+} moiety would exhibit a

single infrared active stretching band of $\nu_{as}(\text{O}=\text{Mo}=\text{O})$. The presence of two infrared bands in the 899-910 and 940-949 cm^{-1} regions due to $\nu_{as}(\text{O}=\text{Mo}=\text{O})$ and $\nu_s(\text{O}=\text{Mo}=\text{O})$, respectively, in the present complexes is strong indicative of the *cis*- MoO_2^{2+} structure⁴.

The IR spectra of these ligands exhibit a strong band at 1613-1625 cm^{-1} , assignable to $\nu(\text{C}=\text{N})$ (azomethine). In the spectra of the respective complexes, this band is shifted to lower frequency³² and appears at 1574-1590 cm^{-1} . This suggests the coordination of the azomethine nitrogen to the MoO_2^{2+} moiety.

For a carbonyl donor, a significant shift of $\nu(\text{CO})$ to lower wave number takes place because of the coordination through carbonyl oxygen. The $\nu(\text{CO})$, for the cyclic carbonyl group at 1675, 1660, 1650, 1664 and 1675 cm^{-1} in uncoordinated Schiff base ligands I, II, III, IV and V, respectively, is shifted to lower wave numbers and appears at 1642, 1627, 1637, 1642 and 1632 cm^{-1} in the respective complexes (see Table 4). This indicates that the cyclic carbonyl oxygen³⁹ is bonded to MoO_2^{2+} moiety in these complexes.

The coordination of the enolic oxygen after deprotonation should be reflected by the disappearance of a broad band centered at 3453-3485 cm^{-1} present in the IR spectra of the ligands (*vide supra*). But due to the presence of a broad band (*vide infra*) for lattice water in the complexes, it is difficult to confirm with certainty regarding the coordination of the enolic oxygen after deprotonation. However, such coordination is supported by the shifting of the $\nu(\text{C}-\text{O})$ (enolic) mode to higher³⁵ wave numbers (see Table 4) in the complexes compared to $\nu(\text{C}-\text{O})$ (enolic) mode of the respective ligands (see Table 2). The presence of a broad band centered at 3475-3547 cm^{-1} may be due to the $\nu(\text{OH})$ mode of the lattice water present in all the complexes.

Electronic spectra

Electronic spectra of all the complexes were recorded in 10^{-3} M dimethylformamide solutions. The compounds, namely, (1), (2) and (4) display only one peak in the range 289-292 nm while the compound (3) displays two peaks at 289 and 331 nm. The compound (5) exhibits three peaks at 280, 289 and 326 nm. Considering the intensity of these transitions, two types of peak assignments, namely, intraligand transition and ligand to metal charge transfer transition seem to be relevant as per the assignments given in the Table 5. The ligand to metal charge transfer transition takes place between the highest occupied ligand molecular orbital and the lowest empty molybdenum d-orbital. This result is comparable with the results reported elsewhere³² for dioxomolybdenum(VI) complexes.

Molar conductance measurements:

The molar conductivities of the complexes in 10^{-3} M DMF solutions are in the range of 8.0-12.1 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, as expected for non-electrolytes⁴⁰. The non-zero molar conductance values are most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligand and change of electrolyte type.

Magnetic measurements

All the complexes, as expected for complexes of dioxomolybdenum(VI), are diamagnetic.

¹HNMR spectra

The ¹HNMR spectra of two representative compounds namely, $[\text{MoO}_2(\text{aatd-admphp})_2]\cdot\text{H}_2\text{O}$ (1) and $[\text{MoO}_2(\text{meacac-admphp})_2]\cdot\text{H}_2\text{O}$ (4) are recorded in DMSO-d₆. The compound (4) displayed a multiplet proton signal due to aromatic protons of the phenyl group at 7.27-7.50 ppm. The proton signals at 5.68, 3.34, 2.83, 2.50 and 2.15 ppm. are most probably due

to proton groups such as $-\text{OCH}_3$ (e), $-\text{NCH}_3$ (a) $-\text{CH}=\text{C}(\text{H})-$ (d), $-\text{CH}_3$ (b) $-\text{CH}_3$ (c), respectively, present in this compound. The indexing of various proton groups are given in the following Fig. 2 (a).

