

to 4.9 BM expected for magnetically dilute Cr^{II} and these increase markedly as the temperature is lowered, the ferromagnetic interactions evidently being transmitted via Cr–Cl–Cr bridges. The electronic spectra consist of the usual absorptions expected for tetragonally distorted octahedral complexes of Cr^{II} but with two sharp and intense bands characteristically superimposed at higher energies (around 15 500 and 18 500 cm^{-1}). These are ascribed to spin-forbidden transitions intensified by the magnetic exchange.

Complexes in which the metal exhibits still lower oxidation states (such as I, 0, –I, –II) occur amongst the organometallic compounds (pp. 1006 and 1037).

23.3.8 Biological activity and nitrogen fixation

It appears that chromium(III) is an essential trace element^(52a) in mammalian metabolism and, together with insulin, is responsible for the clearance of glucose from the blood-stream. Tungsten too has been found to have a role in some enzymes converting CO_2 into formic acid but, from the point of view of biological activity, the focus of interest in this group is unquestionably on molybdenum.

In animal metabolism, oxomolybdoenzymes catalyse a number of oxidation processes. These oxidases contain Mo^{VI} coordinated to terminal O and S atoms, and their action appears to involve loss of an O or S atom along with reduction to Mo^{V} or Mo^{IV} . It is, however, the role of molybdenum in nitrogen fixation which has received most attention.

It is estimated that each year approximately 150 million tonnes of nitrogen are fixed biologically compared to 120 million tonnes fixed industrially by the Haber process (p. 421). In both cases N_2 is converted to NH_3 , requiring the rupture of the $\text{N}\equiv\text{N}$ triple bond which has the highest dissociation energy (945.41 kJ mol^{-1})

of any homonuclear diatomic molecule. This is an inescapable toll exacted by N_2 no matter how the fixation is achieved. In the Haber process it is paid by using high temperatures and pressures. Nature pays it by consuming 1 kg of glucose for every 14 g of N_2 fixed, but does so *under ambient conditions*. It is this last fact which provides the economic spur to achieve an understanding of the mechanism of the natural process.

Nitrogen fixation takes place in a wide variety of bacteria, the best known of which is *rhizobium* which is found in nodules on the roots of leguminous plants such as peas, beans, soya and clover. The essential constituents of this and all other nitrogen-fixing bacteria are:

- (i) adenosine triphosphate (ATP) which is a highly active energy transfer agent (p. 528), operating by means of its hydrolysis which requires the presence of Mg^{2+} ;
- (ii) ferredoxin, $\text{Fe}_4\text{S}_4(\text{SR})_4$ (p. 1102), which is an efficient electron-transfer agent that can be replaced in artificial systems by reducing agents such as dithionite, $[\text{S}_2\text{O}_4]^{2-}$;
- (iii) a metallo-enzyme.

These metallo-enzymes are “nitrogenases” which have been isolated in an active form from several different bacteria and in a pure form from a number of these. The presence of Mo is not essential in all cases⁽⁵³⁾ (a vanadium nitrogenase is known — see p. 999) but is evidently a necessary component of most nitrogenases even though its precise function is unclear. These molybdenum nitrogenases consist of two distinct proteins. One, containing Fe but no Mo and therefore known as “Fe protein”, is yellow and extremely air-sensitive. Its molecular weight is about 60 000 and its structure involves an Fe_4S_4 , ferredoxin-like cluster. The other protein contains both Mo and Fe and is known as “MoFe protein.” It is brown, air-sensitive, has a molecular weight in the approximate range 220 000 to 240 000, and

^{52a} S. A. KATZ and H. SALEM, *The Biological and Environmental Chemistry of Chromium*, VCH, Weinheim, 1994, 214pp.

⁵³ R. R. EADY, *Adv. Inorg. Chem.* **36**, 77–102 (1991).

