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Studies on a New Schiff Baselig and H_3 (pte-tsc) synthesized by condensing 7–Acetonyl–xanthopterin [H_2 (pte)] with thiosemicarbazide [H(TSC)] and its molybdenum complexes exhibiting reactivity towards $Me_3N \rightarrow O$, $PyN \rightarrow O$ and PPh_3; crystal structure of 2–pivaloylamino–7–acetonyl–xanthopterin – water (1/1).

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A B S T R A C T

A new Schiff base ligand,H_3 (pte-tsc) was synthesized by the condensation of 7-acetonyl-xanthopterin [H_2(pte)] and thiosemicarbazide [H(tsc)]. The pterin starting material obtained by modifying a published method was characterized through single crystal X-ray diffraction analysis of its 2-pivaloylamino derivative and other data. Three new Mo(IV,V,VI) complexes synthesized using this ligand and characterized by different physico-chemical methods including elemental analysis, ESIMS, Λ_M data, ^{1}H NMR, IR, UV-VIS, fluorescence spectroscopy, CV data and CHEM3D representations. Here the H_3(pte-tsc) ligand acts as a reducing agent, reducing the metal centre of the molybdenum starting materials during synthesis in most cases. These complexes show reactivity towards oxygen atom donor agents, e.g., $Me_3N \rightarrow O$ or $PyN \rightarrow O$ and their kinetics have been studied. They have negative values for entropy of activation [$\Delta S^{\#}$ = (–208.29 to –198.63) J mol^{-1} deg^{-1}], suggesting associative type enzyme-substrate reactions. Kinetic data [e.g., k_{obs}=(3.82×10^{-3} – 71.00×10^{-3}) s^{-1}] are at par with the available literature.

Keywords: Pterin Schiff base, single crystal X-ray structure, Pterin-Mo (IV,V,VI) complexes, Mo-centred O-transfer redox reaction, negative $\Delta S^{\#}$ value.

A R T I C L E I N F O

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1. Introduction

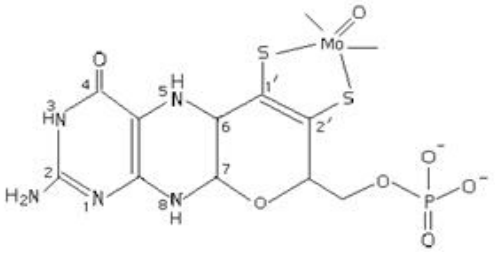
Molybdenum containing enzymes catalyse a wide range of reactions in carbon, sulphur and nitrogen metabolism. Apart from nitrogenase (with a multinuclear active site), the other class of enzymes (nearly 50 such enzymes contain molybdenum in their active sites) generally function catalytically to transfer an oxygen atom either to or from a physiological acceptor/donor molecule[1-5]. In general, these enzymes utilize water as the ultimate source of oxygen in the overall catalytic reaction (equation 1) and the reaction is coupled to electron transfer between substrate X / XO, on Fe – S centre, heme or flavin.

$$X + H_2O \rightleftharpoons XO + 2H^+ + 2e^- \quad \text{------ (1)}$$

Considering the metal centre the overall reaction can be represented by equation (2).

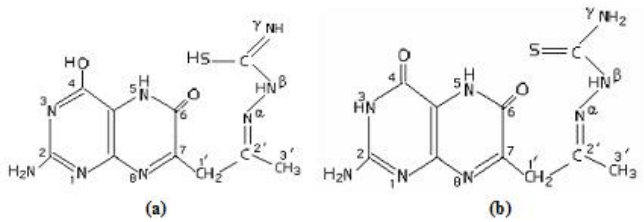
$$X + H_2O + Mo^{VI} \rightleftharpoons Mo^{IV} + XO + 2H^+ \quad \text{------ (2)}$$

The enzymes are referred to as oxotransferases when the substrate is transformed by primary oxygen atom transfer and as hydroxylases when bound or unbound water or hydroxide is directly involved in the substrate transformation reaction. Among others, the oxidation of sulphite to sulphate and the reduction of DMSO to DMS (dimethyl sulphide) can be viewed as oxygen atom (= O, oxo group) transfer reaction. Members of the xanthine oxidase family catalyse the oxidative hydroxylation of a diverse range of aldehydes and aromatic heterocycles in reactions that necessarily involve the cleavage of a C – H bond, e.g., conversion of xanthine to uric acid. Enzymes of this type are characterized by a pterin cofactor having a basic structure as per Scheme 1. Majority of these enzymes possess a Mo=O unit in their active sites; however, some of them do not catalyse oxygen atom transfer (e.g., polysulphide reductase and possibly formate dehydrogenase) and others do not possess a Mo=O unit. The pyranopterin structure (Scheme 1) has been established crystallographically in several cases[1,2, 4,5].



