# SUMMARY

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# CONCLUDING REMARKS

Now, it is time for an assessment of the experimental findings of this thesis vis – a – vis the objectives stated in Chapter I.

The pterin ligands $[H_2(pte_1)]$, $[H_2(pte_2)]$ or $[H_3(pte_2 - tsc)]$ act here as reducing agents and reduce the molybdenum starting materials in the higher oxidation state to a lower one ($Mo^V$ / $Mo^{IV}$) in the complex, which has been assignment using different physicochemical methods. Besides this, new oxomolybdenum cores are formed during such synthetic steps. For example, in Chapter IV, Section – I, the mononuclear $Mo^V$ – starting material used for the synthesis of (**4**) $\{(Et_4N)[(Mo^V_2O_3)(Hpte_1)(Hcys)Cl_3].CH_3OH\}$ was converted to a binuclear species $(Mo^V_2O_3)^{4+}$. In case of (**1**) $\{[(Mo^{VI}_2O_5)(Kpte_1)(Hcys)(CH_3OH)].2CH_3OH\}$ DMSO used during its synthesis, oxidized the intermediate $Mo^{IV}$ complex to a higher oxidation state with $(Mo^{VI}_2O_5)^{2+}$ core ; its reactivity towards $PPh_3$ verified the assignment of higher oxidation state (e.g., VI).

The role of the solvent used for the preparative purpose (e.g., $CH_3OH$) is to be assessed with respect to that of $H_2O$ in the catalytic cycle of oxomolybdoenzymes. Loss of an oxo group from the $Mo^{VI}$ species during enzyme turnover is made up by the $H_2O$ molecule giving $Mo - OH_2$ and undergoes facile deprotonation to Mo – OH or Mo = O species accompanied by changes in the oxidation state of the metal centre [26]. Incorporation of the solvent (e.g., $CH_3OH$) in the coordination sphere of several complexes during their synthesis, points towards the important role played by it during the synthetic process.

Chemical compositions of the new complexes have been established with the help of elemental analysis, ESIMS, IR and $^1$NMR data. Their optimized molecular geometries have been obtained by molecular modelling studies [CHEM3D models obtained through MM2 calculations] along with their bond lengths and bond angles data, which are in agreement with the published X-ray structural data on different molybdenum – pterin coordination compounds. Besides this, the molecular structure of the ligand $[H_2(pte_2)]$ has been established by X-ray crystallography. The spectroscopic data are consistent with the frame work of the above molecular structures.

The present molybdenum – pterin complexes undergo oxygen atom transfer reaction with typical enzyme substrates like DMSO, $Me_3N \rightarrow O$, $PyN \rightarrow O$ or $PPh_3$, as per the oxidation state of the molybdenum centre. Complex (7) {[$(Mo_2^{VI}S_5)$ {$H(pte_2$ -tsc)} $(CH_3OH)_3$].$CH_3OH$} in Chapter III, contains a $(Mo_2^{VI}S_5)^{2+}$ core and undergoes sulphur atom transfer reaction with $PPh_3$, indicating a higher oxidation state for the Mo – centre here. Most of the above reactions conform to substrate saturation type kinetics with negative entropy of activation values, indicating associative type reaction mechanism. The kinetic parameters of these reactions are comparable to the available literature data for similar type of reactions. Nature of such group transfer reactions has been substantiated by reaction stoichiometry studies as well as ESIMS data in a few cases. The sulphur containing secondary ligands (Chapter IV, Section – I) help to manifest different tautomeric forms of the pterin ligand residue in the relevant complexes in solution, which are evident from the $^1H$ NMR spectral data. These data also indicate electron flow from the $NH_2(2)$ group of the pterin ligand residue towards the molybdenum centre in the relevant complexes, thereby promoting the reactivity as mentioned above. Probably such property (that is, flexibility of the pterin ligand residue with respect to electron flow coupled with the possibility of different tautomeric forms) has promoted Nature to select pterin as the essential component of the molybdenum – containing enzymes (except nitrogenase).

The CV data as well as fluorescence spectral data throw light on the changes in electronic structures during different redox reactions involving these complexes. It is evident from the discussions (in the different chapters of this thesis) that the ligand – centred as well as the metal – centred redox systems supplement each other in the new molybdenum – pterin complexes, giving them unique oxygen atom transfer reactivity property towards typical enzyme substrates ; electronic as well as fluorescence spectra have proved to be valuable probes in this respect. In other words, at least a few of the above – mentioned new complexes can be considered as functional models of oxomolybdoenzymes.

In Chapter IV, Section – II fresh characterization and reactivity studies of $(Mo^{V}_2O_3)^{4+}$ - aldimine ligand complexes are discussed. The possible skew disposition of the two Mo = $O_t$ bonds about the Mo – $O_b$ – Mo bond [of the $(Mo^{V}_2O_3)^{4+}$ - core] leads to two sets of MO levels with a paramagnetic ground state (S = 1). This aspect coupled with the chiral ligand backbone casts its influence on the relevant EPR and CD spectra, associated with electronic transitions of the oxometal entity and the L → M charge transfers. Complexes (**4**), (**5**) and (**6**) possess almost similar type of chemical compositions, but different physicochemical and spectroscopic properties (e.g., $\mu_{eff}$ values, IR, EPR and CD spectral data); they also differ with respect to their oxygen atom transfer and electron transfer reactivities. Most of these differences can be attributed to the different arrangements of the $(Mo^{V}_2O_3)^{4+}$ - core, viewed in the light of their CHEM3D models (MM2 method). This conformational control of reactivity / property may prove vital in understanding the behaviour of oxomolybdoenzymes or their model systems.

Chapter V deals with the fresh characterization (ESIMS data as well as X-ray structural study in one case) and reactivity studies on $UO_2^{2+}$ - complexes with aldimine ligands. These complexes serve as excellent vehicle for correlating the $^1$H NMR and CD spectra of the aldimine ligands, using the diamagnetic $UO_2^{2+}$ - entity as a chiroptical probe. The L → M $\pi$ – bonding ability of the $UO_2^{2+}$ - entity as evident from $^1$H NMR data, may be valuable for a search of $UO_2^{2+}$ - complexes with purposefully modified chemical / physical behaviour. These uranyl complexes react with $Na_2SO_3$, undergoing reduction to the $U^{IV}$ state with second order rate constants. The kinetic data are at par with the available literature data. The novelty of this work is the kinetic aspect where the two step reduction of the $UO_2^{2+}$ - entity to the $U^{IV}$ state, is distinctly presented.

Before closing the concluding remark, the author feels that the investigations presented in this thesis will be helpful to the researchers working in the field of molybdenum – pterin chemistry in particular and coordination chemistry of redox "non-innocent" ligands in general.

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