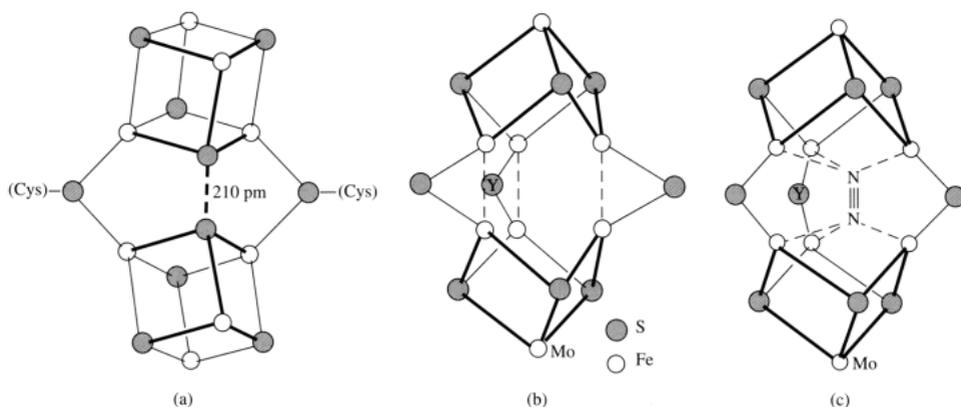


Figure 23.13 Metal centres in the FeMo protein of nitrogenase. (a) P-cluster pair. Each of the four outer Fe atoms is further coordinated to the S of a cysteine group. (b) FeMo cofactor. (Y is probably S, O or N.) Fe–Fe bridge distances are in the range 240–260 pm, suggesting weak Fe–Fe interactions. The Mo achieves 6-coordination by further bonds to N (of histidine) and two O atoms (of a chelating homocitrate), while the Fe at the opposite end of the cofactor is tetrahedrally coordinated by attachment of a cysteine. (c) Possible intermediate in the interaction of N_2 with FeMo cofactor.

contains the actual site of the N_2 reduction.[†] Most of the isolated forms of MoFe protein contain 2 atoms of Mo and about 30 atoms each of Fe and S. These atoms are arranged in 6 metal centres: 4 so-called P-clusters each made up of Fe_4S_4 units, and 2 Fe–Mo cofactors (FeMoco) in which the Mo is thought to be present as Mo^{IV} . Unfortunately, investigation of the structures of these proteins is hampered by the extreme sensitivity of nitrogenase to oxygen and the inherent difficulty of obtaining pure crystalline derivatives from biological materials. (Bacteria evidently protect nitrogenase from oxygen by a process of respiration, $O_2 \rightarrow CO_2$, but if too much oxygen is present the system cannot cope and nitrogen fixation ceases.) The recent determination of the structure of the nitrogenase from *Azotobacter vinelandii*⁽⁵⁴⁾ is therefore a remarkable achievement of X-ray crystallography, building upon results previously obtained from esr, Mössbauer spectroscopy and X-ray absorption spectroscopy (analysis of the

“extended X-ray absorption fine structure” or EXAFS).⁽⁵⁵⁾

It turns out that each of the two FeMo cofactors consists of an Fe_4S_3 and an Fe_3MoS_3 incomplete cubane cluster. These are linked by two S bridges and a third bridging atom (Y), not identified with certainty, but possibly a well-ordered O or N or, alternatively, a less well-ordered S. Three atoms in each cluster are close enough to form interacting pairs across the bridge (Fig 23.13a). The P-clusters form two pairs, each pair consisting of two Fe_4S_4 cubane clusters linked by two cysteine thiol bridges and a disulfide bond (Fig. 23.13b). Cleavage and re-formation of this disulfide bridge *could* provide the mechanism for a $2e^-$ redox process. Mössbauer studies suggest that, in their most reduced form, the iron atoms of the P-clusters are in the 2+ oxidation state, unprecedented in biological Fe_4S_4 systems. The reduction of N_2 apparently involves the following steps:

- (i) reduction by ferredoxin of the Fe protein’s Fe_4S_4 cluster, which is situated in an exposed position at the surface of the protein;

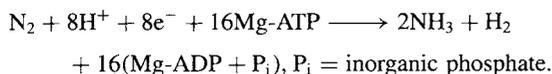
[†] Isolated nitrogenases will also reduce other species such as CN^- and N_3^- containing a triple bond, as well as reducing acetylenes to olefins.

