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Molybdenum−Pterin Chemistry. 3. Use of X-ray Photoelectron Spectroscopy To Assign Oxidation States in Metal Complexes of Noninnocent Ligands

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A series of molybdenum−pterin complexes produced from reactions of molybdenum and pterin reagents in various oxidation states has been investigated by X-ray photoelectron spectroscopy (XPS). Prior difficulties in making oxidation state assignments for the metal center and coordinated pterin can be resolved through comparison of Mo 3d binding energies (BE) for these new complexes with the BEs of standard molybdenum complexes. XPS analysis of molybdenum−pterin complexes produced from reactions of Mo(VI) reagents with tetrahydropterins show binding energies that are shifted by 1.5−1.8 eV to lower energies as compared to the BEs observed for the oxo-Mo(VI) reagents. The opposite shift in BE values is observed for complexes prepared from Mo(IV) chloride and fully oxidized pterins where BEs shift to higher values with respect to those for the starting Mo(IV) reagents. Remarkably, the BEs obtained for Mo−pterin complexes originating from Mo(VI)−tetrahydropterin reactions are nearly identical with those from Mo(IV)-oxidized pterin reactions. Both shifts are consistent with a Mo oxidation state of approximately +5. Both results indicate a significant delocalization of electron density over the molybdenum−pterin framework. This electronic redistribution is bidirectional since in the first system electron density flows from the reduced pterin to Mo(VI) and in the second case it flows from the Mo(IV) center to the electron-deficient oxidized pterin. Also described are syntheses of several tris(pteridine) complexes of Mo(0) that are diamagnetic molecules having intense MLCT absorptions near 500 nm. The electronic spectroscopic properties suggest that the pterin ligands in these complexes behave as strong pi-acids for Mo(0). This idea is verified by XPS analysis of Mo(piv-pterin)$_3$, where higher BEs are observed than for standard Mo(0) or Mo(+2) compounds. X-ray photoelectron spectroscopy may be one of the optimal spectroscopic tools for studying the poorly understood electronic interactions of molybdenum and pteridine heterocycles.

Introduction

There are several classes of metalloenzymes that require a reduced pterin cofactor. Chief among these are the aromatic amino acid hydroxylases,[1] the molybdenum and tungsten oxidoreductases,[2] and nitric oxide synthases.[3] These biological systems have encouraged recent studies of metal−pteridine coordination chemistry.[4] It is clear that molecules of the pterin, pteridine, and alloxazine families can bind to many different transition metals and that they can do so in a variety of oxidation

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(1) Kappock, T. J.; Caradonna, J. P. *Chem. Rev.* **1996**, *96*, 2659.

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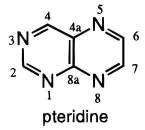
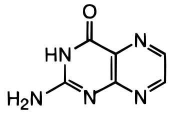
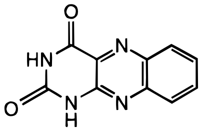
states. Since pterins and metals individually are redox-active species, it is not surprising that reactions between them lead to metal−pterin redox events.[5] We and others have previously reported such reactivity in copper,[6] iron,[7] and molybdenum[8−13] systems.



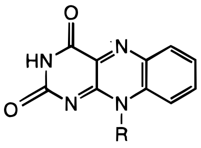
pteridine



pterin



alloxazine



flavin (isoalloxazine)

R = -$CH_2(CHOH)_3CH_2OPO_3^{2-}$ in FMN

R = -$CH_2(CHOH)_3CH_2$-ADP in FAD

A characteristic of transition metals coordinated to pterins in all oxidation states is a high degree of electronic delocalization between the metal and the coordinated pteridine. This is most easily detected by the intense electronic absorptions in the visible spectrum and is most precisely observed by the bond distances obtained from X-ray structural determinations. Because the extent of delocalization is variable, a problem ensues when formal oxidation states are assigned to the metal and pterin in these complexes. In the specific case of molybdenum complexes of reduced pterins, different oxidation state assignments have been made for Mo and the pterin ligand.[9,10]

In this paper X-ray photoelectron spectroscopy (XPS) is used to estimate molybdenum oxidation states for a variety of pterin complexes prepared from molybdenum reagents that span the range from Mo(0) to Mo(VI). For the complexes produced from reactions of Mo(VI) reagents and reduced *tetrahydro*pterins, we describe how the experimental results from XPS confirm previous computational predictions[10] where both methods favor a formal Mo(V) oxidation state assignment for the molybdenum center. These products may be best formulated as Mo(V) complexed by a trihydropterin radical. The diamagnetic behavior of the Mo(V)−H_3pterin molecule is explained by invoking a strong antiferromagnetic coupling between the Mo d^1 electron and the trihydropterin radical ligand. The reactivity of compounds in this group can be rationalized by considering this coupled electron pair available to both the molybdenum and the pterin, a trait consistent with a highly covalent interaction. XPS measurements on molybdenum complexes of oxidized pterins confirm the proposal from one of us that pterin coordination to molybdenum effects a partial molybdenum oxidation and pterin reduction.[4b] Finally the synthesis and characterization of tris(pteridine) complexes of Mo(0) are reported.