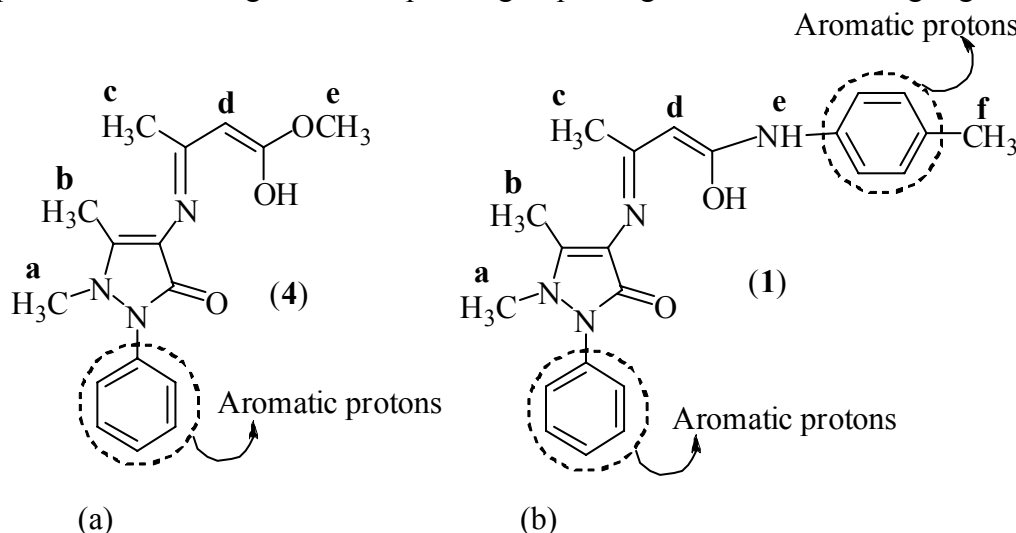


Fig. 2. Indexing of various protons in compounds (1) and (4)

The absence of a proton signals around 12 ppm in the complex suggests the absence of any hydroxyl proton, and hence it concludes the coordination of enolic oxygen of the ligand after deprotonation. The compound (1) also exhibited almost similar pattern of proton signals, the indexing of which is given in the following Fig. 2 (b). Unfortunately, the proton signal of $-\text{NHC}_6\text{H}_4-$ could not be detected. Similar to compound (4), the absence of a proton signal around 12 ppm in the complex indicates the absence of any hydroxyl proton, and hence again concludes the coordination of enolic oxygen of the ligand after deprotonation.

Thermogravimetric analyses

One of the representative compounds, namely, $[\text{MoO}_2(\text{aatd-admphp})_2] \cdot \text{H}_2\text{O}$ (1) was subjected to thermogravimetric analysis. Thermogram of this compound shows a weight loss of 1.9% (calcd. 2.0%, assuming weight loss for 1 mole of H_2O molecule per mole of the compound) at 98°C . This may be due to the presence of one lattice⁴¹ water in this complex. This is consistent with the infrared spectral data (vide supra). Unfortunately, the other weight losses could not be correlated due to unknown fragmentation of the bulky ligand molecule.

3D-Molecular Modeling and Analysis:

Based on the proposed structures (Fig. 4), the 3D molecular modeling of one of the representative compounds, viz., $[\text{MoO}_2(\text{aaa-admphp})_2] \cdot \text{H}_2\text{O}$ (3) was carried out by the CS Chem 3D Ultra Molecular Modeling and Analysis Programme⁴². The details of bond lengths and bond angles as per the 3D structure (Fig. 3), are given in Table 6 and 7, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the compound in question are numbered in Arabic numerals. In all, 280 measurements of the bond lengths (96 in number), plus the bond angles (184 in number) are listed in the Tables. Except few cases, optimal values of both the bond lengths and the bond angles are given in the Tables along with the actual ones. The actual bond lengths/bond angles given in Tables 6/7 are calculated values as a result of energy optimization in CHEM 3D Ultra, while the optimal bond length/optimal bond angle values are the most desirable/favourable (standard) bond lengths/bond angles established

by the builder unit of the CHEM 3D Ultra. The missing of some values of standard bond lengths/bond angles may be due to the limitations of the software, which we had already noticed in modeling of other systems^{43,44}. In most of the cases, the observed bond lengths and bond angles are close to the optimal values, and thus the proposed structure of compound **3** (and also others) is acceptable

