Chemical Models of the Active Site Cores of Some Nickel Containing Enzymes

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ABSTRACT

The active site core structures of the nickel containing metalloenzymes carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS) and nickel-iron hydrogenase have recently been resolved by X-ray crystallography and each catalyses reactions of industrial and environmental importance. Here, existing nickel and iron complexes have been utilised to prepare new, and refine existing, models of the active site cores with a view to expanding the knowledge of the mechanisms of the enzymes and developing new catalysts that are cheaper and cleaner.

The complex $[NiCl_2(dppp)]$, dppp = 1,3-bis(diphenylphosphino)propane, and its close analogue $[NiCl_2(dppe)]$, dppe = 1,2-bis(diphenylphosphino)ethane, on reaction with a complex containing nickel in an N_2S_2 coordination environment, $[NEt_4]_2[Ni(ema)]$, H_4ema = *N,N'*-ethylenebis(2-(acetylthio)acetamide), gave new dinuclear nickel compounds, [Ni(ema-*S,S'*)Ni(diphos)], diphos = dppp or dppe, which are very good structural models of the dinickel subsite of the ACS active site 'A' cluster. They have been fully characterised and the crystal structure of one resolved. Their redox chemistry and reactivity has been investigated. The metal chelating compound 1,10-phenanthroline was used to explore the lability of the nickel atoms and a comparison made to the 'A' cluster. In both, the nickel not in the N_2S_2 coordination environment was removed. A new ligand, which could encapsulate two metal centres, with N_2S_2 ligation to one metal and all sulfur ligation to the other, is proposed.

Other Group 10 metal-bisphosphine complexes were used to give heterometallic compounds, [Ni(ema)M(diphos)], M = Pd or Pt, analogous to the dinuclear nickel complexes. The crystal structures of the four compounds were resolved and compared. To give dimetallic complexes that supercede the nickel-iron hydrogenase models previously prepared in this laboratory, $[NiCl_2(dppp)]$ was reacted with $[NEt_4][Fe(NS_3)CO]$, $NS_3 = N(CH_2CH_2S)_3^{3-}$, and its nitrosyl analogue. The crystal structures of $[\{Fe(NS_3)(CO)_2\text{-}S,S'\}NiCl(dppp)]$ and related complexes were resolved. An unusual bis(dicyano-nickel) complex, $[\{Ni(CN)_2(dppp)\}_2\mu\text{-}(dppp)]$, was also prepared and structurally characterised.