Experimental Section

All chemicals were purchased from Aldrich unless otherwise noted and used without further purification except as noted below. $MoO_2(acac)_2$ and $MoO_2(detc)_2$ have been prepared according to literature methods.[14,15] Preparation of the compounds **1**−**9** and **13** has been reported elsewere (refs for **1**−**9** are in Table 1, for **13** in ref 9). The synthesis of 2-pivaloylpterin followed the procedure in ref 4b. Solvents were dried over 4 Å molecular sieves except methanol, which was dried over 3 Å molecular sieves, stored under N_2, and used without further purification. All molybdenum reactions were performed in standard laboratory glassware under a nitrogen atmosphere in a Vacuum Atmospheres drybox or on a Schlenk line. FT-NMR spectra were obtained using an IBM 300 MHz FT-NMR, and chemical shifts are reported in parts per million referenced to internal TMS or solvent. Infrared spectra of samples of KBr disks were recorded on a Perkin-Elmer FT-IR Model 2000 instrument and are referenced to the 1601.4 cm^{-1} absorption of polystyrene. Electronic spectra were recorded using a Hewlett-Packard 8452A spectrophotometer. Solution conductivities were measured using a Barnstead PM-70CB conductivity bridge equipped with a Yellow Springs Instruments 3403 dip cell. Microanalyses were performed by Robertson Microanalytical Labs, Madison, NJ, or Galbraith Labs.

Syntheses. Mo(piv-pterin)$_3$ (10). 2-Pivaloylpterin (0.268 g, 1.1 mmol) was partially dissolved in deaerated acetonitrile (80 mL) to form a pale yellow slurry in a Schlenk flask. $Mo(CO)_6$ (0.136 g, 0.51 mmol) was added to the flask, and a reflux condensor connected to a bubbler was attached. The solution was heated at reflux for 8 h, cooled, and allowed to sit overnight. The dark purple brown solid was filtered using an emersion filter, isolated, and taken into the drybox for further workup. The pale red brown filtrate was discarded. In the drybox, the solid was washed with ether, filtered, and dried under vacuum. Yield of Mo(piv-pterin)$_3$ (**10**): 0.27 g, 91%. ^1H NMR (CD_3OD): 11.15 br s (1H) H3; 9.29 br s (1H) H(N2); 7.16 d, 6.14 d (2H) H6, H7; 1.27 s (9H) *t*-Bu.

Mo(ethp)$_3$ (11). 2-Ethylthiohydroxypteridine (ethp) (0.627 g, 3.0 mmol) was combined with $Mo(CO)_6$ (0.265 g, 1.0 mmol) and dimethylformamide (25 mL) in a Schlenk flask and purged with nitrogen. The solution was heated to 85 °C for 1 h. After cooling to ambient temperature, the reaction solution was filtered to yield a dark purple solid. The solid was washed several times with methylene chloride and then dried. The addition of methylene chloride to the filtrate induced precipitation of a second crop of product. Yield of Mo(ethp)$_3$ (**11**): 0.52 g, (73%). ^1H NMR (d_6-DMSO): 10.4 (1H, br s, *H*3, ethp); 6.87, 5.83 (2H, d, *H*6, *H*7, ethp); 2.98, 2.96 (2H, q, −CH_2−, ethp); 1.25 (3H, t, −CH_3 ethp). Anal. Calcd for $MoO_3N_{12}C_{24}H_{23}S_3$ [Mo(ethp)$_3$]: C, 40.00; H, 3.36; N, 23.32; S, 13.35; Mo, 13.31. Found: C, 39.51; H, 3.64; N, 22.88; S, 13.84; Mo, 13.62.

Mo(hp)$_3$ (12). This compound was prepared following the method for **11** with these changes. The reaction solution was heated to 115 °C for 3 h. The isolated dark purple solid was washed with diethyl ether. Yield of Mo(hp)$_3$·DMF (**11**): 0.52 g, (96%). ^1H NMR (d^6-dmso): 10.4 (1H, br s, *H*3, hp); 7.71 (2H, s, *H*2); 6.87, 5.83 (2H, d, *H*6, *H*7, hp). Anal. Calcd for $MoO_4N_{13}C_{21}H_{19}$ [[Mo(hp)$_3$]·DMF]: C, 41.12; H, 3.12; N, 29.68; Mo, 15.60. Found: C, 40.48; H, 3.52; N, 29.48; Mo, 14.97.