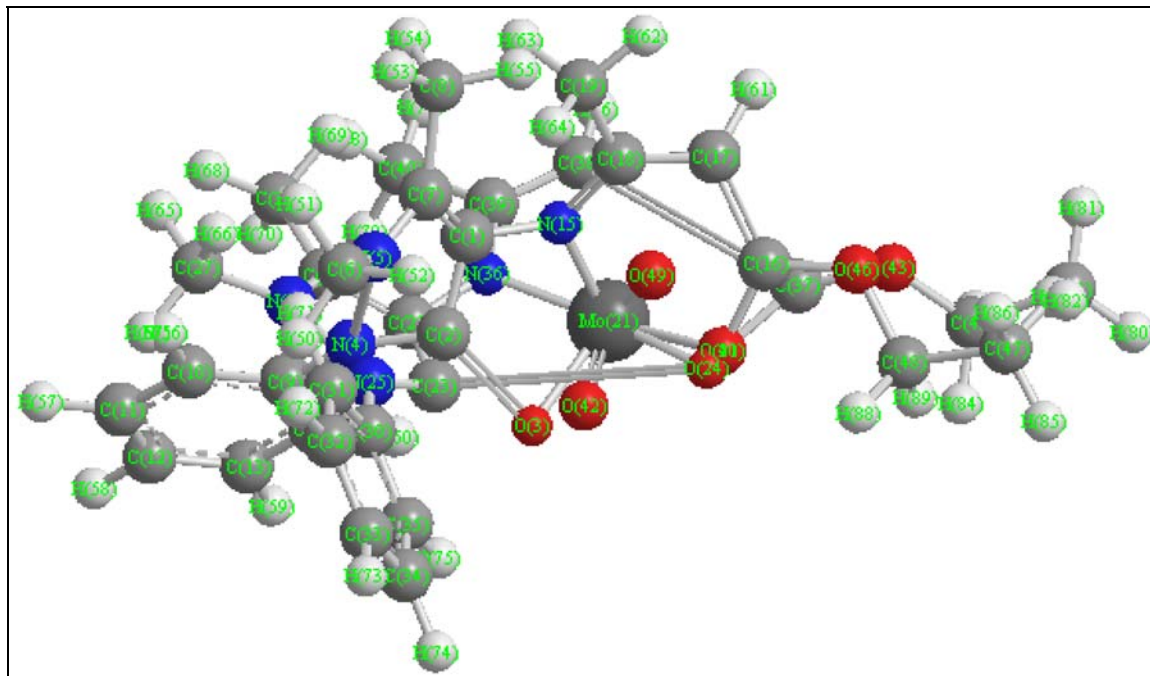


Fig. 3: 3D-structure of $[\text{MoO}_2(\text{aaa-admphp})_2] \cdot \text{H}_2\text{O}$ (**3**). Out of six coordinating oxygens, two oxygens (O_{41} and O_{20}) are overlapping near O_{24} .

CONCLUSION

The satisfactory analytical data and all the results presented above suggest that the resulting complexes are of the compositions $[\text{MoO}_2(\text{L})_2] \cdot \text{H}_2\text{O}$ where LH = N-(*o*-acetoacetotoluidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*o*-aatd-admphpH, I), N-(*o*-acetoacetanisidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (*o*-aans-admphpH, II), N-(acetoacetanilidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (aaa-admp-hpH, III), N-(methylacetoacetidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (meacac-admphpH, IV) or N-(ethylacetoacetidene)-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (etacac-admphpH, V). The tentative octa-coordinated structures proposed for these complexes are shown in the Fig. 4. X-ray crystallographic studies, which might confirm the proposed structures, could not be carried out, as we failed to grow crystals of any of these complexes.

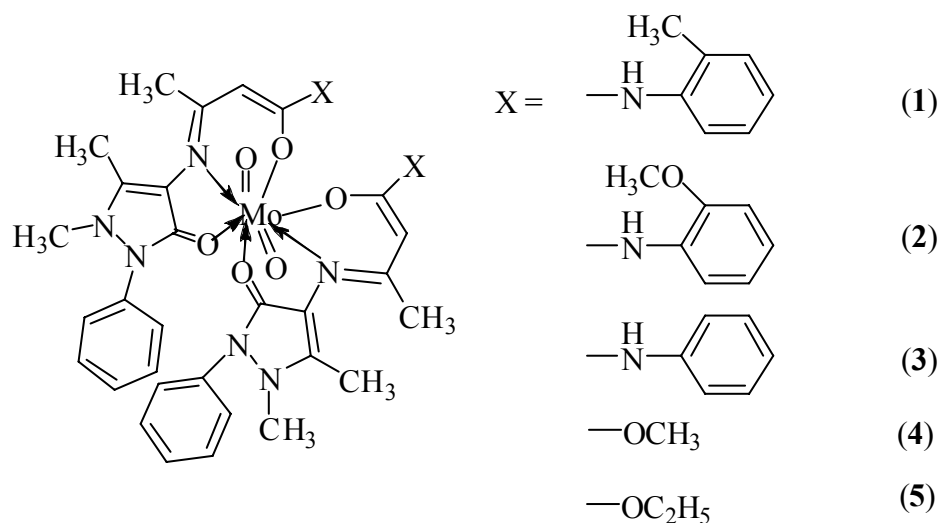


Fig. 4. Proposed octacoordinate structure of complexes

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Table 1. Characterization data of the synthesized ligands