Scheme 1: Pyranopterindithiolate–molybdenum coordination[5]

Considering the composition of the metal centred functional unit (McFU) of oxomolybdoenzymes[1, 2], this paper embodies the synthesis of a new ligand, H_3(pte-tsc), its corresponding molybdenum complexes as well as their reactivity, especially towards the relevant enzyme substrates. This new ligand (Scheme 2a) was synthesized by condensing a 7–substituted pterin [7–acetonyl–xanthopterin, H_2(pte)] with thiosemicarbazide [H(tsc)]. Scheme 2b reflects another tautomeric form of this ligand involving the thiocarbonyl group (S = C <) and NH_2 (γ) as well as the NH (3) and O (4) amide functions:



(Scheme 2)

As far as [H_3(pte-tsc)] ligand is concerned there are three possible de-protonation sites e.g., OH(4), NH(5) and the thiol group [Scheme 2a & 2b]. Actual state of de-protonation of the ligand residue in complex compounds depends on reaction conditions, oxidation state of the metal centre, presence of secondary ligands etc. The optimized bond length and bond angle data of the present systems have been compared with the literature X – ray structural data of related systems.

The notable aspect of the stability of the hydrogen bond between the pterin ligand and its constituent water molecule in (**a**) {[H_2(2-piv-pte)].H_2O} is verified through single crystal X-ray structure determination of 2-pivaloylamino-7-acetonyl-xanthopterin monohydrate. Here the H_2O molecule is bonded to the NH(2) group. This strongly hydrogen bonded H_2O molecule is not removed even during the reaction of 7-acetonyl-xanthopterin with pivalic anhydride. This pivalatedpterin was characterized by other physico-chemical methods in addition to its single crystal X-ray structure determination. Chelating property of this N,O,S – donor Schiff base ligand (Scheme 2a & 2b) towards different molybdenum starting materials, characterization of the resulting complexes isolated in the solid state as well as their reactivity aspects are also delineated.

2. Experimental

General Remarks:

All chemicals were obtained from commercial sources and used as received. Solvents were purified following literature procedures[6]. Spectroscopy grade DMF (SRL Chemical). Bu_4NClO_4 (TBAP) and PyN→O were prepared following literature procedures[7-9]. 7-acetonyl-xanthopterin monohydrate [H_2(pte)].H_2O was prepared in this laboratory[10] (pH,4–4.5). MoO_2 (acac)$_2$, $(Et_4N)_2[MoS_4]$ and $(Bu_4N)_4[Mo_8O_{26}]$ were prepared following published methods [11].

Physical Measurements:

All reactions under N_2in Schlenk technique, elemental analysis (C,H,N) data from the IACS, Kolkata. Molybdenum estimated by atomic absorption spectroscopy.

IR spectra (4000–400 cm^{-1}) recorded at 27^0C (Shimadzu FTIR 8300, KBr). ^{1}H NMR (DMSO–d_6) from R.S.I.C., Lucknow (300MHz DRX NMR spectrometer).The electrospray mass spectra (CH_3OH) from RSIC, Lucknow (Micromass Quattro II triple quadrupole mass spectrometer).Electrical conductivity in DMF/DMSO (0.8 mmol dm^{-3} solution) (Systronics, model 304 digital conductivity meter).CHEM 3D representations (CHEM 3D Ultra, V. 8.0, 2004), Cambridge Soft Corporation, USA and in higher versions. CV measurements (dry DMF, 0.1 M tetraethyl ammonium perchlorate, BAS CV–27 model). Electronic spectra (800–200nm) and kinetic data (27^0C, Shimadzu UV–240 spectrophotometer), with thermostatic conditions (± 0.5 K, dry DMF). Pseudo-first-order (35-70 times $PyN\rightarrow O$, $Me_3N\rightarrow O/PPh_3$) rate constants (k_{obs}, s^{-1}) by the least square method from the plots of $\log(A_\infty - A_t)$ vs. time, which were linear for at least three half-lives[12(a,b), 13, 14]. Activation parameters calculated through Eyring plot [$\ln(k_{obs}/T)$ vs. $(1/T)$]. Magnetic susceptibility measurement with a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant.

