Abstract

Synthesis and Characterisation of Low-valent Nickel Thiolate Complexes

Although transition metal thiolate chemistry is well known and studied since 35 years, there is less insight into the specific synthesis of low-valent nickel thiolate complexes with sulphur-only ligand sphere. Nickel complexes with sulfur containing ligands are well known in biological systems, and so interest is focussed on complexes with the oxidation states +2 and +3. We suppose this is erroneous, particularly as in more reduced nickel complexes with sulphur-only ligand sphere exceptional bonding properties are existent. The nickel complexes synthesized and characterized in this work adduce excellent evidence of these properties and it is obvious to suppose, that they could be of some importance with regard to metallo-enzymes. With the results of this work we enhance our previous understanding of low-valent nickel thiolato complexes.

Investigating the reactions of nickel(II) chloride and nickel(II) bromide respectively with the *tert*-butanethiolato ligand in a mixture of acetonitrile/methanol, new five-, seven-, eight-, seventeen, and twenty-nuclear complexes with unusual trigonal-planar coordination and in some cases additional tetrahedral coordination of the nickel centres were synthesized and structurally characterized:

- $[BzEt_3N][Ni_5S(S^tBu)_5]$ (**1**)
- $[BzEt_3N][Ni_7S(S^tBu)_8]$ (**2**)
- $[(Ph_3P)_2N]_3[Ni_7S(S^tBu)_9]_2[Ni_7S(S^tBu)_8]$ (**3**)
- $[(Ph_3P)_2N][Ni_8S(S^tBu)_9]\cdot½MeOH$ (**4**)
- $[Ni_8S(S^tBu)_9]$ (**5**)
- $[Ni_{17}S_5(S^tBu)_{15}]$ (**6**)
- $[(Ph_3P)_2N]_2[Ni_{20}S_{12}(S^tBu)_{10}]\cdot 2MeCN$ (**7**)

Reactions of low-valent nickel tert-butanethiolato complexes with N-heterocyclic carbenes (NHCs) afforded the novel complexes $[Ni_4S_2(S^tBu)_4(^iPr_2Me_2NHC)_2]$ (**8**), $[Ni_3O(S^tBu)_2(Me_2NHC)_5]I_2$ (**9**) and $[Ni(S^tBu)_2(^iPr_2Me_2NHC)_2]$ (**10**).