Synthesis, Characterization of New Tungsten(IV)–Pterin Complexes and their Reactivity Studies towards Trimethylamine N-Oxide, Sodium Borohydride and Potassium Ferricyanide

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Abstract

2-Pivaloylamino-6-acetyl-isoxanthopterin (1). H_L has been reacted with Na2WO4.2H2O under suitable conditions leading to the formation of Na(WIV(1)(OH))(3) (2). Na(WIV(L)(dedt))2. CH2OH (3) and (Ph4P)2[WIL(L)(aet)] (4) have been prepared by the reaction of (2) with PPh3, in presence of the ancillary ligands like sodium diethyl dithiocarbamate trihydrate and 2-aminoethanethiol hydrochloride, respectively. These new compounds have been purified by flash chromatography and characterized by elemental analysis, different physico-chemical and spectroscopic methods. Such data particularly H NMR and fluorescence spectra indicate the redox noninnocent nature of the pterin ligand. Reactivities of these compounds with different substrates have been followed kinetically; using the data of (3) as their representative, it appears that the electron transfer process (kobs =1.1x10^-2 s^-1) involving K3[Fe(CN)6] is twice as fast as the group transfer processes associated with Me3N+→O and NaBH4. The corresponding negative ΔS° values are consistent with associative pathways in all these cases.

Keywords: Tungsten(IV)–Pterin complexes; Potassium ferricyanide; Reactivity studies

Introduction

Pterins (2-amino-4-oxopteridines) are important in a wide range of biological functions including a large number of metal–containing enzymes (e.g., Fe, Mo, W) [1-3]. The redox noninnocent nature of the pterin ring is associated with the ability of its pyrazine ring to exist in a number of oxidation states [4]. In the above enzymes, this redox capability of the pterin moiety is matched by the ability of the metal centres to display multiple oxidation states [5]. This aspect has catalysed research work on the coordination chemistry of pteridines in general and pterins in particular [5-8]. Literature survey reveals the existence of only a limited amount of data on the synthetic tungsten–pterin complexes [9] and provides with the impetus for the present endeavour using 2-pivaloylamino-6-acetyl-isoxanthopterin (1, H_L) (Figure 1). Its 1,1'-pivaloyl group plays a crucial role in enhancing solubility of the unsubstituted pterin and facilitating the synthetic and purification steps [10,11]. Here (1) acts as a reducing agent towards the tungsten(VI) starting material Na2WO4.2H2O leading to the formation of the present tungsten (IV) complexes (2), (3) and (4). Their characterization aspects, spectroscopic analysis and reactivity studies towards biologically relevant substrates are delineated here [12-15].

Experimental

Materials

Extra pure AR grade solvents were used as received. Pivalic anhydride, trimethylamine N–oxide and triphenyl phosphine were obtained from Aldrich, USA and Riedel, Hannover respectively. Tetraphenyl phosphonium bromide and 2–aminoethanethiol hydrochloride (H2aet.HCl) were purchased from Lancaster, England. Sodium diethyl dithiocarbamate trihydrate (Na dedtc. 3H2O) and Na2WO4.2H2O were obtained from Merck, India. Silica gel (230–400 mesh) for flash chromatography (dried at 453K for 6 h before use) and silica gel (GF254) for t.l.c. were procured from SRL, Mumbai.

Methods

All synthetic steps were carried out under a dinitrogen atmosphere using the Schlenk procedure as well as under subdued light [16,17]. All heating operations including boiling under reflux, were carried out on a paraffin oil bath. Flash chromatography was performed under a dinitrogen flow as well [18]. For the two above steps, the dinitrogen gas was purified using a BTS column [19]. Column dimensions for the flash chromatographic purification of the pivalated pterin ligand and the corresponding tungsten (IV) complex were 2.5 cm ID×70 cm and 1.2 cm ID×50 cm respectively; in each case the overall column length included a 250–200 ml bulb at the top. The above systems provided with 500–600 mg of the pivalated pterin ligand and 40–50 mg of the corresponding complex respectively, in the pure form per batch operation. Synthesis of the 2–pivaloylamino–6–acetyl-
isoxantherptin (1, H₂L) and most of the instrumental methods have been described elsewhere [9,20].