X–ray Data Collection and Crystal Structure Determination: A red coloured monoclinic crystal of (**a**) was obtained by slow evaporation of CH_3OH–CH_2Cl_2 (1:1,v/v) solution of (**a**) over silica-gel in a desicator for 10 days in darkness. This crystal was used for single crystal X-ray diffraction study at the SAIF, Madras as a paid technical service (Enraf Nonius CAD 4 automatic diffract meter).

Syntheses:

(a) H_2 (2-piv-pte$_2$)·H_2O:

7–acetonyl-xanthopterin monohydrate (2.0g, 7.9mmol) and pivalic anhydride (3.213g, 10.072mmol, 3.5mL) was taken in a 25 mL round bottomed flask and fitted with a micro condenser. The mass was subjected to reflux in an oil bath under N_2-atmosphere and darkness for three hours. A deep brown solution was formed which on concentration in a rotary evaporator at 70^0C a brown residue was obtained. This was subjected to high pressure column chromatography (silica-gel, 400 mesh). The fraction in CH_2Cl_2 was collected as a dark brown solution and concentrated in rotary evaporator to get a dirty–brown solid, dried in vacuo over silica-gel for 48 hours. (Yield 70%).Anal.Calcd.for $C_{14}H_{19}N_5O_5$**(a)**: C,49.9; H,5.6; N,20.8. Found: C,53.7; H,6.4; N,19.9 %.

(1) H_3(pte-tsc)·DMF.

A DMF solution (110mL) of 7-acetonyl-xanthopterin monohydrate (0.253g, 1mmol) and a methanolic solution (10mL) of sodium acetate (anhydrous) (0.123g, 1.5mmol) mixed together in a flask and stirred for 5 min. A solution of thiosemicarbazide (0.091g, 1mmol) in DMF (40mL) added to the above reaction mixture. Within 10 min. the solution turned greenish-yellow with a flocculants precipitate; stirring was continued for one hour at 70-80^0C under N_2-atmosphere and darkness,. After settling for 10 min., the reaction mixture was evaporated in rotary evaporator at 70^0C. The reddish-yellow residue was triturated with CH_3OH (5mL) and then added diethyl ether. The reddish-brown crystalline precipitate so obtained, filtered(glass-fritte), washed(CH_3OH, ether),dried in vacuo(silica-gel). (Yield 85%).Anal.Calcd.for $C_{13}H_{19}N_9O_3S$ **(1)**: C,40.9; H,4.9; N,33.1; S,8.4. Found: C,40.5; H,5.0; N,32.7; S,8.2 %.

(2) [Mo^{IV}(pte-tsc)(OCH_3)(CH_3OH)]·0.5CH_3OH.A

DMF solution (100mL) of **(1)**, (0.381g, 1mmol) added to a DMF solution (100mL) of [$Mo^{VI}O_2$(acac)$_2$] (0.326g, 1mmol) in a Schlenk flask. Heating and stirring (40-50^0C,N_2-atmosphere, darkness) for three hours. The yellow solution so formed allowed to settle for one hour. The solvent removed in a rotary evaporator (70^0C). The red oily residue formed was triturated with CH_3OH (15mL); diethyl ether (10mL) added, a red crystalline precipitate was obtained. It was filtered (dinitrogen, glass-fritte), washed (CH_3OH, diethyl ether), dried in vacuo(silica-gel). (Yield 65%).Anal.Calcd.for $MoC_{12.5}H_{18}N_8O_{4.5}S$ **(2)**: C,31.2; H,3.8; N,23.3; S,6.7; Mo,20.0 . Found: C,29.0; H,3.6; N,23.0; S,6.9; Mo,20.1%.

(3) [($Mo_2^VO_4$){H(pte-tsc)}$(DMF)_3$]·DMF·CH_3OH.

