Preparation and Characterization of Mononuclear Ni Complexes of Tetradentate Amine-thioether and Amine-thiolate Ligands

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A short route for the preparation of tetradentate amine-thioether and amine-thiolate ligands derived from thiosalen is reported. The ligating properties of several of the synthesized ligands towards Ni(II) has been examined. The diamine-dithiophenolate ligands $(L^6)^{2-}$ [H_2L^6 = *N,N′*-dimethyl-*N,N′*-di(2-mercaptobenzyl)-ethane-1,2-diamine] and $(L^7)^{2-}$ [H_2L^7 = *N,N′*-di(2-mercaptobenzyl)-piperazine] support the formation of four-coordinate $Ni^{II}N_2S_2$ complexes [$Ni^{II}(L^6)$] (**10**) and [$Ni^{II}(L^7)$] (**11**). By contrast, the amine-thioethers **2** [*N′,N″-bis*(2-(*tert*-butylthio)benzyl)ethane-1,2-diamine], L^2 [8,11-diaza-5,13-dibenzo-1,4-dithia-cyclotetradecane] and its N-methylated derivative $L^{2,Me}$ were found to produce the six-coordinate Ni(II) complexes [$Ni^{II}Cl_2$(**2**)$_2$] (**9**), [$Ni^{II}_2(\mu$-Cl$)_2(L^2)_2][ClO_4]_2$ (**12**), [$Ni^{II}(NCS)_2(L^2)$] (**13**), and [$Ni^{II}Cl_2(L^{2,Me})$] (**14**). The results of IR, NMR and UV/vis spectroscopy and the crystal structures of complexes **9** – **13** are reported.

Key words: Nickel Complexes, Macrocyclic Ligands, N Donor, S Donor