S. No.	Ligands (Empirical Formula)(F.W)	Found (Calcd.), %			Colour	Decomp. Temp.(°C)
		C	H	N		
I	<i>o</i> -aatd-admphpH (C ₂₂ H ₂₄ N ₄ O ₂) (376)	70.62 (70.21)	6.10 (6.38)	14.57 (14.89)	Macrame	145
II	<i>o</i> -aans-admphpH (C ₂₂ H ₂₄ N ₄ O ₃) (392)	67.14 (67.35)	6.34 (6.12)	14.56 (14.29)	Sugarcane	195
III	aaa-admphpH (C ₂₁ H ₂₂ N ₄ O ₂) (362)	69.34 (69.61)	6.22 (6.08)	15.21 (15.47)	Spl. off-cream	195
IV	meacac-admphpH (C ₁₆ H ₁₉ N ₃ O ₃)(301)	63.45 (63.79)	6.45 (6.31)	13.76 (13.95)	Straw	125
V	etacac-admphpH (C ₁₇ H ₂₁ N ₃ O ₃) (315)	64.43 (64.76)	6.32 (6.67)	13.10 (13.33)	Bone white	120

Table 2. Important IR spectral bands (cm⁻¹) of the Ligands

S. No.	Ligand	v(C=O) (cyclic)	v(C=N) (azometh.)	v(C-O) (enolic)	v(OH)	v(NH)
I	<i>o</i> -aatd-admphpH	1675	1625	1143	3466	3300
II	<i>o</i> -aans-admphpH	1660	1620	1155	3460	3315
III	aaa-admphpH	1650	1617	1160	3485	3383
IV	meacac-admphpH	1664	1613	1157	3450	-
V	etacac-admphpH	1675	1616	1136	3443	-

Table 3. Characterization data of the synthesized complexes

S. No.	Complexes (Empirical Formula, F. W.)	Found (Calcd.), %				Colour	Decomp. Temp.(°C)	Yield (%)	Λ_m ($\Omega^{-1}\text{cm}^2\text{-mol}^{-1}$)
		C	H	N	Mo				
(1)	[MoO ₂ (<i>o</i> -aatd-admphp) ₂].H ₂ O (C ₄₄ H ₄₈ N ₈ O ₇ Mo) (895.94)	58.56 (58.93)	5.12 (5.36)	12.79 (12.50)	10.54 (10.71)	Mushroom	210	50	12.1
(2)	[MoO ₂ (<i>o</i> -aans-admphp) ₂].H ₂ O (C ₄₄ H ₄₈ N ₈ O ₉ Mo) (927.94)	56.76 (56.90)	5.36 (5.17)	12.34 (12.07)	10.57 (10.34)	Mist grey	220	45	10.5
(3)	[MoO ₂ (aaa-admphp) ₂].H ₂ O (C ₄₂ H ₄₄ N ₈ O ₇ Mo) (867.94)	58.35 (58.07)	5.26 (5.07)	12.35 (12.90)	11.25 (11.05)	Venetian green	195	44	10.0
(4)	[MoO ₂ (meacac-admphp) ₂].H ₂ O (C ₃₂ H ₃₈ N ₆ O ₉ Mo) (745.94)	51.21 (51.48)	5.28 (5.09)	11.46 (11.26)	12.54 (12.86)	Mist grey	195	40	8.0
(5)	[MoO ₂ (etacac-admphp) ₂].H ₂ O (C ₃₄ H ₄₂ N ₆ O ₉ Mo) (773.94)	52.34 (52.72)	5.74 (5.43)	10.56 (10.85)	12.73 (12.40)	Summer sand	220	40	9.0

Table 4. Important IR spectral bands of the synthesized complexes

S. No	Complexes	$\nu(\text{C}=\text{O})$ (cyclic)	$\nu(\text{C}=\text{N})$ (azometh.)	$\nu(\text{C}-\text{O})$ (enolic)	$\nu_s(\text{O}=\text{Mo}=\text{O})$	$\nu_{as}(\text{O}=\text{Mo}=\text{O})$	$\nu(\text{H}_2\text{O})$
(1)	$[\text{MoO}_2(o\text{-aatd-admphp})_2]\cdot\text{H}_2\text{O}$	1642	1590	1164	939	839	3531
(2)	$[\text{MoO}_2(o\text{-aans-admphp})_2]\cdot\text{H}_2\text{O}$	1627	1590	1174	940	890	3475
(3)	$[\text{MoO}_2(\text{aaa-admphp})_2]\cdot\text{H}_2\text{O}$	1637	1582	1169	945	899	3531
(4)	$[\text{MoO}_2(\text{meacac-admphp})_2]\cdot\text{H}_2\text{O}$	1642	1590	1164	945	899	3547
(5)	$[\text{MoO}_2(\text{etacac-admphp})_2]\cdot\text{H}_2\text{O}$	1632	1574	1164	940	904	3547