A DMF solution (100mL) of **(1)**, (0.381g, 1mmol) added to another DMF solution (80mL) of $(Bu_4N)_4[Mo_8^{VI}O_{26}]$ (269g, ⅛mmol) in a Schlenk flask underN_2-atmosphere. Heated at 65^0C for two hours, stirring(N_2-atmosphere, darkness). The solution turned deep greenish-yellow. Then, the solvent removed in a rotary evaporator (70^0C),a brownish, oily residue formed.On trituration with CH_3OH (10mL) a green precipitate obtained, filtered (glass-fritte, N_2), washed (CH_3OH, diethyl ether),dried in vacuo(silica-gel). (Yield 60%).Anal.Calcd.for $Mo_2C_{23}H_{42}N_{12}O_{11}S$ **(3)**: C,31.1; H,4.7; N,18.9; S,3.6; Mo,21.7. Found: C,32.1; H,4.2; N,18.5; S,3.7; Mo,21.8 %.

(4) [($Mo_2^{VI}S_5$){H(pte-tsc)}$(CH_3OH)_3$]·CH_3OH.A

DMF solution (100mL) of **(1)**, (0.381g, 1mmol) charged slowly to a methanolic solution (30mL) of $(Et_4N)_2[MoS_4]$ (0.484g, 1mmol) under stirring in a Schlenk flask at 28^0C. The pH of the reaction mixture adjusted (6.0,HCl in dioxane). Stirred for two hours (60^0C,N_2, darkness). A dark red solution formed,concentrated (70^0C, rotary evaporator),an oily residue formed, triturated with CH_3OH (5mL), a pink-brown precipitate resulted,filtered(glass-fritte), washed (CH_3OH, diethyl ether), dried in vacuo(silica-gel). (Yield 45%).Anal.Calcd.for $Mo_2C_{14}H_{27}N_8O_6S_6$ **(4)**: C,21.35; H,3.43; N, 14.23; S,24.4; Mo,24.4. Found: C,21.9; H,3.4; N,13.7; S, 25.0; Mo,24.3 %.

3. Results and Discussion

The molecular structure of **(a)** along with its numbering scheme is shown in Figure 1. The data (Table 2) clearly shows the xanthopterin structure (7-oxo) of this ligand[15]. The crystal contains one water molecule hydrogen bonded to the N(1) atom of the pterin as well as O(4) and N(5), as evident from Table 3.

Table 1: Crystal data and details of structure refinement for (**a**):

Empirical formula	$C_{14}H_{19}N_5O_5$
Formula weight	337.34
Temperature	293(2) K
Wave length	0.71073 Å
Crystal system	Monoclinic

Space group	P21/a
Unit cell dimensions	a = 15.722(5) Å alpha = 90 deg. b = 6.598(4) Å beta =104.76(3) deg. c = 16.382(6) Å gamma = 90 deg.
Volume	1643.4(14) $Å^3$
z	4
Calculated density	1.363 mg/ m^3
Absorption coefficient	0.105 mm^{-1}
F(000)	712
Crystal size	0.3 x 0.2 x 0.2 mm
Theta range for data collection	2.57 to 24.96 deg.
Limiting indices	0 < = h < = 18, 0 < = k < = 7, -19 < = l < = 18
Reflections collected / unique	2980 / 2860 [R(int) = 0.0279]
Completeness to theta = 24.96	99.3 %
Absorption correction	Psi- scan
Max. and min. transmission	0.9972 and 0.9032
Refinement method	Full- matrix least-squares on F^2
Data / restraints / parameters	2860 / 0 / 230
Goodness- of- fit on F^2	0.847
Final R indices [I > 2 sigma(I)]	RI = 0.0572, wR2 = 0.1269
R indices (all data)	RI = 0.1869, wR2 = 0.1664
Extinction coefficient	0.0007(9)
Largest diff. peak and hole	0.250 and – 0.211 e. A^{-3}

