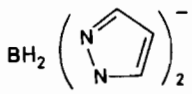
Normally, such reductions give oxo bridged Mo(V) dimers; the presence of bulky groups on the ligands, however, inhibits the dimerization.

Representative ligands:

L:

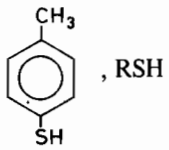
$RNHCH_2C(R')_2SH$
R = Me, Et, Ph, Bz
R′ = Me, Et



L′:

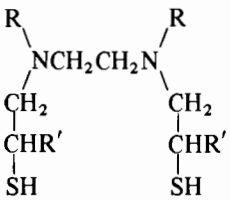
$R_2NCH_2CH_2NHCH_2C(R')_2SH$
R = Me; R′ = Me, Et

L″:

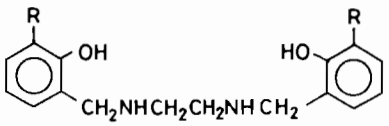


R = i-pr, t-but

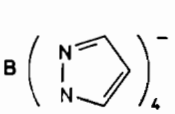
L‴:



R = Me, Et
R′ = Me



R = i-pr, t-but



Synthetic methods for the preparation of the complexes and their properties (IR, electronic and EPR spectra; electrochemistry) are reported. The relationships between EPR and electrochemical parameters and structures of the complexes are explored and the implications for the molybdenum hydroxylases are discussed.

Current problems in modeling the molybdenum centers of the hydroxylases and possible directions for research toward the solution of these problems are presented.

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Nickel Containing Hydrogenases

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Hydrogenases have been purified from different biological sources. They are highly diversified enzymes in terms of active centers constitution, although they catalyze the simplest oxidation–reduction process: $H_2 \rightleftharpoons 2H^+ + 2e$.

Hydrogenases have been recognized so far to be iron–sulfur proteins. Generally they contain from four to twelve atoms of non-haem iron arranged in Fe–S clusters representative of the known basic structures, *e.g.*, [2Fe-2S], 3Fe-xS], and [4Fe-4S] [1–7].

Recently, nickel joined the group of transition metals relevant in biological oxidation–reduction

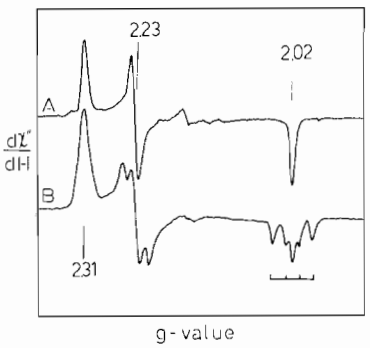

Fig. 1. EPR spectra of *D. gigas* hydrogenase enriched (B) and unenriched (A) ^{61}Ni enzyme. The EPR experiments were performed with a Bruker 200-series EPR-spectrometer. EPR data was taken at ~100 K, using 100 KHz modulation frequency and 9.256 GHz microwave frequency. Adapted from ref. 9.

processes. It was shown to be a structural component of the hydrogenases isolated from *Desulfovibrio gigas* [1, 2], *Desulfovibrio desulfuricans* (ATCC 27774) [3], *Desulfovibrio desulfuricans* (Norway strain) [4], *Methanosarcina barkeri* [5], *Methanobacterium thermoautotrophicum* [6] and *Chromatium vinosum* [8]. With the exception of the last one, they were demonstrated to contain EPR nickel redox dependent signals. As an example, *D. gigas* hydrogenase exhibits rhombic EPR signals, with g-values 2.31, 2.23 and 2.02 (see Fig. 1). Using isotopic reconstitution by ^{61}Ni (nuclear magnetic moment I = 3/2), the EPR signal was proven to arise from a nickel species [9]. The same types of experiments were reported for *M. thermoautotrophicum* [6] and *D. desulfuricans* (ATCC 27774) hydrogenases [3].

A detailed EPR study on the oxidation–reduction transition of the EPR detectable species in the presence of reductants (dithionite and hydrogen) indicates [1, 2]:

(a) The reduction of thc Ni EPR active species is an one-electron process (possibly associated with the redox couple Ni(III)–Ni(II)).

(b) No evidence was found so far for exchangeable protons in the vicinity of the nickel center in the oxidized (native) state. However, hydrogen reduced samples originate a different EPR rhombic Ni signal, which may represent an active transient species occuring during the activation of hydrogen molecules [9]. Thus, it is attractive to propose the presence of a hydride intermediate in analogy with nickel catalysts involved in hydrogenation processes [10].

(c) Although the determined mid-point redox potential (–220 mV) is more negative than that expected for nickel compounds [11] it is still more positive than that of the substrate couple H_2/H^+. The value determined was shown to be pH dependent [2].

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Intermediates in the Reduction of Dioxygen by Cytochrome *c* Oxidase and in the Photosynthetic Water Oxidation

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The cycle of oxygen in the biosphere is totally dominated by two processes, photosynthetic oxidation of water to dioxygen on the one hand and reduction of dioxygen to water on the other. There is one problem common to the mechanism of these two reactions; at least at some point, electrons are carried one at a time, whereas the dioxygen–water reaction requires a total of four electrons. In some cases thermodynamic requirements effectively prevent four consecutive one-electron transfers, which