⁵⁴ D. C. REES, M. K. CHAN and J. KIM, *Adv. Inorg. Chem.* **40**, 89–119 (1993).

⁵⁵ C. D. GARNER, *Adv. Inorg. Chem.* **36**, 303–39 (1991).

- (ii) one-electron transfer from the Fe protein to a P-cluster pair of the FeMo protein, by a process involving the hydrolysis of ATP;
- (iii) two-electron transfer, within the FeMo protein, from a P-cluster pair (whose environment is essentially hydrophobic) to an FeMo cofactor (whose environment is essentially hydrophilic);
- (iv) electron and proton transfer to N₂ which is almost certainly attached to the FeMo cofactor.

The overall reaction can be represented as:



Aspects of the process still requiring clarification include details of the electron flow between redox centres; the pathways for entry and exit of N₂, NH₃ and H₂ (presumably structural rearrangements are needed); the role of Mg-ATP; and the nature of the interaction between N₂ and the FeMo cofactor which is central to the whole process. Persuasive arguments had been advanced for an intermediate involving 2 Mo atoms bridged by N₂⁽⁵⁶⁾, yet in the determined structure the Mo atoms are too far apart to form a binuclear intermediate of this kind. On the other hand it has been plausibly suggested⁽⁵⁵⁾ that a reduced form of the FeMo cofactor might be sufficiently open at its centre to allow the insertion of N₂ so forming a bridged intermediate in which Fe-N interactions replace weak Fe-Fe bonds (Fig. 23.13c). The concomitant weakening of the N≡N bond would facilitate subsequent reduction of the N₂ bridge.

Further developments in this field may be confidently expected.

23.3.9 Organometallic compounds^(57,58)

In this group a not-insignificant number of M-C σ-bonded compounds are known but are very unstable (MMe₆ is known only for W and this

explodes in air and can detonate in a vacuum) unless stabilized either by ligands lacking β-hydrogen atoms (p. 925) or by dimerizing and forming M-M bonds. Thus trimethylsilylmethyl (-CH₂SiMe₃) yields [Cr(tms)₄] and the dimers [(tms)₃M≡M(tms)₃], (M = Mo, W). As with the preceding group, however, the bulk of organometallic chemistry is concerned with the metals in low oxidation states stabilized by π bonding ligands such as CO, cyclopentadienyl and, in this group, η⁶-arenes. Cyanides have been discussed on pp. 1025-32.

Stable, colourless, crystalline hexacarbonyls, M(CO)₆, are prepared by reductive carbonylation of compounds (often halides) in higher oxidation states and are octahedral and diamagnetic as anticipated from the 18-electron rule (p. 1134). Replacement of the carbonyl groups by either π-donor or σ-donor ligands is possible, giving a host of materials of the form [M(CO)_{6-x}L_x] or [M(CO)_{6-2x}(L-L)_x] (e.g. L = NO, NH₃, CN, PF₃; L-L = bipy, butadiene). [M(CO)₅X]⁻ ions (X = halogen, CN or SCN) are formed in this way. The low-temperature reaction (-78°) of the halogens with [Mo(CO)₆] or [W(CO)₆] (but not with [Cr(CO)₆]) produces the M^{II} carbonyl halides, [M(CO)₄X₂] from which many adducts, [M(CO)₃L₂X₂], are obtained. Although not all of these have been fully characterized, those that have are 7-coordinated and mostly capped octahedral. Reduction of the hexacarbonyls with a borohydride in liquid ammonia forms dimeric [M₂(CO)₁₀]²⁻ which are isostructural with the isoelectronic [Mn₂(CO)₁₀] (p. 1062). Hydrolysis of these dimers produces the yellow hydrides [(CO)₅M-H-M(CO)₅] which maintain the 18 valence electron configuration by means of a 3-centre, 2-electron M-H-M bond. Neutron diffraction studies show these bridges to be non-linear as expected, the actual degree of bending probably being influenced by crystal-packing forces arising from different counter-cations. A