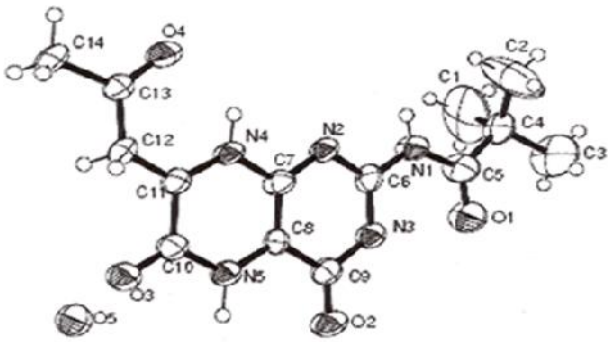


Figure 1

Mass Spectra: FAB mass spectrum of (**1**) contains the molecular ion peak without solvent molecule (DMF) of crystallization at m/z =307, $[M–DMF–H]^+$ (relative intensity 100%), where 'M' is the molecular formula of (**1**)[7(a), 16-19] (F.W.= 381). The de-solvated ESIMS molecular ion peak of (**2**) appeared at m/z=464, $[M– 0.5CH_3OH]^+$; where 'M' is the molecular formula of (**2**) (F.W.=479.94)[7(a), 16, 17].Compound (**3**) shows the partly de-solvated ESIMS peak for the species $[M–CH_3OH–2DMF–H]^+$ at m/z=707.4, where 'M' is the relevant molecular formula (F.W.=885.88)[7(a), 16, 17]. In case of **7,** the ESIMS data shows a fragment $[M–CO+H]^+$ at m/z=760.

The following peaks are found to be common in almost all the complexes reported here: m/z=331.1 $[Mo\{H_2(pte)\}]^+$; m/z=307.1, $[H_2(pte\text{-}tsc)]^+$. This supports that the new Schiff base ligand, H_3(pte-tsc) is a stable one and is able to retain its identity throughout its reactions with a variety of molybdenum starting materials, leading to pure products.

Conductivity Measurements:

The Λ_M [(9.12–32.2) ohm^{-1} cm^2 mol^{-1}, 301K, CH_3OH)] values for (**2**),**(3)**&**(4)** support the non-electrolytic formulation of these complexes[20].

IR Spectra:

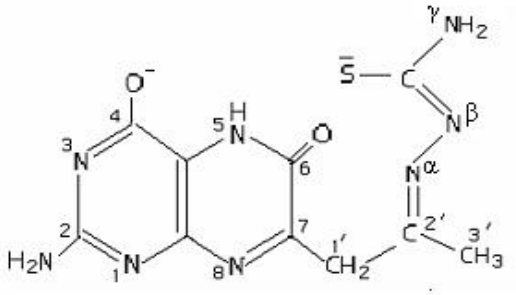
Two intense bands with fine structure at 1690cm^{-1} and 1650cm^{-1} of H_2(pte) corresponding to different types of ν(C=O) modes, are replaced by a band at 1647 cm^{-1} in (**1**) corresponding to ν(C=O) of O(6) and ν(C=N) of C(2′) (Scheme 2). These two bands are present in slightly modified form in most of these complexes. As per X-ray structural data on different metal–pterin complexes[21-24], the M–N(5) bond plays a pivotal role in the pterin ligand chelation process. Again in the free ligand, (**1**) (Scheme 2) the ν(C–O) and ν(C-O) + δ(OH) modes of the OH(4) group could be located at 1458cm^{-1} and 1236cm^{-1} respectively, indicating its existence in the enol form e.g., involving the amide function in positions 3, 4 (Scheme 2a), in some amount.

There is no ν(Mo=O_t) or ν(Mo–O_b–Mo) band in the IR spectrum of (**2**) in the region 800–1000cm^{-1} corresponding to its formulation here as devoid of any oxomolybdenum core. In (**3**) two new peaks characteristic of the $(Mo_2{}^{V}O_4)^{2+}$ core appear at 945cm^{-1}, [ν(Mo=O_t)] and 790cm^{-1}, [ν(Mo–O_b–Mo)] respectively. In (**4**) no IR band is observed in the region 800–1000cm^{-1}, but a peak at 503cm^{-1} [ν(Mo=S_t)] and another at 470cm^{-1} [ν(Mo–S_b–Mo)] assignable to $(Mo_2{}^{VI}S_5)^{2+}$ core are observed[25].