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XPS. X-ray photoelectron spectroscopy (XPS) investigations were carried out using a Kratos S800 XPS instrument. The samples were insulators and the energy scale of the spectra therefore shifted due to electrostatic charging. The energy scale was calibrated using Cl 2p = 198.4 eV and/or C 1s = 285.0 eV (aromatic and aliphatic carbon). The spectrometer was operated at a constant pass energy of 40 eV which resulted in a resolution of 1.0 eV for Ag $3d_{5/2}$. The spectra were measured with Mg $K\alpha$ radiation at a pressure of typically $<3 \times 10^{-8}$ mbar. The samples were pressed on an indium foil, then transferred into the XPS machine high vacuum as quickly as possible and investigated without further treatment. The binding energy data for the compounds will always refer to the Mo $3d_{5/2}$ line of the Mo 3d doublet where the $3d_{3/2}$ line is 3.2 eV apart from the $3d_{5/2}$ line with an ideal intensity ratio of $3d_{5/2}$:$3d_{3/2}$ of 3:2. These binding energies were obtained by deconvolution fitting of the spectra to fix the energy of the main peak (Mo $3d_{5/2}$) as correctly as possible while keeping the $3d_{5/2}$:$3d_{3/2}$ doublet line separation to approximately 3.2 eV. Due to the line broadening (charging effects, etc.) and poor overall intensities inherent in some of the spectra, the intensity ratio of the $3d_{5/2}$:$3d_{3/2}$ doublet in some optimized spectral fits deviated from the ideal 3:2 value. In particular, the fitting of **5** was difficult due to low intensity and the additional S 2s peak in the spectrum which resulted in a $3d_{5/2}$:$3d_{3/2}$ doublet intensity ratio of 5:4. Standard errors are about ±0.3 eV.

Results

Synthesis. A list of the molecules used in this XPS study for which X-ray crystal structures have been determined are in Table 1, including structural digrams, formula abbreviations, and references. One compound, $MoOCl_3$(riboflavin-(OAc)) (**13**), has not been structurally characterized by X-ray diffraction but is presumed to have a structure analogous to **9**.[9] All of the oxo-molybdenum−pterin complexes used in the XPS investigation have been prepared previously according to eqs 1 and 2.

$$\mathrm{Mo(VI)O_2L} + \mathrm{H_4pterin} + \mathrm{H^+} \rightarrow \mathrm{MoO(L)(H_3pterin)} + \mathrm{H_2O} \qquad (1)$$

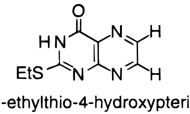
$$\mathrm{Mo(IV)Cl_4(MeCN)_2} + \mathrm{pterin} \xrightarrow[-\mathrm{HCl},\ -\,2\mathrm{MeCN}]{+\,\mathrm{H_2O}} \mathrm{MoOCl_3(pterinH)} \qquad (2)$$

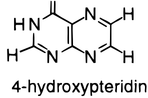
Equation 1 is a general description of the reaction between dioxo-molybdenum(VI) reagents with tetrahydropterins (H_4-pterin) that yields compounds **1**−**6**.[8−13] Equation 2 shows the reaction between desoxo molybdenum(IV) chloride and oxidized pterins which yields oxo-molybdenum−pterin compounds **7**−**9** through oxygen abstraction from trace water in the solvent.[4b]

The preparation of zerovalent Mo−tris(pteridine) complexes is reported here for the first time. These materials are easily synthesized from molybdenum hexacarbonyl and 3 equiv of pterin under thermal ligand substitution conditions (eq 3). The reaction fails for pteridines bearing any substituent other than hydrogen at the pterin position 6. For example, reaction of $Mo(CO)_6$ with 3 equiv of 6,7-dimethylpterin produces a tetracarbonyl species $Mo(CO)_4(dmp)$ from partial carbonyl substitution. No $Mo(dmp)_3$ is formed.

$$\mathrm{Mo(CO)_6} + 3\,\mathrm{L} \longrightarrow \mathrm{MoL_3}\ (\mathrm{L} = \text{piv-pterin, ethp, hp}) + 6\,\mathrm{CO}_{(g)} \qquad (3)$$

10: Mo(piv-pterin)$_3$
11: Mo(ethp)$_3$
12: Mo(hp)$_3$


2-ethylthio-4-hydroxypteridine
ethp


4-hydroxypteridine
hp

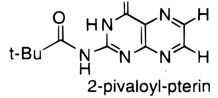
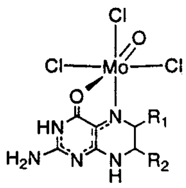
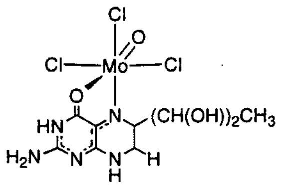
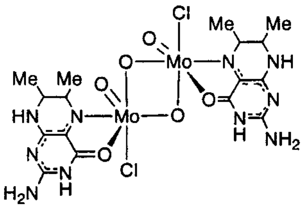
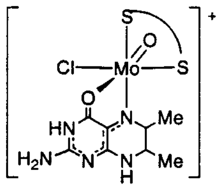
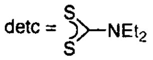
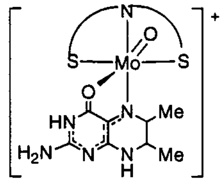
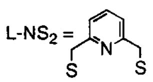
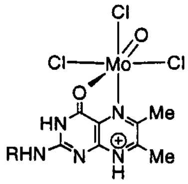
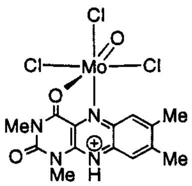
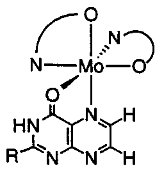