⁵⁷ S. W. KIRTLLEY, R. DAVIS and L. A. P. KANE-MAGUIRE, Chap. 26, pp. 783-1077, Chap. 27, pp. 1079-253 and Chap. 28, pp. 1255-384 in *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1982.

⁵⁸ pp. 277-402 of ref. 2.

⁵⁶ A. E. SHILOV, *Pure Appl. Chem.* **64**, 1409-20 (1992).

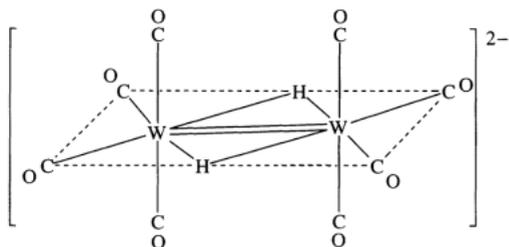


Figure 23.14 Structure of $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$.

related compound, $[\text{NEt}_4]_2^+[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ is of interest because it has 2 hydrogen bridges and a W–W distance indicative of a W–W double bond (301.6 pm compared to about 320 pm for a W–W single bond) (Fig. 23.14). The compound also illustrates the improved refinement now possible with modern X-ray methods (p. 1013) and it was, in fact, the first case of the successful location of hydrogens bridging third-row transition metals. Reduction of the hexacarbonyls using Na metal in liquid NH_3 yields the super-reduced, 18-electron species $[\text{M}(\text{CO})_4]^{4-}$.

$\text{M}(\text{CO})_6$ and other Mo and W compounds catalyse alkene metathesis[†] by the formation of

[†] This general reaction involves the cleavage of two C=C bonds and the formation of two new ones:



active alkylidene (p. 930) intermediates. This has stimulated the study of Mo and W alkylidenes (also alkylidyne which are similarly active in alkyne metathesis)⁽⁵⁸⁾

Metallocenes, $[\text{M}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$, analogous to ferrocene would have only 16 valence electrons and could therefore be considered “electron deficient”. Chromocene can be formed by the action of sodium cyclopentadienide on $[\text{Cr}(\text{CO})_6]$. It is isomorphous with ferrocene but paramagnetic and much more reactive. Monomeric molybdocene and tungstocene polymerize above 10 K to red-brown polymeric solids, $[\text{M}^{\text{II}}(\text{C}_5\text{H}_5)_2]_n$. They are obtained by photolytic decomposition of yellow, $[\text{M}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ which are “bent” molecules (Fig 23.15a), themselves prepared by the action of NaBH_4 on MCl_5 and NaC_5H_5 in thf. With Mo and W hexacarbonyls, conditions similar to those used to prepare chromocene produce only $[(\eta^5\text{-C}_5\text{H}_5)\text{M}^{\text{I}}(\text{CO})_3]_2$, (Fig. 23.15b) in which dimerization achieves the 18-valence-electron configuration by means of an M–M bond. The chromium analogue of these dimers has one of the longest M–M bonds found in dinuclear transition metal compounds (328.1 pm). Its reactivity allows ready insertion of a variety of groups which includes S and Se yielding

and can be used to convert propylene into ethylene for subsequent polymerization or oligomerization.

⁵⁸ See for instance: J. KRESS and J. A. OSBORN, *Angew. Chem. Int. Edn. Engl.* **31**, 1585–7 (1992); A. MAYR and C. M. BASTOS, *Prog. Inorg. Chem.* **40**, 1–98 (1992).