\[ \text{Na}_2[W_2^{IV} (\mu-O)(L)_2(\text{CH}_3 \text{OH})_2] \]

A solution of (1) (H₂L, 0.19 g, 0.6 mmol) in CH₂OH (80 ml) was reacted with Na₂WO₄ 2H₂O (0.1 g, 0.3 mmol) in H₂O (10 ml). The resulting solution was boiled under reflux for 6 h, maintaining the pH at 5.6. After removing the solvent under reduced pressure in a rotary evaporator, the crude product was purified by flash chromatography using CH₂Cl₂: C₂H₅OH (96:4 v/v) as the eluant; removal of the solvent under reduced pressure yielded a red compound (yield: 40%). It was dried in vacuo over silica gel. Its purity was checked through t.l.c. (UV lamp) using its 0.5% solution in CH₂OH and utilizing the above eluant.

[Found: C, 40.5; H, 4.1; N, 15.9%. C₃₄H₄₄N₁₁S₂O₉WNa (MW 1020.84) Calcd.: C, 39.9; H, 3.9; N, 15.4%]. UV–VIS [CH₃OH, λ max/nm (log ε)]: 275sh (4.70), 334br (4.52), 391 (4.47), 419sh (4.31), 460sh (4.02).

\[ \text{Na}[W^{IV}(L)_2(dedtc)] \cdot \text{CH}_2\text{OH} \]

A solution of (1) (0.19 g, 0.6 mmol) in CH₂OH (80 ml) was reacted with Na₂WO₄ 2H₂O (0.1 g, 0.3 mmol) in H₂O (10 ml). The resulting solution was boiled under reflux at pH 5.6. The solvent was removed under reduced pressure and dried overnight in vacuo over silica gel. The brown product so obtained was dissolved in CH₂OH (100 ml) and reacted with Nadedtc 3H₂O (0.07 g, 0.3 mmol) in CH₃OH (20 ml), followed immediately by Ph₄PBr (0.25 g, 0.6 mmol) in CH₂OH (15 ml). The resulting solution was stirred at 313 K for 1 h. After the removal of the solvent, the crude product was purified by flash chromatography. At first, a pet ether fraction eluted Ph₃PO, then the CH₂Cl₂:C₂H₅OH (96:4 v/v) fraction (checked through t.l.c.) was collected and removal of the solvents afforded a red compound (yield, 50%). [Found: C, 40.5; H, 4.2; N, 15.1%. C₃₈H₄₈N₂₀O₁₉W₂Na₂ (MW 1761.68) Calcd.: C, 39.5; H, 3.9; N, 15.9%]. UV–VIS [CH₂OH, λ max/nm (log ε)]: 285 (3.91), 341 (4.06), 391 (3.93), 413 (3.94), 436sh (3.77).

\[(\text{Ph}_3\text{P})_2[W^{IV}(L)_2(aet)] \]

This compound (red) was synthesized by a similar procedure as outlined above for (3) and using 2–aminoethanethiol hydrochloride instead of Nadedtc. 3H₂O. At the final stage of reaction, Ph₂PB (0.25 g, 0.6 mmol) in CH₂OH (15 ml) was added and the reaction was continued at 313 K for 1 h more; yield, 50%. [Found: C, 58.9; H, 5.0; N, 9.3%. C₇₈H₇₅N₁₁S₂O₉P₂W (MW 1570.84) Calcd.: C, 59.6; H, 4.8; N, 9.8%]. UV–VIS [CH₂OH, λ max/nm (log ε)]: 260sh (4.69); 268 (4.72), 275sh (4.70), 334br (4.52), 391 (4.47), 419sh (4.31), 460sh (4.02).