Table 5. Electronic spectral peaks of synthesized complexes

S. No.	Complexes	λ_{max} (nm)	ν (cm^{-1})	(ϵ , litre $\text{mol}^{-1} \text{cm}^{-1}$)	Peak Assignment
(1)	$[\text{MoO}_2(o\text{-aatd-admphp})_2]\cdot\text{H}_2\text{O}$	291	34364	3356	Intraligand transition
(2)	$[\text{MoO}_2(o\text{-aans-admphp})_2]\cdot\text{H}_2\text{O}$	289	34602	3377	Intraligand transition
(3)	$[\text{MoO}_2(\text{aaa-admphp})_2]\cdot\text{H}_2\text{O}$	289 331	34602 30211	3481 6200	Intraligand transition Ligand \rightarrow metal charge transfer transition
(4)	$[\text{MoO}_2(\text{meacac-admphp})_2]\cdot\text{H}_2\text{O}$	292	34246	3387	Intra ligand transition
(5)	$[\text{MoO}_2(\text{etacac-admphp})_2]\cdot\text{H}_2\text{O}$	280 289 326	35714 34602 30674	3484 3544 5097	Intraligand transition Intra ligand transition Ligand \rightarrow metal charge transfer transition

Table 6. Various bond lengths of compound $[\text{MoO}_2(\text{aaa-admphp})_2]\cdot\text{H}_2\text{O}$ (3)

S. No.	Atoms	Actual Bond length	Optimal Bond length	S. No.	Atoms	Actual Bond length	Optimal Bond length
1	C(48)-H(89)	1.113	1.111	49	C(22)-N(36)	1.266	-
2	C(48)-H(88)	1.113	1.111	50	C(22)-C(28)	1.337	1.337
3	C(47)-H(87)	1.113	1.113	51	C(22)-C(23)	1.337	1.517
4	C(47)-H(86)	1.113	1.113	52	Mo(21)-O(49)	1.2921	-
5	C(47)-H(85)	1.113	1.113	53	N(36)-Mo(21)	1.976	-
6	C(47)-C(48)	1.523	1.514	54	Mo(21)-O(42)	1.5397	-
7	O(46)-C(48)	1.402	1.389	55	Mo(21)-O(24)	1.94	-
8	C(45)-H(84)	1.113	1.111	56	O(41)-Mo(21)	1.94	-
9	C(45)-H(83)	1.113	1.111	57	O(20)-Mo(21)	1.94	-
10	C(44)-H(82)	1.113	1.113	58	C(19)-H(64)	1.113	1.113
11	C(44)-H(81)	1.113	1.113	59	C(19)-H(63)	1.113	1.113
12	C(44)-H(80)	1.113	1.113	60	C(19)-H(62)	1.113	1.113
13	C(44)-C(45)	1.523	1.514	61	C(18)-C(19)	1.497	1.497
14	O(43)-C(45)	1.402	1.389	62	C(17)-H(61)	1.1	1.1
15	C(40)-H(79)	1.113	1.113	63	C(17)-C(18)	1.337	1.503
16	C(40)-H(78)	1.113	1.113	64	C(16)-O(46)	1.355	1.355
17	C(40)-H(77)	1.113	1.113	65	C(16)-O(20)	1.355	1.355
18	C(39)-C(40)	1.497	1.497	66	C(16)-C(17)	1.592	1.337
19	C(38)-H(76)	1.1	1.1	67	N(15)-Mo(21)	1.976	-
20	C(38)-C(39)	1.337	1.503	68	N(15)-C(18)	1.266	-
21	O(43)-C(37)	1.355	1.355	69	C(14)-H(60)	1.1	1.1
22	C(37)-O(41)	1.355	1.355	70	C(13)-H(59)	1.1	1.1
23	C(37)-C(38)	4.446	1.337	71	C(13)-C(14)	1.337	1.42
24	N(36)-C(39)	1.266	-	72	C(12)-H(58)	1.1	1.1
25	C(35)-H(75)	1.1	1.1	73	C(12)-C(13)	1.337	1.42
26	C(34)-H(74)	1.1	1.1	74	C(11)-H(57)	1.1	1.1
27	C(34)-C(35)	1.337	1.42	75	C(11)-C(12)	1.337	1.42
28	C(33)-H(73)	1.1	1.1	76	C(10)-H(56)	1.1	1.1
29	C(33)-C(34)	1.337	1.42	77	C(10)-C(11)	1.337	1.42
30	C(32)-H(72)	1.1	1.1	78	C(9)-C(14)	1.337	1.42
31	C(32)-C(33)	1.337	1.42	79	C(9)-C(10)	1.337	1.42
32	C(31)-H(71)	1.1	1.1	80	C(8)-H(55)	1.113	1.113
33	C(31)-C(32)	1.337	1.42	81	C(8)-H(54)	1.113	1.113
34	C(30)-C(35)	1.337	1.42	82	C(8)-H(53)	1.113	1.113
35	C(30)-C(31)	1.337	1.42	83	C(7)-C(8)	1.497	1.497
36	C(29)-H(70)	1.113	1.113	84	C(6)-H(52)	1.113	1.113
37	C(29)-H(69)	1.113	1.113	85	C(6)-H(51)	1.113	1.113
38	C(29)-H(68)	1.113	1.113	86	C(6)-H(50)	1.113	1.113
39	C(28)-C(29)	1.497	1.497	87	N(5)-C(7)	1.266	1.462
40	C(27)-H(67)	1.113	1.113	88	N(5)-C(6)	1.47	1.47
41	C(27)-H(66)	1.113	1.113	89	N(4)-C(9)	1.266	1.345
42	C(27)-H(65)	1.113	1.113	90	N(4)-N(5)	2.3505	-
43	N(26)-C(28)	1.266	1.462	91	O(3)-Mo(21)	1.94	-
44	N(26)-C(27)	1.47	1.47	92	C(2)-N(4)	1.266	1.369