2-pivaloyl-pterin
piv-pterin

Table 1. Structures f Molybdenum Pteridine Complexes in This Work

	abbreviation	*[ref.]*
	$MoOCl_3(H_3pterin)$ **1** $R_1 = R_2 =$ H:	[11]
	$MoOCl_3(H_3dmp)$ **2** $R_1 = R_2 =$ Me:	[4b]
	$MoOCl_3(H_3biopterin)$ **3**	[9]
	$Mo_2O_4Cl_2(H_3dmp)_2$ **4**	[10]
	$[MoOCl(detc)(H_3dmp)]Cl$ **5** detc = 	[12]
	$[MoO(L\text{-}NS_2)(H_3dmp)]Cl$ **6** L-NS$_2$ = 	[13]
	$MoOCl_3(dmpH)$ **7** R = H	[4b]
	$MoOCl_3$(piv-dmpH) **8** R = t-BuC(O)-	[4b]
	$MoOCl_3(tmazH)$ **9**	[4b]
	Mo(piv-pterin)$_3$ **10** R = t-BuC(O)NH	this work
	Mo(ethp)$_3$ **11** R = EtS	this work
	Mo(hp)$_3$ **12** R = H	this work

A compilation of the spectroscopic data used to confirm the formulation Mo(pteridine)$_3$ is given in Table 2. The tris-

Table 2. Spectroscopic Data for Molybdenum(0) Tris(Pteridine) Complexes

UV/vis

	λ, nm (ϵ, M^{-1} cm^{-1})		
	Mo(piv-pterin)$_3$ (**10**)		
DMF	282	318	506(24 500)
DMSO	306(sh)	382(sh)	512(48 100)
methanol	254	332(sh)	516(23 300)
	Mo(ethp)$_3$ (**11**)		
DMF	272 (49 200)	388 (10 100)	504 (43 000)
	Mo(hp)$_3$ (**12**)		
DMSO	292 (13 100)	382 (4000)	502 (32 000) 778 (2200)

IR, cm^{-1}

	ν(CO,CN)				
Mo(piv-pterin)$_3$	1701	1624	1541	1483	1445
Mo(ethp)$_3$	1620	1570	1515	1455	
Mo(hp)$_3$	1621	1585	1527	1450	1432

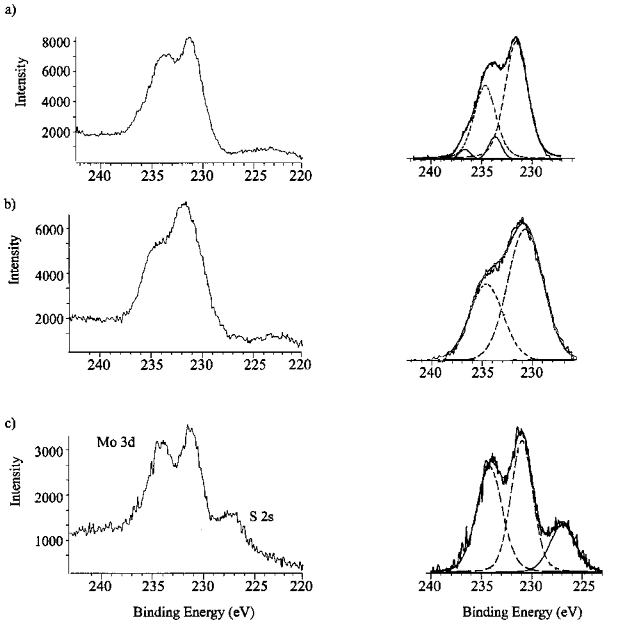


Figure 1. Mo 3d XPS spectra of (a) MoOCl$_3$(H$_3$dmp) (**2**), (b) MoOCl$_3$-(dmpH) (**7**), (c) [MoOCl(detc)(H$_3$dmp)]Cl (**5**). The illustrations on the right side show the deconvoluted XP spectra which were fitted to a 3.2 eV separation between the 3d$_{5/2}$:3d$_{3/2}$ lines of the doublet with resulting intensity ratios of approximately 3:2 for **2** and **7** and 5:4 for **5**.