Results and Discussion

The low solubility problem associated with pterin compounds, is overcome to a large extent here by replacing one of the hydrogen atoms of the pterin NH₂ (2) group by a pivaloyl group [(CH₃)₃CCO] through reaction with pivalic anhydride [10,11]. Careful control of the reaction conditions, e.g. the use of subdued light, paraffin oil bath heating, dinitrogen atmosphere as well as the flash chromatographic purification of the resulting compounds under dinitrogen flow, ensures pure product formation, free from artifacts.

Electrospray Ionization mass spectrometry (ESIMS) involving a soft ionization technique, is valuable for characterizing coordination compounds [25,26]. ESIMS data of the present compounds assist in assigning some of the important fragments through comparison of experimental and simulated isotope distribution patterns [27]. For example, in case of Na₂[W₁^{IV} (\mu-O)(L)(\text{CH}_3 \text{OH})_2] (2) the species [(M–O)/2–2CH₂CO–3H]⁺ at m/z =830 could be characterized in this way (Figure 3); here M is the relevant molecular formula and the (CH₃CO) unit corresponds to the 6–substituent of the pterin ligand residue (Figure 2). This data also support Scheme 1, indicating the formation of a mononuclear species relevant to (3) and (4) on the mass spectrometry timescale. Similarly, the desolvated species [(M–O)/2–CH₂OH–(CH₃)₂CO+H]⁺ could also be identified in the region m/z=769.

IR spectral data (KBr pellets) of the present compounds, are helpful in characterizing some of their functional groups. For the pterin ligand (1) (Figure 1 shows the structural formulas of its tautomers) two medium intensity broad bands at 1363 cm⁻¹ and 1209 cm⁻¹ could be assigned to the δ(N–H) and δ(N–H)+ν(C–N) vibrations respectively, of its NH(3) and NH(5) groups [28]. Absence of such vibrations in the corresponding complexes (2,3,4) indicate deprotonation of such functional groups in forming the pterin ligand anion, L⁻ (Figure 2). On the other hand, a new distinct band of variable intensity is observed at 1261 cm⁻¹ for the present complexes, which may be assigned to the ν(C=O) mode of the O(4) phenoxy group [28]. For (1) the ν(C=N) and ν(C=C) vibrations of the pterin ring appear at 1660 cm⁻¹, 1589 cm⁻¹ and 1481 cm⁻¹ as strong-to-medium intensity bands [29]; the positions and shapes of these bands undergo moderate alteration in the corresponding complexes due to tautomerism/deprotonation/electronic redistribution during the complex formation process involving the N(3)-(C4)-(N5)-(C6)-(C1)’ system (Figures 1 and 2). For (2) an intense broad band assignable to the ν(W=O) mode, is observed at 800.4 cm⁻¹ (Figure 4a); it is absent in case of both (3) (Figure 4b) and (4). Scheme 1 summarizes this aspect and shows that the careful
use of a combination of PPh3 and the ancillary ligands, leads to the formation of the desired complexes (3) and (4) from (2) [21,22]. Here in each compound, the W(IV) centre attains a coordination number of six (octahedral geometry) with the pterin ligand anion (Figure 2) acting as a bidentate binegative O(4), N(5) donor [8,29]; the latter view is also supported by the 1H NMR data as discussed in the next section.

Figure 4: IR spectra (KBr) of 2 [Figure 4a] & 3 [Figure 4b] indicating removal of the μ-O atom from 2 through reaction with PPh3 and Na(dedtc). 3H 2O (vide Scheme 1).

Scheme 1: Reaction pathway (details are given in the experimental section) leading to the formation of 3 [Figure 4b] & 4 from 2 [Figure 4a], reflecting removal of the ν(W-Ο-W) mode at 800.4 cm⁻¹ of 2.

Table 1: Relevant ¹H NMR signals in DMSO-d₆ (300 MHz, δ ppm, internal TMS) of the free ligand 1, the corresponding complexes 2, 3 and 4 and Δ (=δ(complex)–δ(ligand)) values. ss=sharp singlet; wb=weak broad. *vide Figure 1 for the proton numbering system.