45	N(25)-C(30)	1.266	1.345	93	C(2)-O(3)	1.816	-
46	N(25)-N(26)	1.6127	-	94	C(1)-N(15)	1.266	-
47	C(23)-N(25)	1.266	1.369	95	C(1)-C(7)	1.337	1.337
48	C(23)-O(24)	3.7427	-	96	C(1)-C(2)	1.337	1.517

Table 7. Various bond angles of compound $[\text{MoO}_2(\text{aaa-admphp})_2] \cdot \text{H}_2\text{O}$ (3)

S. No.	Atoms	Actual Bond Angles	Optimal Bond Angles	S. No.	Atoms	Actual Bond Angles	Optimal Bond Angles
1	H(87)-C(47)-H(86)	109.5201	109	93	H(58)-C(12)-C(13)	119.9998	120
2	H(87)-C(47)-H(85)	109.4623	109	94	H(58)-C(12)-C(11)	120.0005	120
3	H(87)-C(47)-C(48)	109.4618	110	95	C(13)-C(12)-C(11)	119.9997	-
4	H(86)-C(47)-H(85)	109.4418	109	96	H(57)-C(11)-C(12)	119.9994	120
5	H(86)-C(47)-C(48)	109.4414	110	97	H(57)-C(11)-C(10)	120.0003	120
6	H(85)-C(47)-C(48)	109.5	110	98	C(12)-C(11)-C(10)	120.0003	-
7	H(89)-C(48)-H(88)	109.5199	109.4	99	H(60)-C(14)-C(13)	119.9999	120
8	H(89)-C(48)-C(47)	109.4616	109.41	100	H(60)-C(14)-C(9)	120.0003	120
9	H(89)-C(48)-O(46)	109.4615	106.7	101	C(13)-C(14)-C(9)	119.9997	-
10	H(88)-C(48)-C(47)	109.4422	109.41	102	H(56)-C(10)-C(11)	119.9997	120
11	H(88)-C(48)-O(46)	109.442	106.7	103	H(56)-C(10)-C(9)	120.0006	120
12	C(47)-C(48)-O(46)	109.5	107.4	104	C(11)-C(10)-C(9)	119.9997	-
13	H(82)-C(44)-H(81)	109.5202	109	105	C(37)-O(41)-Mo(21)	109.5	-
14	H(82)-C(44)-H(80)	109.4618	109	106	C(39)-N(36)-C(22)	128.9981	-
15	H(82)-C(44)-C(45)	109.462	110	107	C(39)-N(36)-Mo(21)	119.9985	-
16	H(81)-C(44)-H(80)	109.4419	109	108	C(22)-N(36)-Mo(21)	110.9999	-
17	H(81)-C(44)-C(45)	109.4417	110	109	C(23)-O(24)-Mo(21)	38.4005	-
18	H(80)-C(44)-C(45)	109.4997	110	110	Mo(21)-O(20)-C(16)	109.4999	-
19	H(84)-C(45)-H(83)	109.5201	109.4	111	H(64)-C(19)-H(63)	109.52	109
20	H(84)-C(45)-C(44)	109.462	109.41	112	H(64)-C(19)-H(62)	109.4624	109
21	H(84)-C(45)-O(43)	109.4616	106.7	113	H(64)-C(19)-C(18)	109.4614	110
22	H(83)-C(45)-C(44)	109.4421	109.41	114	H(63)-C(19)-H(62)	109.4423	109
23	H(83)-C(45)-O(43)	109.4416	106.7	115	H(63)-C(19)-C(18)	109.4415	110
24	C(44)-C(45)-O(43)	109.4999	107.4	116	H(62)-C(19)-C(18)	109.4997	110
25	C(45)-O(43)-C(37)	119.9998	110.8	117	H(61)-C(17)-C(18)	124.4386	120
26	O(43)-C(37)-O(41)	138.4365	-	118	H(61)-C(17)-C(16)	124.4392	120
27	O(43)-C(37)-C(38)	138.4364	124.3	119	C(18)-C(17)-C(16)	111.1223	-
28	O(41)-C(37)-C(38)	83.127	124.3	120	C(19)-C(18)-C(17)	120	121.4
29	H(74)-C(34)-C(35)	120.0002	120	121	C(19)-C(18)-N(15)	120.0004	-
30	H(74)-C(34)-C(33)	119.9996	120	122	C(17)-C(18)-N(15)	119.9996	-
31	C(35)-C(34)-C(33)	120.0001	-	123	C(14)-C(9)-C(10)	120.0006	120
32	H(73)-C(33)-C(34)	120.0005	120	124	C(14)-C(9)-N(4)	120	120
33	H(73)-C(33)-C(32)	119.9992	120	125	C(10)-C(9)-N(4)	119.9994	120
34	C(34)-C(33)-C(32)	120.0003	-	126	H(52)-C(6)-H(51)	109.5199	109
35	H(72)-C(32)-C(33)	120.0005	120	127	H(52)-C(6)-H(50)	109.4617	109
36	H(72)-C(32)-C(31)	119.9998	120	128	H(52)-C(6)-N(5)	109.4617	-