Table 3. Molybdenum Binding Energies from X-ray Photoelectron Spectroscopy

	3d$_{5/2}$ binding energy (eV)
Mo Standards	
Mo(VI)O$_2$(acac)$_2$	233.3
Mo(VI)O$_2$(detc)$_2$	232.3
Mo(VI)O$_2$(L−NS$_2$)	232.1
Mo(IV)Cl$_4$(acetonitrile)$_2$	230.8
Mo(IV)Cl$_4$	229.7
Mo(IV)O(detc)$_2$	230.1
Mo Reduced Pterin Compounds	
MoOCl$_3$(H$_3$dmp) (**2**)	231.6
MoOCl$_3$(H$_3$biopterin) (**3**)	231.6
MoOCl$_3$(H$_3$pterin) (**1**)	231.6
Mo$_2$O$_4$Cl$_2$(H$_3$dmp)$_2$ (**4**)	231.7
[MoOCl(detc)(H$_3$dmp)]Cl (**5**)	231.0
[MoO(LNS$_2$)(H$_4$pterin)]Cl (**6**)	230.8
Mo Oxidized Pterin Compounds	
MoOCl$_3$(dmpH) (**7**)	231.7
MoOCl$_3$(piv-dmpH) (**8**)	231.3
MoOCl$_3$(tmazH) (**9**)	231.7
MoOCl$_3$(riboflavin-(OAc)) (**13**)	231.7
Mo(piv-pterin)$_3$ (**10**)	230.1

(pteridine) complexes are dark purple solids due to an intense absorption near 500 nm (ϵ > 20 000 M^{-1} cm^{-1}). Typical of many zerovalent molybdenum compounds, they decompose rapidly in air. The highly polar and coordinating solvents, such as DMF, DMSO, and methanol, that are required to solvate the pterin portions of the structures also cause degradation although at a much slower rate than in air. For example, **10** degrades at the rate of 1% per day in DMF and approximately 40% per day in DMSO. The compounds are nonelectrolytes in solution. Molybdenum coordination at the carbonyl oxygen O4 and the pyrazine nitrogen N5 is indicated by infrared spectroscopy. The shifts to lower energy for absorptions due to ν(C=N,C=O) modes is already documented in the literature for transition metals chelated at the O4, N5 sites.[4] The coordination of a neutral, i.e., undeprotonated pterin, is confirmed by the presence of the amide proton H3 in the NMR spectrum. A single set of resonances observed for the pteridine protons in complexes **10**−**12** (^{1}H NMR) is the basis for the *fac* isomer depicted in Table 1.

All of the oxo-molybdenum complexes **1**−**9** in this study have been structurally characterized by X-ray diffraction. The molecularity of **13** and the new Mo−tris(pteridine) series is supported by spectroscopic and microanalytical data.

X-ray Photoelectron Spectroscopy (XPS). This method allows the determination of the oxidation state of a metal ion provided the compound is reasonably stable and standard compounds are available. The energy scale of the spectra can be shifted due to electrostatic charging of samples that are insulators. In this case it is crucial to calibrate the energy scale which has been done by using the lines of C 1s = 285.0 eV (aromatic and aliphatic carbon) and Cl 2p = 198.4 eV. The results from the measurements of the Mo 3d binding energies of all molybdenum−pterin and −pteridine complexes studied in this work are listed in Table 3. Some examples of measured spectra of the Mo 3d binding energies of different complexes are depicted in Figure 1 and give an overview of characteristics found. In the spectra of compounds from reactions of Mo(VI) reagents with tetrahydropterins such as MoOCl$_3$(H$_3$dmp) (**2**) (Figure 1a, left side), deconvolution of the Mo 3d spectrum (Figure 1a, right side) indicates that the spectrum is the result of a superposition of two different Mo 3d spectra. The second component, amounting to about 9%, may be the result of surface oxidation due to short exposure to air. The spectrum in Figure 1b shows a compound from reaction of a Mo(IV) reagent with oxidized pterin like MoOCl$_3$(dmpH) (**7**), where the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ doublet is strongly broadened due to extensive electrostatic charging of the sample. In Figure 1c the spectrum of [MoOCl(detc)(H$_3$dmp)]Cl **5** gives additional information with the appearance of the S 2s peak of the sulfur signal. Figure 2 provides a graphical representation of the complete data and, for purposes of comparison, data for the molybdenum standards measured in this study or obtained from the literature.

Figure 2 includes representative literature data of molybdenum compounds which are mostly oxo, halide, or oxo-halide complexes. Inspection of the data shows that changing the metal environment can also greatly change binding energies even though the formal oxidation state of the metal center is unchanged. Two types of molybdenum standards were measured in this study: one group of complexes with Mo in a +6