- Most of the ¹H NMR signals of (1) (Figure 1) including that of the NH(2) group, have been assigned on the basis of the ¹H–¹H COSY data (Figure 5a); they indicate predominance of the vinylogous amide tautomer (Figure 1b). The NH proton signals (weak broad/singlet) of the pterin ring are not connected by any cross peaks and they are located (Figure 5b) on the basis of literature data [30-33] as well as their change over during the metal coordination process. For (1) the CH₃(2´) (δ 1.097) and CH(1´) (δ 6.15) signals (each a sharp singlet) could be read off from the ¹H–¹H COSY spectrum (Figure 5a); the same is true for the three CH₃(2´´) (δ 1.24, 6H, double doublet; δ 1.15, 3H, doublet) and NH(2) (δ 4.30) signals. The last signal is practically invisible in the 1D spectrum. The CH₃(2´) and CH(1´) proton signals along with their Δ values for (2), (3) and (4) are shown in Table 1; such low Δ values indicate that the O(2´) atom is not involved in the metal coordination process [9,34].

Figure 5: (a) ¹H–¹H COSY data (symmetrized) of 1 (H₂L) in DMSO –d₆ over the region δ 7.0–0.0; (b) different NH signals of 1 are located here (vide text for details).

Table 1: Relevant ¹H NMR signals in DMSO-d₆ (300 MHz, δ ppm, internal TMS) of the free ligand 1, the corresponding complexes 2, 3 and 4 and Δ (=δ(complex)–δ(ligand)) values. ss=sharp singlet; wb=weak broad.

- (vide Figure 1 for the proton numbering system.
- CH₃OH signals of these complexes appear at δ 13.65 (-OH) and δ 3.40 (CH₃-)
- Due to low solubility of 4, neither the multiplicity of the CH(1´) signal could be characterized nor the NH(8) signal could be located.
- Structural formulas of the ancillary ligand anions, dedtc′ and aet2- along with the proton numbering system of the latter, are shown in Scheme 1. The 2D NMR spectral data of the corresponding free ligands are included in the supplementary materials (Figures S–1 and S–2).
- The phenyl ring proton signals of the Ph4P(+) countercation of 4, appear at δ 8.20 (2H, quartet) and δ 7.83 (3H, complex multiplet); the corresponding signals of Ph4PBr appear at δ 7.97 and δ 7.78 respectively.

Most of the ¹H NMR signals of (1) (Figure 1) including that of the NH(2) group, have been assigned on the basis of the ¹H–¹H COSY data (Figure 5a); they indicate predominance of the vinylogous amide tautomer (Figure 1b). The NH proton signals (weak broad/singlet) of the pterin ring are not connected by any cross peaks and they are located (Figure 5b) on the basis of literature data [30-33] as well as their change over during the metal coordination process. For (1) the CH₂(2´) (δ 1.097) and CH(1´) (δ 6.15) signals (each a sharp singlet) could be read off from the ¹H–¹H COSY spectrum (Figure 5a); the same is true for the three CH₂(2´´) (δ 1.24, 6H, double doublet; δ 1.15, 3H, doublet) and NH(2) (δ 4.30) signals. The last signal is practically invisible in the 1D spectrum. The CH₂(2´) and CH(1´) proton signals along with their Δ values for (2), (3) and (4) are shown in Table 1; such low Δ values indicate that the O(2´) atom is not involved in the metal coordination process [9,34].
The NH(3) and NH(5) proton signals could not be located for any of the present complexes indicating their deprotonation during the chelation process, associated with the formation of the ligand anion L2– through tautomerism (Figures 1 and 2) and strengthening the inference regarding bidentate pterin coordination involving the O(4) and N(5) atoms [8,29].

The higher frequency shift (downfield) of the NH(8) proton signal in the present complexes (Table 1), as compared to that in (1) is noteworthy; it is related to the electron density withdrawal from NH(8) through mesomeric interaction by the O(4) atom, as discussed by different authors [8,39].

Now a closer look at the 1H NMR spectral data (Figure 6) of (3) reveals several interesting aspects.