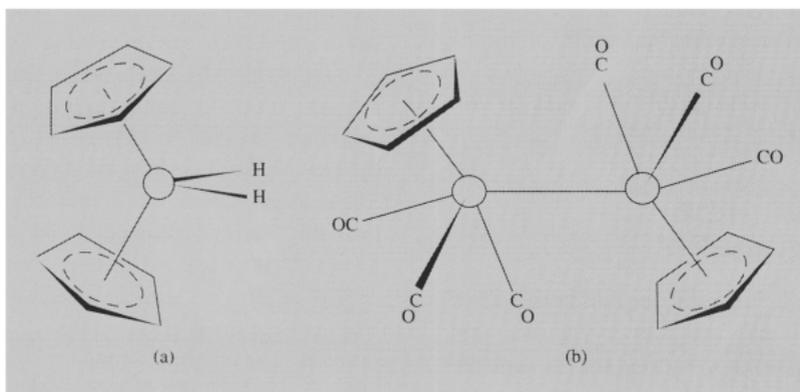


Figure 23.15 (a) The “bent” molecules $[\text{M}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ (b) $[\text{M}^{\text{I}}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ (M = Mo, W).

products such as $[\text{Cr}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4\text{E}_2]$, while cleavage of the bond with Ph_2E_2 gives $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{EPh})]$ ($\text{E} = \text{S}, \text{Se}$)⁽⁵⁹⁾. Of the many other cyclopentadienyl derivatives the Mo and W halides $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]$ and dimeric $[\text{M}_2(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_4]$, which are useful precursors in other syntheses⁽⁶⁰⁾ may be mentioned.

Of greater stability than the monomeric metallocenes in this group are the dibenzene sandwich compounds which are isoelectronic with ferrocene and of which the dark brown $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ was the first to be prepared (p. 940) and remains the best known. The green $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)_2]$ and yellow-green $[\text{W}(\eta^6\text{-C}_6\text{H}_6)_2]$ are also well characterized and all contain the metal in the formal oxidation state of zero. As the 12 C atoms in $[\text{M}(\eta^6\text{-C}_6\text{H}_6)_2]$ are equidistant from the central metal atom, the coordination number of M is 12, though, of course, only 6 bonding molecular orbitals are primarily involved in linking the

two ligand molecules to M. The compounds are more susceptible to oxidation than is the isoelectronic ferrocene and all are converted to paramagnetic salts of $[\text{M}^I(\eta^6\text{-C}_6\text{H}_6)_2]^+$: the ease with which this process takes place increases in the order $\text{Cr} < \text{Mo} < \text{W}$. Since CO groups are evidently better π -acceptors than C_6H_6 , replacement of one of the benzene ligands in $[\text{M}(\text{C}_6\text{H}_6)_2]$ by three carbonyls giving, for instance, $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$, appreciably improves the resistance to oxidation because the electron density on the metal is lowered. $[\text{W}(\eta^6\text{-C}_6\text{H}_6)_2]$ is reversibly protonated by dilute acids to give $[\text{W}(\eta^6\text{-C}_6\text{H}_6)_2\text{H}]^+$.

As in the previous group, a potentially productive route into C₇-ring chemistry is provided by the reduction of a metal halide with Na/Hg in thf in the presence of cycloheptatriene. With MoCl_5 , $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^7\text{-C}_7\text{H}_9)]$ is produced and a variety of derivatives have already been obtained.⁽⁶¹⁾

⁵⁹L. Y. GOH, Y. Y. LIM, M. S. TAY, T. C. W. MAK and Z. Y. ZHOU, *J. Chem. Soc., Dalton Trans.*, 1239–42 (1992).

⁶⁰M. L. H. GREEN and P. MOUNTFORD, *Chem. Soc. Revs.* **21**, 29–38 (1992).

⁶¹M. L. H. GREEN, D. K. P. NG and R. C. TOVEY, *J. Chem. Soc., Chem. Commun.*, 918–9 (1992).