37	C(33)-C(32)-C(31)	119.9997	-	129	H(51)-C(6)-H(50)	109.4419	109
38	H(75)-C(35)-C(34)	119.9999	120	130	H(51)-C(6)-N(5)	109.442	-
39	H(75)-C(35)-C(30)	120.0003	120	131	H(50)-C(6)-N(5)	109.5001	-
40	C(34)-C(35)-C(30)	119.9998	-	132	H(55)-C(8)-H(54)	109.5197	109
41	H(71)-C(31)-C(32)	120.0003	120	133	H(55)-C(8)-H(53)	109.4613	109
42	H(71)-C(31)-C(30)	119.9999	120	134	H(55)-C(8)-C(7)	109.4619	110
43	C(32)-C(31)-C(30)	119.9999	-	135	H(54)-C(8)-H(53)	109.4418	109
44	C(35)-C(30)-C(31)	120.0003	120	136	H(54)-C(8)-C(7)	109.4424	110
45	C(35)-C(30)-N(25)	119.9996	120	137	H(53)-C(8)-C(7)	109.5003	110
46	C(31)-C(30)-N(25)	120	120	138	C(7)-N(5)-C(6)	136.1024	108
47	H(67)-C(27)-H(66)	109.52	109	139	C(7)-N(5)-N(4)	87.7951	-
48	H(67)-C(27)-H(65)	109.4616	109	140	C(6)-N(5)-N(4)	136.1025	-
49	H(67)-C(27)-N(26)	109.462	-	141	Mo(21)-N(15)-C(18)	119.9989	-
50	H(66)-C(27)-H(65)	109.4418	109	142	Mo(21)-N(15)-C(1)	111.0001	-
51	H(66)-C(27)-N(26)	109.4417	-	143	C(18)-N(15)-C(1)	128.9976	-
52	H(65)-C(27)-N(26)	109.5002	-	144	C(8)-C(7)-N(5)	124.5001	125.3
53	H(70)-C(29)-H(69)	109.5202	109	145	C(8)-C(7)-C(1)	124.5002	121.4
54	H(70)-C(29)-H(68)	109.4616	109	146	N(5)-C(7)-C(1)	110.9997	120
55	H(70)-C(29)-C(28)	109.4623	110	147	O(49)-Mo(21)-N(36)	124.7376	-
56	H(69)-C(29)-H(68)	109.4419	109	148	O(49)-Mo(21)-O(42)	87.358	-
57	H(69)-C(29)-C(28)	109.442	110	149	O(49)-Mo(21)-O(24)	49.6554	-
58	H(68)-C(29)-C(28)	109.4994	110	150	O(49)-Mo(21)-O(41)	45.7247	-
59	C(28)-N(26)-C(27)	128.2504	108	151	O(49)-Mo(21)-O(20)	45.7247	-
60	C(28)-N(26)-N(25)	103.4988	-	152	O(49)-Mo(21)-N(15)	47.3358	-
61	C(27)-N(26)-N(25)	128.2508	-	153	O(49)-Mo(21)-O(3)	103.3574	-
62	C(29)-C(28)-N(26)	124.5005	125.3	154	N(36)-Mo(21)-O(42)	110.6566	-
63	C(29)-C(28)-C(22)	124.4994	121.4	155	N(36)-Mo(21)-O(24)	165.8938	-
64	N(26)-C(28)-C(22)	111	120	156	N(36)-Mo(21)-O(41)	169.9999	-