1. Figure 6a shows two sets of NH(2) and CH(3′′) signals, that is, its two pterin ligand residues (L2–) are nonequivalent on the NMR time scale.

2. A comparison of Figure 6c and 6d indicates nonequivalence of the two –CH2– protons of the ancillary ligand residue as well (dedtc′; vide Scheme 1 for its structural formula); the attendant additional spin–spin splittings convert the original quartet signal (Figure 6d) into a complex multiplet (Figure 6c). That is, (3) possesses a distorted octahedral coordination geometry around its W(IV) atom, associated with both nonequivalent pterin and (dedtc′) coordination.

3. The 1H NMR spectral data of the (aet2–) residue of (4) support the above view. In spite of the low solubility of (4), the –CH2–(1) and –CH2–(2) signals of the ancillary ligand residue (vide Scheme 1 for the structural formula of aet2– and supplementary information Figure S-2 for the 2D NMR spectral assignment of 2-aminoethanethiol hydrochloride) could be located at δ 7.69 and δ 7.64, with the corresponding Δ values of δ 4.78 and δ 4.45 respectively. In other words, a substantial electron flow aet2–→W(IV) is indicated for (4), thereby supporting the hypothesis regarding the lowering of ligand pKa value through coordination and assisting the deprotonation process (H2aet → aet2–) [23,24]. Such deprotonation of the coordinated –NH group (of H2aet), is also supported by the structural data of a related ligand-containing complex [24].

Although the free ligand (1) is nonfluorescence, the present complexes possess intense fluorescence property (Figure 7), which can
complexes possess intense fluorescence property (Figure 7), which can be ascribed partly to the aromatic (oxidized) nature of the pyrimidine ring in the pterin ligand anion, L^2− (Figure 2) as well as to the overall rigidity of the chelated ligand/complex molecules, preventing dissipation of the excitation energy in manners other than by the emission of fluorescent light [35-38]. In short the fluorescence property is a good probe for understanding the overall oxidation state of the pterin ring and following its transformations [e.g. H2L (Figure 1)→L^2− (Figure 2)].

Figure 8 shows typical cyclic voltammetric (CV) responses of these complexes. Although the free ligand (1) is characterized by a single irreversible reduction peak at −0.93 V, for the corresponding complexes two such peaks (in the ranges −1.13 to −1.33 V and −1.37 to −1.50 V respectively), are observed for the pterin ligand residue (L^2−) in (2)–(4). A substantial electronic redistribution during the process H2L→L^2− may be inferred. For (3) an irreversible reduction peak at −0.45 V corresponds to the W(IV)→W(III) reduction, followed by decomposition through solvent attack; in case of (4) the corresponding metal–centred reduction occurs at −0.63 V. For the binuclear complex (2), two such irreversible reduction peaks are observed at −0.63 V and −0.77 V respectively, indicating nonequivalence of its two W(IV) centres on the CV timescale.

The above characterization data could be collated together in the form of CHEM 3D models of (2)–(4) (Figure 9) [40]. Such CHEM 3D models may be utilized for visualizing the corresponding frontier orbitals (extended Huckel surfaces) and evaluating their energies (eV). Now the forgoing inference about the molecular structure of (3) (e.g., nonequivalent pterin/dedtc’ coordination as per Figure 6, as well as the energy information about its frontier orbitals (Figure 9, Δ1=0.15 eV, Δ2=0.34 eV) may be utilized for understanding its reactivity data (Figure 10 and Table 2) with a wide variety of substrates, affecting both the W(IV) and pterin centres [12-15]. They include an one–electron oxidant K3[Fe(CN)6], an oxygen atom transfer agent (Me3N→O) and NaBH4 which can affect the pyrazine part of the pterin ring [14]. Besides this, K3[Fe(CN)6] and NaBH4 fail to react with each other as evident from the absorption spectral studies (vide the supplementary information Figure S3). In the other words, (3) is able to mediate
mediator like the NAD+/NADH couple where NAD+ can be reduced nonenzymatically by the reducing agents like Na2S2O4 or NaBH4. NADH can in turn be nonenzymatically reoxidized with K3[Fe(CN)6], but it is not oxidized directly by molecular O2 [13]. Me3N → O involves a metal–centred oxygen atom transfer process leading ultimately to a μ-oxo W(V) dimer; this inference has been verified through a stoichiometric experiment on a related system [30]. K3[Fe(CN)6] oxidizes the metal centre [W(IV) → W(V)] in (3) and from the overall similarity of the absorption spectral changes with that of Me3N →O (Figures 10b and 10c), it appears that the formation of a μ–oxo W(V) dimer is the end product of this reaction process as well.