^{1}H NMR Spectra:

^{1}H NMR data in DMSO-d_6 of (**1** – **4**) have been assigned on the basis of protonic integration, multiplicity, $^1H–^1H$ COSY and literature value[18, 26] For (**1**) (Scheme 2) the –OH(4), NH(3) and NH(5) signals are observed at δ,12.49(bs), δ,11.63(bs), and δ,10.04(bs) respectively indicating the presence of two tautomers in DMSO solution. The NH_2(γ), NH(β) and NH_2(2) signals are observed at δ,7.46(bs), δ,7.30(bs) and δ,7.11(bs) respectively. The CH_2(1′) and CH_3(3′) signals are observed at δ,3.57(d, br) and δ,2.22(t) respectively. In the pertinent complexes the –OH(4) signal is absent indicating its de-protonation. The NH(5) signal appears at downfield (δ,11.10–10.98,bs) as compared to the free ligand value in most cases indicating involvement of the NH(5) group in metal coordination process[21-24]. Both the CH_2(1′) and CH_3(3′) signals are shielded in the complexes and appear in the region δ,3.21–3.19(q) and δ,1.20–1.18 (t) respectively. The NH_2 (γ) and NH_2(2) signals appear in the region δ,7.06–6.75 (bs) and δ,6.99–

6.65 (bs) respectively, i.e., shielding is observed for these signals as well.



Scheme 3

Although the –OH signal of CH_3OH appears around δ,5.0, in (**2**) and (**4**) it appears atδ,12.34 (bs) indicating strong coordination of the – OH group of CH_3OH to the Mo – atom[21-23, 27].

CHEM 3D Study:

CHEM 3D data suggest that the bond lengths and bond angles of the ligand residue have undergone a visible change due to complexation with molybdenum metal. In (**2**), the bonds C (1)–N(7) from 1.35Å to 1.40Å, C(3)–O(13) from 1.23Å to 1.38Å and C(19)–S from 1.58Å to 1.83Å have increased. This suggests N (7), O (13) and S atoms' bonding with the molybdenum atom. The C (5)–N (12) bond length has undergone a decrease from 1.37Å to 1.30Å on complexation indicating the N(12) [N(2) as per Scheme 2) lone pairs' participation in metal coordination via the pterin rings. Some other bond lengths, such as, N (4)–C(5), C(19)–N(20), C(19)–N(17) etc. have also suffered visible change due to redistribution of overall electron density on metal coordination.

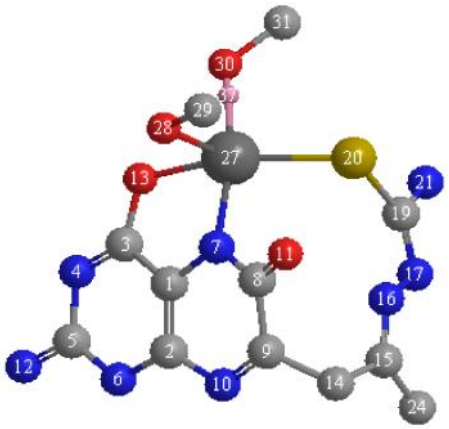


Figure 2: The optimized geometry (CHEM3D model through MM2 calculations) of (2), steric energy 13.68 Kcal mol^{-1}. Its numbering system is set by the software used28 and is different from that in Schemes 2.

This model contains slightly distorted trigonal bi-pyramidal (TBP) geometry around the Mo^{IV}-centre. The case of CH_3O- coordination is an X-ray crystallographically established one [7(a), 22].

In molybdenum–pterin complexes the pivotal role of the Mo-N (5) bond has been verified through X-ray crystallography[23(a), 27, 31-30].

UV-vis Data. Three bands of (**1**) at 310nm, 355.5nm and 408nm are completely modified in the metal complexes and appear at lower wave lengths and with larger intensity, except in (**3**), where 408nm ligand peak is missing. A sharp increase in intensity of the UV-vis absorption bands in the metal complexes can be accounted for[33] electronic drift from $–NH_2$(2) group (Scheme 3) towards metal–ligand bonding site via the pterinring[21, 23(a)]which is substantiated by ^{1}H NMR and fluorescence study.

