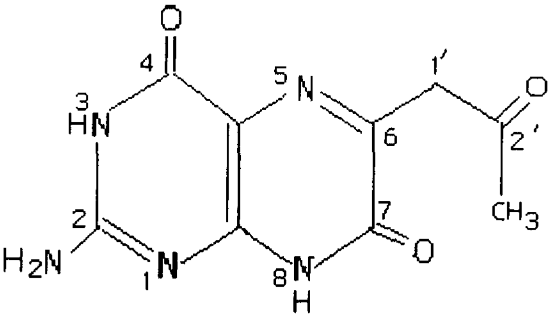
PREFACE

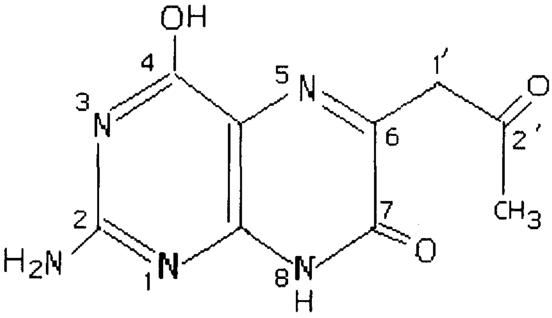
The research work embodied in this thesis entitled, " *Synthetic, Physico-chemical and Reactivity Aspects of Co-ordination Compounds of Molybdenum and dioxouranium (VI) with Pterin and Aldimine Ligands*", has been carried out in the laboratory of Professor Parag S. Roy, Department of Chemistry, University of North Bengal. The thesis consists of five chapters. In Chapter I, a general introduction stresses the importance of the works reported here, along with the highlights of the available knowledge in these fields and the necessary references (indicated by superscript numbers), which are grouped together at the end of this treatise. The aims and objectives of this work as described in Chapter I (Introduction), points out the scope of the present work, research goals to be achieved and the outlines of the experimental techniques used for realizing them. Chapter II, III and the first Section of Chapter IV are concerned with the investigation on coordination compounds of molybdenum with the following pterin ligands (schematic structures of both keto and enol forms, IUPAC and trivial nomenclatures, together with their abbreviations used here, are indicated below).



(keto – form)

Scheme – (P-1)

2 – amino – 6 – (2′ - oxopropyl) pteridin – 4,7(3H, 8H) – dione (IUPAC)



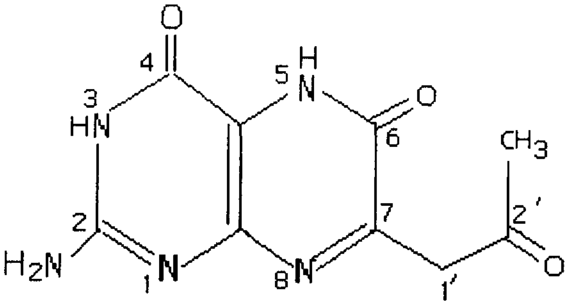
(enol – form)

Scheme – (P-2)

2 – amino – 4 – hydroxy – 6 – (2′ - oxopropyl) pteridin – 7(8H) – one (IUPAC)

6 – acetonyl – isoxanthopterin (Trivial)

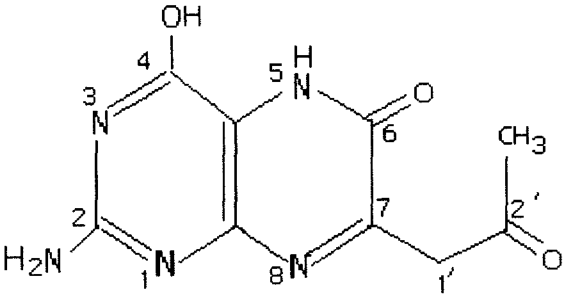
$[H_2(pte_1)]$ (abbreviation)



(keto – form)

Scheme – (P-3)

2 – amino – 7 – (2′ - oxopropyl) pteridin – 4,6(3H,5H) – dione (IUPAC)



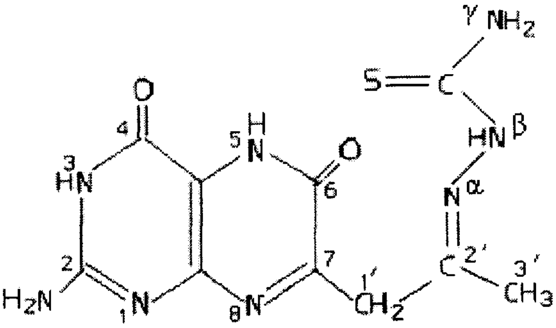
(enol – form)

Scheme – (P-4)

2 – amino – 4 – hydroxy – 7 – (2′ - oxopropyl) pteridin – 6(5H) – one	(IUPAC)
7 – acetonyl – xanthopterin	(Trivial)
[$H_2(pte_2)$]	(abbreviation)

2 – pivaloylamino derivative of this compound has been crystallized and its crystal as well as molecular structures have been determined through single crystal X-ray diffraction study.