2W(IV)+2Fe(CN)6^3-+3H2O→[OWV–O–WVO]^4++2Fe(CN)6^4-+6H^+

Participation of the water molecule in the reaction cycle catalysed by the pterin–containing Mo/W enzymes is well-known [12]; the above reaction possibility also follows the principle of single electron transfer. A comparison of the kinetic parameters (Table 2) is quite instructive; the reaction with K3[Fe(CN)6] involving an electron transfer process is quite faster as compared to the other two group transfer processes. All these reaction pathways are of the associative type as evident from their negative ΔS# values. Few related data of (2) and (4) are shown in Figure 11.

In recent years synthetic molecules with exceptionally small (<0.5 V) HOMO–LUMO gaps (HLG) have received considerable attention due to their interesting properties, e. g. electrochemical/redox amphoteric behavior [41]. The different locations of the HOMO–LUMO orbitals in a single molecule hinders the electron transition between them, unlike systems with extended conjugation. However, facile electron transfer may occur between two such covalently linked centres in solution with thermal excitation at room temperature. The reactivity of (3) with both oxidizing and reducing agents (Figure 10 and Table 2) may be correlated at least partly with the small band gaps (Figure 9) among its HOMO, LUMO and the (LUMO+1) (lowest–energy virtual orbital) levels [41]. Besides this, the compact ancillary ligand (dedtc) helps to sustain its solution structure during the reaction with NaBH4 as evident from the tight isosbestic point present in Figure 10a.

The mode of action of the Mo/W cofactors in pterin–containing enzymes [5,12], involves redox processes at the metal centre, possibly linked to changes in the pyrazine ring oxidation level. Some of the present data may be helpful in understanding such electron exchange cooperativity.

Table 2: Comparison of kinetic parameters for the reaction of 3 with different substrates.

| Kinetic Parameters | Reaction with Me3N→O in CH3OH | Reaction with K3[Fe(CN)6] in CH3OH–H2O 3:1 v/v | Reaction with NaBH4 in CH3OH |
|--------------------|-------------------------------|-----------------------------------------------|-----------------------------|
| Kobs (s⁻¹)         | 5.3x10⁻³                      | 1.1x10⁻²                                    | 5.9x10⁻³                    |
| ΔS# (JK⁻¹mol⁻¹)     | -278.0                        | -284.0                                      | -286.5                      |

(a) measurements were done at 3: substrate ratio of 1:7-8 and the absorbance changes were followed at 337 nm, 412 nm and 412nm for Me3N→O, K3[Fe(CN)6] and NaBH4, respectively (vide Figure 10 for the relevant absorption spectral changes).
Conclusion

Here successful use of a derivatized pterin ligand (1) leads to the isolation of several tungsten (IV) complexes in the pure form. Their facile reactivity towards $\text{M}_3\text{N}_2\text{O}$ indicates a lower oxidation state for the metal centre [e.g., W(IV)], as compared to the tungsten starting material (Na$_2$WO$_4$. 2H$_2$O). Different spectroscopic studies, especially 1H NMR data indicate considerable electronic redistribution for (1) during the complex formation process as well as strong bonding interaction with the ancillary ligand anions (dedtc`, aet$_2^-$) in case of (3) and (4). The ability of such complexes to react with diversified reagents is highlighted by (3) and it may be related to its electronic structure, e.g., the presence of spatially separated HOMO–LUMO orbitals with exceptionally small energy gap.

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