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SYNTHESIS AND STRUCTURAL STUDIES ON SOME DIOXOMOLYBDENUM (VI) COMPLEXES BEARING 1-(1-HYDROXYPHTHALEN-2-YL) ETHANONE MOIETY

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A number of molybdenum complexes $\text{Cis-MoO}_2(\text{NE})_2 \cdot \text{CH}_3\text{OH}$, $\text{Cis-MoO}_2(\text{HRSB})_2 \cdot n\text{H}_2\text{O}$ {R= H, 4-Br, 4-OCH₃, 4-CH₃ and n= 0, 1, 2} $\text{Cis-MoO}_2(\text{HL})(\text{acac})n\text{H}_2\text{O}$ {HL= HNEBH, HNEINH, HNENH, HNEPH, n=0,1}, $\text{Cis-[MoO}_2(\text{L})_2 \cdot n\text{H}_2\text{O]}$, {L= HNE-2-ABH, HNE-4-ABH, n = 0, 2} and $\text{Cis-[MoO}_2\text{O}_5(\text{HNEAH})_2]$ have been synthesized and characterization by magnetic, spectroscopic (FT-IR, ¹H and ¹³C-NMR spectra) and electrochemical techniques. The complexes were made reaction of $\text{Cis-MoO}_2(\text{acac})_2$ with the ligands, (1-hydroxynaphthalen-2-yl)ethanone (HNE), 2-amino-N-(1-(1-hydroxynaphthalen-2-yl) ethylidene)benzohydrazide (HNE2-ABH), 4-amino-N-(1-(1-hydroxynaphthalen-2-yl)ethylidene)benzohydrazide (HNE4-ABH), N-(1-(1-hydroxynaphthalen-2-yl) ethylidene)benzohydrazide (HNEBH), N-(1-(1-hydroxynaphthalen-2-yl)ethylidene)acetohydrazide (HNEAH), N-(1-(1-hydroxynaphthalen-2-yl)ethylidene)nicotinohydrazide (HNENH), N-(1-(1-hydroxynaphthalen-2-yl) ethylidene)isonicotinohydrazide (HNEINH), N-(1-(1-hydroxynaphthalen-2-yl)ethylidene)picolinohydrazide (HNEPH), they coordinate as dibasic tridentate (OON) or (E)-2-(1-(phenylimino)ethyl)naphthalen-1-ol (HASB), (E)-2-(1-(p-tolylimino)ethyl)naphthalen-1-ol (HTSB), E-2-(1-(4-methoxyphenylimino)ethyl)naphthalen-1-ol (HMSB) and (E)-2-(1-(4-bromophenylimino)ethyl)naphthalen-1-ol (HBrSB) monobasic bidentate (NO). Both the molecular and the spectroscopic studies showed that, the complexes are octahedrally coordinated. The redox properties, of the electrode couples and the stability of some complexes towards reduction were linked to the electron withdrawing or ability releasing of the substituent in the Schiff bases and the hydrazones. Results show that, changes in E_{1/2} for the complexes due to remote substituent effects could be related to changes in basicity of the carbonyl oxygen of the hydrazide moiety in the hydrazone ligand. The electron-donating substituents stabilized Mo (VI) complexes while electron-withdrawing groups favored lower oxidation state of Mo (V) and/or Mo (IV) species. The nature of mechanism and kinetic parameters of the electroactive chelates are strongly dependent on the substituent. The EHOMO and ELUMO level of hydrazones, from both electrochemical and theoretical data also back-donation energy ($\Delta E_{\text{back-donation}}$), ionization potential (I), molecular dipole moment (μ), electronegativity (χ), softness (σ) electron affinity (A), global hardness (η) and electrophilicity index (ω) were calculated.

BIOGRAPHY

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