Kinetic Measurements and Fluorescence Study:

All the complexes (**2**–**4**) are susceptible to oxygen atom transfer (OAT) reactions, along with coupled electron proton transfer (CEPT) reactions in some cases. Compounds (**2**)&(**3**) having Mo–atom in lower oxidation states (IV/V) show reactivity with potent oxygen donor specieslike $PyN\rightarrow O$, $Me_3N\rightarrow O$but not with oxygen abstractor, like, PPh_3. They oxidize Mo-pterin compounds to some higher oxidation state and itself getting reduced to pyridine (PyN) or trimethyl amine (Me_3N). (**4**)undergoes reaction with a typical sulphur abstractor like $PPh_3$from the Mo(VI)–centre. Exceptional nature of (**4**) with a Mo^{VI}–centre (i.e., the Mo–centre not undergoing reduction during complex synthesis), can be correlated with oxidizing property of the $(MoS_4)^{2-}$ starting material; formation of $(Mo^{VI}_2S_5)^{2-}$ core is also in line with the unique behavior of the Mo–S duo[34] in nature as well as in synthetic system. Reaction stoichiometry was checked as per the following equations [3(a) and 3(b) are different steps leading to overall reaction (3)]:

2 x compound (**2**)+ $2PyN\rightarrow O$ → $2[Mo^{VI}O]^{4+}$ complex + 2PyN---3(a)

$2[Mo^{VI}O]^{4+}$ complex+$2PyN\rightarrow O+H_2O\rightarrow[Mo_2{}^{VI}O_5]^{2+}$ complex +2PyN+$2H^+$---3(b)

The overall reaction:

2 x compound (**2**)+ $4PyN\rightarrow O + H_2O\rightarrow[Mo_2{}^{VI}O_5]^{2+}$ complex + 4PyN + $2H^+$---(3)

Physicochemical studies indicate the composition $[(Mo^{VI}_2O_5)\ \{H(pte\text{-}tsc)\ (DMF)_3]$. The ν(Mo=O) and ν(Mo–O–Mo) modes characteristic of the $[Mo_2{}^{VI}O_5]^{2+}$ core are observed at $925cm^{-1}$, $888cm^{-1}$ and $825cm^{-1}$ respectively[23]. H_2O used in Equation 1(b), most probably came from moisture in the solvent.[23(c),35]. Kinetics of these OAT reactions was followed spectrophotometrically at 400nm for (**2**)&(**3**) and at 510nmfor(**4**). Rate constants measured by least square method. $\Delta H^{\#}$ and $\Delta S^{\#}$-values obtained from the slope and intercept of the Eyring plots respectively. $\Delta G^{\#}$-values from the Gibb's–Helmholtz equation, $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$.

The negative ($\Delta S^{\#}$) is in conformity with the enzyme–substrate type associative mechanism[33,36]. High k_{obs} values are obtained in cases involving oxygen or sulphur abstraction by PPh_3. As a substrate, $Me_3N\rightarrow O$ provides higher k_{obs} values than $PyN\rightarrow O$. Higher E_a(activation energy) value is observed for (**2**)&(**3**)where the ligand coordination around the Mo^{IV} centre is most compact, with lowest steric energy.

CV Data:

The CV data of (**1**) shows a quasi–reversible couple in the region –0.85V (reduction) and –0.68V (oxidation). ΔE_p (E_{pc}–E_{pa}=170mV) value essentially for two–electron transfer process. (**2**) is characterized by the quasi–reversible peak as well as additional peaks on for the metal centre; at –0.105V a reduction of the metal–centre ($Mo^{IV} \rightarrow Mo^{III}$) followed by chemical attack of the solvent leading to its partial decomposition. A weak signal at +0.45V characterizes the reoxidation process of the metal–centre. In (**3**) the metal reduction ($Mo^{V} \rightarrow Mo^{IV}$) peak is observed at +0.13V and the subsequent reoxidation occurs at +0.47V. In (**4**), the metal reduction ($Mo^{VI} \rightarrow Mo^{V}$) takes place at –0.26V.