65	C(30)-N(25)-N(26)	128.2506	-	157	N(36)-Mo(21)-O(20)	169.9999	-
66	C(30)-N(25)-C(23)	128.2517	122	158	N(36)-Mo(21)-N(15)	80.0001	-
67	N(26)-N(25)-C(23)	103.4977	-	159	N(36)-Mo(21)-O(3)	89.9999	-
68	N(25)-C(23)-O(24)	119.9999	-	160	O(42)-Mo(21)-O(24)	58.8558	-
69	N(25)-C(23)-C(22)	111.0003	112.74	161	O(42)-Mo(21)-O(41)	68.8546	-
70	O(24)-C(23)-C(22)	110.8105	-	162	O(42)-Mo(21)-O(20)	68.8546	-
71	H(79)-C(40)-H(78)	109.5201	109	163	O(42)-Mo(21)-N(15)	89.1791	-
72	H(79)-C(40)-H(77)	109.4616	109	164	O(42)-Mo(21)-O(3)	21.1628	-
73	H(79)-C(40)-C(39)	109.4621	110	165	O(24)-Mo(21)-O(41)	10	-
74	H(78)-C(40)-H(77)	109.4414	109	166	O(24)-Mo(21)-O(20)	10	-
75	H(78)-C(40)-C(39)	109.442	110	167	O(24)-Mo(21)-N(15)	89.9998	-
76	H(77)-C(40)-C(39)	109.5	110	168	O(24)-Mo(21)-O(3)	79.9999	-
77	H(76)-C(38)-C(39)	126.7993	120	169	O(41)-Mo(21)-O(20)	0	-
78	H(76)-C(38)-C(37)	126.7984	120	170	O(41)-Mo(21)-N(15)	89.9998	-
79	C(39)-C(38)-C(37)	106.4023	-	171	O(41)-Mo(21)-O(3)	89.9999	-
80	C(40)-C(39)-C(38)	119.9997	121.4	172	O(20)-Mo(21)-N(15)	89.9998	-
81	C(40)-C(39)-N(36)	119.9999	-	173	O(20)-Mo(21)-O(3)	89.9999	-
82	C(38)-C(39)-N(36)	120.0004	-	174	N(15)-Mo(21)-O(3)	89.9999	-
83	N(36)-C(22)-C(28)	120.0001	-	175	C(9)-N(4)-N(5)	144.67	-
84	N(36)-C(22)-C(23)	111	-	176	C(9)-N(4)-C(2)	144.6696	122

85	C(28)-C(22)-C(23)	110.9999	117.6	177	N(5)-N(4)-C(2)	70.6604	-
86	C(48)-O(46)-C(16)	120.0002	110.8	178	Mo(21)-O(3)-C(2)	90.5513	-
87	O(46)-C(16)-O(20)	117.7324	-	179	N(4)-C(2)-O(3)	120	-
88	O(46)-C(16)-C(17)	117.7327	124.3	180	N(4)-C(2)-C(1)	111	112.74
89	O(20)-C(16)-C(17)	124.5349	124.3	181	O(3)-C(2)-C(1)	121.4167	-
90	H(59)-C(13)-C(14)	119.9998	120	182	N(15)-C(1)-C(7)	120	-
91	H(59)-C(13)-C(12)	120.0001	120	183	N(15)-C(1)-C(2)	110.9998	-
92	C(14)-C(13)-C(12)	120	-	184	C(7)-C(1)-C(2)	111.0002	117.6

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