A new Schiff base ligand has been synthesized by condensing 7 – acetonyl – xanthopterin [$H_2(pte_2)$] with thiosemicarbazide [$NH_2C(=S)NHNH_2$, H(tsc)]:



Scheme – (P-5)

α – N (7 – acetonylidene – xanthopterin) thiosemicarbazide

[$H_3(pte_2–tsc)$] (abbreviation)

Studies on μ – oxo binuclear molybdenum (V) complexes [possessing the $(Mo^{V}{}_2O_3)^{4+}$ core] of aldimine derivatives of L - / D – amino acids, constitute the subject matter of Section - II of Chapter IV. In Chapter V dioxouranium (VI) complexes of chiral aldimine ligands derived from asparagines, arginine and glutamine are discussed.

In each Chapter Tables, Figures and Schemes have been numbered using a combination of Roman and Arabic numbers; for example, the first Table of Chapter I is numbered (I – 1), the second Table is numbered (I – 2), whereas the first Table of Chapter II is numbered (II – 1), the second Table as (II – 2) and so on. For Chapters containing two sections, the same procedure is followed without any break. In each Chapter (and for each Section of Chapters containing two Sections), the compounds have been assigned serial numbers (in bold letters within first bracket) and referred to them by these numbers during discussion.

The multiplicities of NMR spectral signals are indicated by the usual abbreviations, e.g., ‘s’ for singlet ; ‘bs’ for broad singlet, ‘d’ for doublet, ‘dd’ for doublet of doublet, ‘t’ for triplet and ‘m’ for multiplet.

The pterin ring numbering system has been used for the Schemes related to the Schematic structures as well and utilized in discussion part. The optimized (lowest steric energy) computational model (CHEM3D) of the pertinent ligands and complex compounds obtained here through molecular mechanics calculations (MM2) are numbered as per the program used [Chem3D ultra, version 8.0 (2004) and the higher version, Cambridge Soft Corporation, U.S.A.]. A correspondence between the two above-mentioned sets of numbering systems has been indicated in the text. The same applies for the ORTEP diagram obtained through X-ray crystallography for the 2 – pivaloylamino derivative of 7 – acetonyl – xanthopterin [$H_2(pte_2)$]. The CHEM3D model of this compound has also been obtained in order to compare the two sets of bond length (Å) and bond angle (deg.) data obtained through the MM2 calculations and single crystal X-ray diffraction study respectively; good agreement (discussed later) between the two sets of data, stresses the reliability of the MM2 method, which has been used here extensively.

For most of the compounds discussed here, the optimized (MM2) bond length (Å) and bond angle (deg.) data, have been compared with the available literature X-ray structural data of related systems, for checking the efficacy of the MM2 method in obtaining the CHED3D models of the present molybdenum – pterin systems as well as the molybdenum – aldimine systems. The following colour code has been used for labeling the different atoms of CHEM3D models:

red coloured ball represents the oxygen atom;
blue coloured ball represents the nitrogen atom;
ash coloured ball represents the carbon atom;
green coloured ball represents the chlorine atom;
yellow coloured ball represents the sulphur atom;
dark-ash coloured ball (larger size) represents the molybdenum atom;
pink coloured ball (small size) represents the lone electron pair.

References are mentioned at the end of this thesis following standard international conventions. In spite of taking outmost care, very few number of references are repeated and the author expresses regret for this.

Preliminary reports involving part of this work have been submitted to CSIR, New Delhi as annual progress reports as well as final technical report. Two papers have already been published out of the subject matter of Chapter II [34]. Materials of other Chapters are presently in the process of publication in different journals. Several publications on coordination compounds of pterin ligands reflect continuing interest of this laboratory on this subject [48, 178, 179]. Parts of this work have been presented in a couple of reference proceedings, e.g., National Seminar on current Trends in Chemistry – II, 4th March, 2008.

Md. Afsar Ali; 19.8.2008

August, 2008 **(MD. AFSAR ALI)**