Table 2: Selected Coordination Bond lengths (Å) and Angles (degrees) for (**a**) With Esds in Parentheses [#]

C(5) – N(1)	1.397 (5)	C(8)–C(7)– N(4)	117.2 (3)
C(6) – N(1)	1.365 (4)	N(5)–C(8)– C(9)	119.6 (3)
C(8) – N(5)	1.383 (4)	O(2)–C(9)– N(3)	122.2 (3)
C(8) – C(9)	1.443 (5)	N(3)–C(9)– C(8)	113.5 (3)
C(9) – O(2)	1.225 (4)	O(3)–C(10) – N(5)	121.4 (3)
C(9) – N(3)	1.389 (4)	N(5)–C(10)– C(11)	115.7 (3)
C(10) – O(3)	1.218 (4)	O(4)–C(13)– C(14)	120.7 (3)
C(10) – N(5)	1.360 (5)	C(6)–N(2)– C(7)	115.2 (3)
C(13) – O(4)	1.228 (4)	C(6)–N(3)– C(9)	123.4 (3)
C(13) – C(14)	1.529 (5)	C(11)–N(4)– C(7)	122.9 (3)
N(2)–C(6)– N(3)	123.2 (3)	C(10)–N(5)– C(8)	122.6 (3)

[#] Symmetry transformations used to generate equivalent atoms

Table 3: Hydrogen Bonds for (**a**) (Åand degrees)

D – H . . . A	d (D – H)	d (H . . . A)	d (D . . . A)	< (DHA)
N(1) – H(1) . . . O(5) # 1	0.80 (3)	2.16 (3)	2.945 (4)	168 (3)
N(4) – H(4) . . . O(4)	0.89 (3)	2.13 (3)	2.687 (4)	120 (2)
N(5) – H(5) . . . O(4) # 2	0.95 (4)	1.92 (4)	2.870 (4)	178 (4)

Symmetry transformations used to generate equivalent atoms:
1 - x, - y +1, - z +1 # 2 x +1/2, - y +1/2, z

Table 4: Comparison of selected computed bond lengths (Å) involving Mo-atom in (**2**) from the optimized geometry (Figure 2) with the available literature data (in parentheses) from X-ray structural studies[*]

Atoms	**Bond Distances(Å)**[+]	**Atoms**	**Bond Distances(Å)**[+]
O (13)-Mo (27)	1.96(2.23)[21(b)]	O(30)-Mo(27)	2.07(2.32)[29]
S (20)-Mo (27)	2.33(2.37)[29, 30]	O(28)-Mo(27)	1.95
N (7)-Mo (27)	1.99(2.02)[21(b)]		

Table 5

Compound NO.S	**Substrate used (in DMF)**	**T (K)**	**k_{obs} (s^{-1}) x 10^3**	**k_2 (s^{-1}) x 10^3**	**K_M (M)x 10^5**	**E_a (KJ, mol^{-1})**	**$\Delta H^{\#}$ (KJ, mol^{-1})**	**$\Delta S^{\#}$ (J,mol^{-1}, deg^{-1})**	**$\Delta G^{\#}$ (KJ, mol^{-1})**
2	$PyN \rightarrow O$	298 304 307.5 312	3.82 7.16 10.12 15.10	9.97	11.9	75.99	74.40	-208.29	137.73
5	$Me_3N \rightarrow O$	302 308.5 313 318	25.50 26.80 27.60 28.60	30.3	21.5	5.78	3.18	-198.63	63.12
6	PPh_3	291 295.5 302.5 308.5	56.60 59.50 65.40 71.00	171.4	1100	9.95	7.09	-200.40	67.72

4. Conclusion

In most cases the pterin ligand acts as a reducing agent during synthesis and oxidation state of the metal centre in the final product depends on the reaction condition as well as the nature of the molybdenum starting material used. The pterin complexes have low solubility due to extensive

intermolecular hydrogen bonding, which leads to failure to get single crystal for X-ray crystallography and low resolution in ^{1}H NMR spectra. These compounds show OAT reactivity towards oxygen/sulphur donors /abstractor, which throws light on the oxidation state of the metal centre. The $k_{obs}(s^{-1})$ values are within the range of enzyme type OAT reactions. Reaction stoichiometry studies and kinetics with negative entropy of activation value support metal-centred OAT reaction. CV data as well as fluorescence spectral data throw light on the changes in electronic structure during different redox steps. Therefore, to the best of our knowledge, the present complexes appear to be the most appropriate functional models to mimic the active site of oxomolybdoenzymes.

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