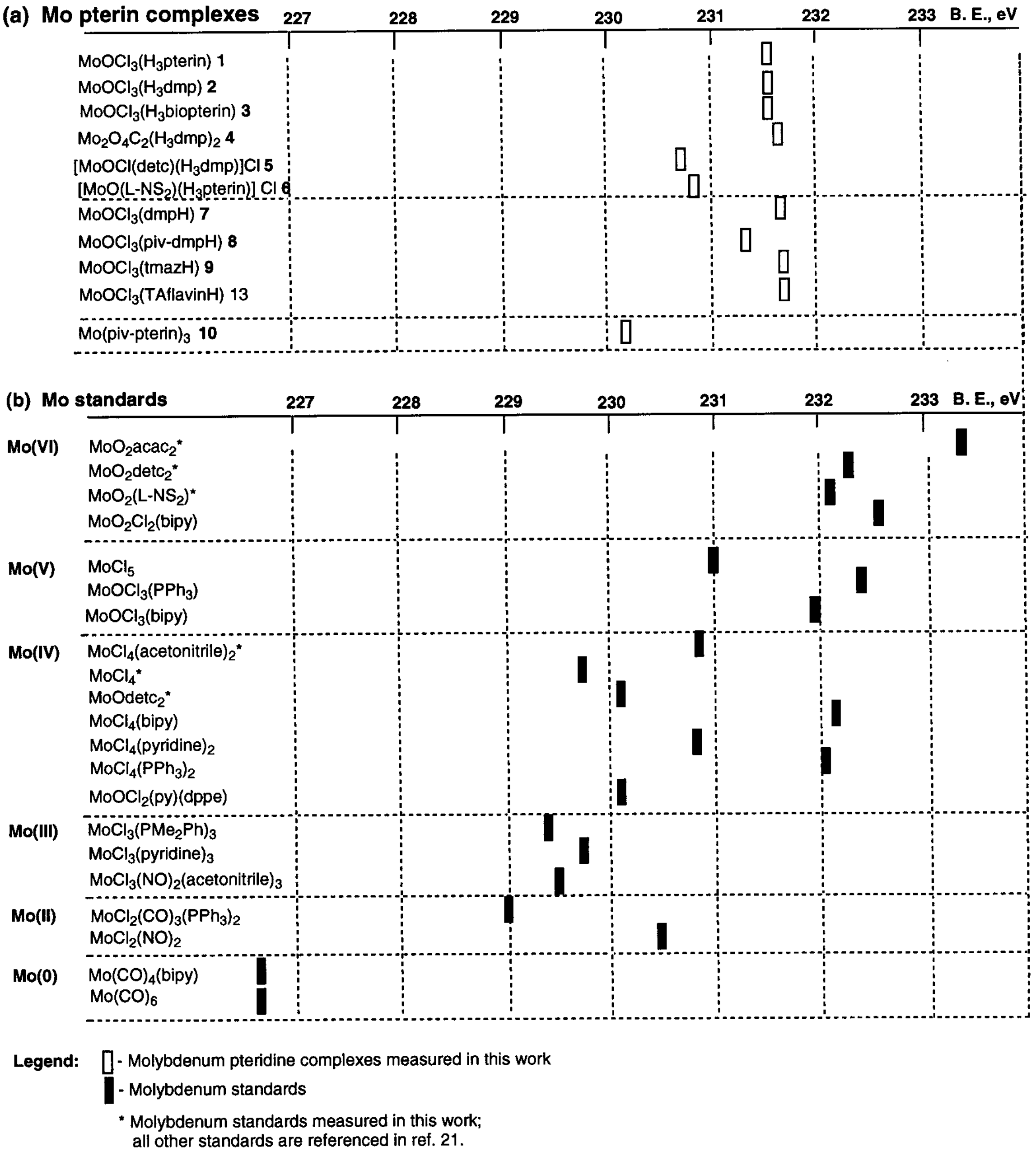


Figure 2. Graphical compilation of the Mo 3d XPS data measured in this work and taken from the literature.[21] (a) Molybdenum−pterin complexes. (b) Molybdenum standards.

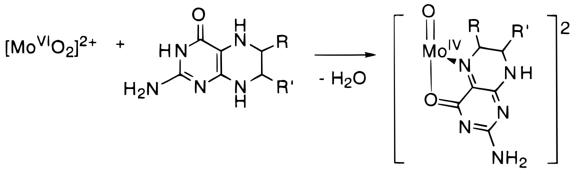
oxidation state and the other group with formally Mo(IV) centers. Each of these two groups included oxo-molybdenum compounds with either chloride or thiolate ligands. All measured standard compounds are either starting compounds for the preparation of the pterin/pteridine complexes or contain only ligands that are also present in the products, i.e., Mo−pterin/pteridine complexes. These properties are crucial conditions for their use as standards. The Mo(VI) standards measured in this study exhibited binding energy (BE) values between 233 and 232 eV while the BE values for the Mo(IV) standards fell in the range between 229 and 231 eV, indicating that a drop of two formal charge units from +6 to +4 correlates with a BE decrease of 2−3 eV. In contrast to the 4 eV range spanned by the standard compounds, all of the molybdenum−pterin and −pteridine compounds have binding energy values in a narrow range (230.7−231.7 eV) that is intermediate between the ranges seen for the Mo(VI) and Mo(IV) standards. Within the group of molybdenum−pterin compounds having only chloride and oxo ligands (complexes **1**−**4** and **7**−**9**), it is seen that all members of this subset have nearly identical BE values (231.3−231.7 eV). This observation underlines the efficient electronic redistribution in molybdenum−pterin compounds, a point receiving further elaboration in the Discussion. When sulfur is substituted for chlorine in the inner coordination sphere of the Mo−pterin compounds (complexes **5** and **6**), the BE shifts by 1 eV to lower energies.

Only one molybdenum compound in this XPS study lacks an oxo ligand. The Mo−tris(piv-pterin) complex **10** shows a BE of 230.1 eV, the lowest BE of all Mo−pterin complexes. Since the Mo is assigned a zerovalent oxidation state in this neutral complex, its BE is better compared with literature values for molybdenum(0) and other low-valent species (Figure 1). This comparison suggests the electron density on the metal in Mo(piv-pterin)$_3$ is considerably less than in Mo(0) and Mo(II) complexes and indicates a very strong electron density transfer from Mo to the electron-deficient oxidized pterin system.

Discussion

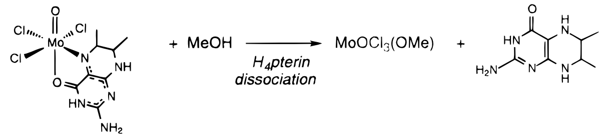
Molydenum and pterins make an unusual reaction system because each have a wide range of oxidation states available. Within this study are complexes that incorporate the two components in both their fully reduced and their fully oxidized oxidation states. Pairing two redox-active species predictably favors electron transfer between them. This prediction has been borne out for transition metal−pterin systems, but oxidation state assignments for the metal and pterin pieces of the product have remained ambiguous and difficult to make. Perhaps the best example of this problem concerns the reactions of dioxo-molybdenum reagents with fully reduced tetrahydropterins. This system was initially explored as a means to understanding potential reactivity available to the molybdenum cofactor (Moco), which at that time was believed to possess both a Mo(VI) center and a tetrahydropterin.[8,9] The premise for the investigations was that Mo in its highest oxidation state would likely react with a pterin in its most reduced oxidation state, predicting a net redox reaction as the anticipated outcome.

The first two reports of dioxo-molybdenum(VI) reactions with tetrahydropterins described the products as oxo-Mo(IV)−dihydropterin species (eq 4).[8,9] The conformation of the chelated dihydropterin was consistent only with a quinonoid isomer of dihydropterin.



(4)

Since quinonoid dihydropterin is a highly reactive and unstable species when generated by other procedures,[16] its coordination and stabilization on Mo was intriguing. However, further study of these and other systems eventually suggested that interpreting eq 4 as a two-electron transfer from tetrahydropterin to molybdenum was an overly simplified view. Results accumulated (eqs 5−9) which illustrated how the chemical behavior of molybdenum was sometimes typical of a tetrahydropterin complex[10] of Mo having a formal oxidation state +6, but in other reactions the observed outcomes were typical of a oxo-Mo(IV) center.[11,12] A comparison of eq 7 with eq 8 shows the subtle difference made by methyl substituents on pterin in determining whether oxygen atom transfer occurs.



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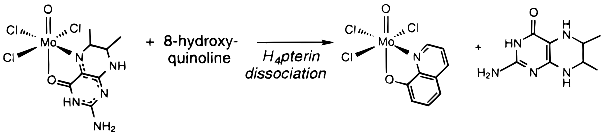

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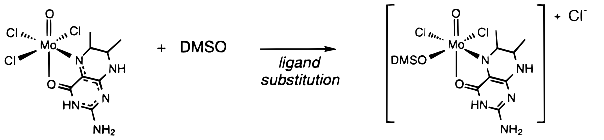

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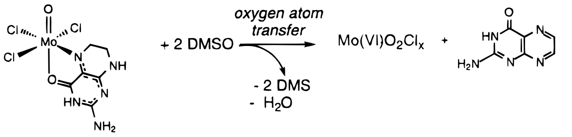
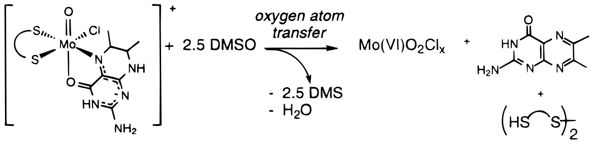
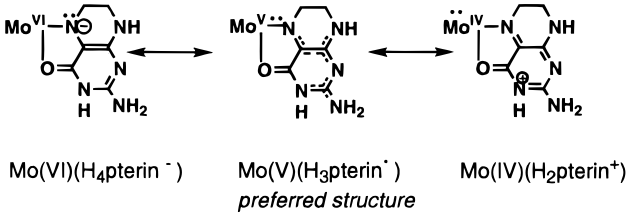


(8)



(9)

The limiting Mo(VI) and (IV) formal oxidation states coordinated by the corresponding tetrahydro- and dihydropterin ligands, respectively, are shown below with an intermediate, delocalized structure. The intermediate structure, which can be described as a Mo(V) ion coordinated by a trihydropterin radical ligand, is the charge distribution favored by theoretical work.[10] It was the goal of the XPS measurements described in this paper to obtain experimental confirmation of a more defined oxidation state of the Mo center and the pterin heterocycle. Consideration of the XPS data in Table 3 and the graphical depiction in Figure 2 confirm that a Mo(V) oxidation state best fits the experimental results.



A **B** **C**

The preferred Mo(V)−trihydropterin radical structure **B** can be used to understand the variable reactivity types of the molybdenum pterin complexes in the following way. An explicitly drawn lone pair of electrons is included in the structures above. Beginning with consideration of structure **A** where the reactants Mo(VI) and H$_4$pterin are initally combined, this lone pair can be considered to originate from the deprotonation of the tetrahydropterin at N5. The shift of this pair to reduce Mo to the +4 oxidation state in structure **C** would result in a net two-electron redox reaction. In the preferred stucture **B** this lone pair is highly covalent and shared between the molybdenum and the pterin chelate. The variable reactivity can then be understood as the shifting of this electron pair to either the Mo (producing the reactivity of eqs 8 and 9) or to the pterin (producing the reactivity of eqs 5−7) depending on the reaction conditions or the environment presented by the ancillary ligands. For example, shifting the shared electron pair in **B** to the pterin at position N5 in **A** would likely result in a favored protonation at N5 followed by dissociation from Mo, the result observed in eqs 5 and 6. The covalent lone pair in structure **B** also emphasizes the strong antiferromagnetic coupling in these complexes instead of the diradical view that is suggested by the Mo(V)−trihydropterin formulation.

XPS measurement of molybdenum complexed by oxidized pterins or flavins, such as in **7**−**9**,[4b] gave binding energies nearly identical with those observed for the molybdenum complexes of reduced pterins. This suggests that oxidized pterin complexes should also be viewed as Mo(V) species with one-electron reduced pterins. Indeed partial pterin reduction has been proposed to account for the protonated form of the chelated pterins in **7**−**9**.[4b] The sum of the XPS results emphasize that electron flow between molybdenum and pterin is bidirectional and that there is an apparent preference of the molybdenum

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atom to acquire the equivalent of a +5 oxidation state regardless of the oxidation state of the coordinated pterin ligand.

Pterins and pteridines join the other classes of chelating ligands that are well-known for "noninnocent" behavior when complexed to transition metals. Prototype examples of noninnocent ligands whose reduced and oxidized forms make a redox pair are dithiolene/dithioketone,[17] *o*-diamine/*o*-diimine,[18] and *o*-catecholate/*o*-benzoquinone.[19] The noninnocent nature of these ligands can be traced to the highly covalent interaction between transition metals and the ligands resulting from well-matched frontier orbital energies and overlap. A facile electronic flow between metal and ligand means that the ligands may effectively serve as "electronic buffers", a term recently coined by Enemark et al. in order to explain the constant first ionization energy of a series of molybdenum dithiolene complexes whose formal oxidation states varied from +2 to +5.[20] Our results presented here corroborate that noninnocent pterin and pteridine ligands also behave as electronic buffers to molybenum.

Conclusion

XPS has been used to investigate the effective charge on molybdenum in a series of molybdenum−pterin complexes in various oxidation states. Prior difficulties in making oxidation state assignments for the metal center and coordinated pterin have been resolved through comparison of Mo 3d binding energies for these complexes with standard molybdenum complexes. Complexes obtained from reaction of Mo(VI) complexes with tetrahydropterins show binding energies that are 1.5−1.8 eV lower than starting metal complexes consistent with a Mo(V)−trihydropterin assignment. We favor this formulation for these products and view the electron pair originating from the tetrahydropterin as covalently shared between Mo and pterin ligands. This electron pair is thus accessible to both the Mo and pterin ligand in subsequent reactions, a view that resolves the diverse reactivity observed for this group of compounds. Complexes prepared from Mo(IV) and fully oxidized pterins show a shift of Mo 3d binding energies to higher values and also correspond to a Mo(V) oxidation state. The synthesis of several tris(pteridine) complexes of Mo(0) is described. These novel pterin compounds are diamagnetic, neutral molecules having intense MLCT absorptions near 500 nm. The Mo 3d binding energy observed in one tris(pterin) complex is higher than observed in other Mo(0) or Mo(2+) compounds and implies a significant flow of electron density from the Mo(0) core to the pterin heterocycle. The XPS results agree with the electronic spectroscopic properties which suggest that the pterin ligands in these tris complexes behave as strong pi-acids for Mo(0). Therefore, all molybdenum−pterin complexes have significant delocalization of electron density over the molybdenum−pterin framework. X-ray photoelectron spectroscopy may be the optimal spectroscopic tool for studying the poorly understood electronic interactions of molybdenum and pteridine heterocycles.

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