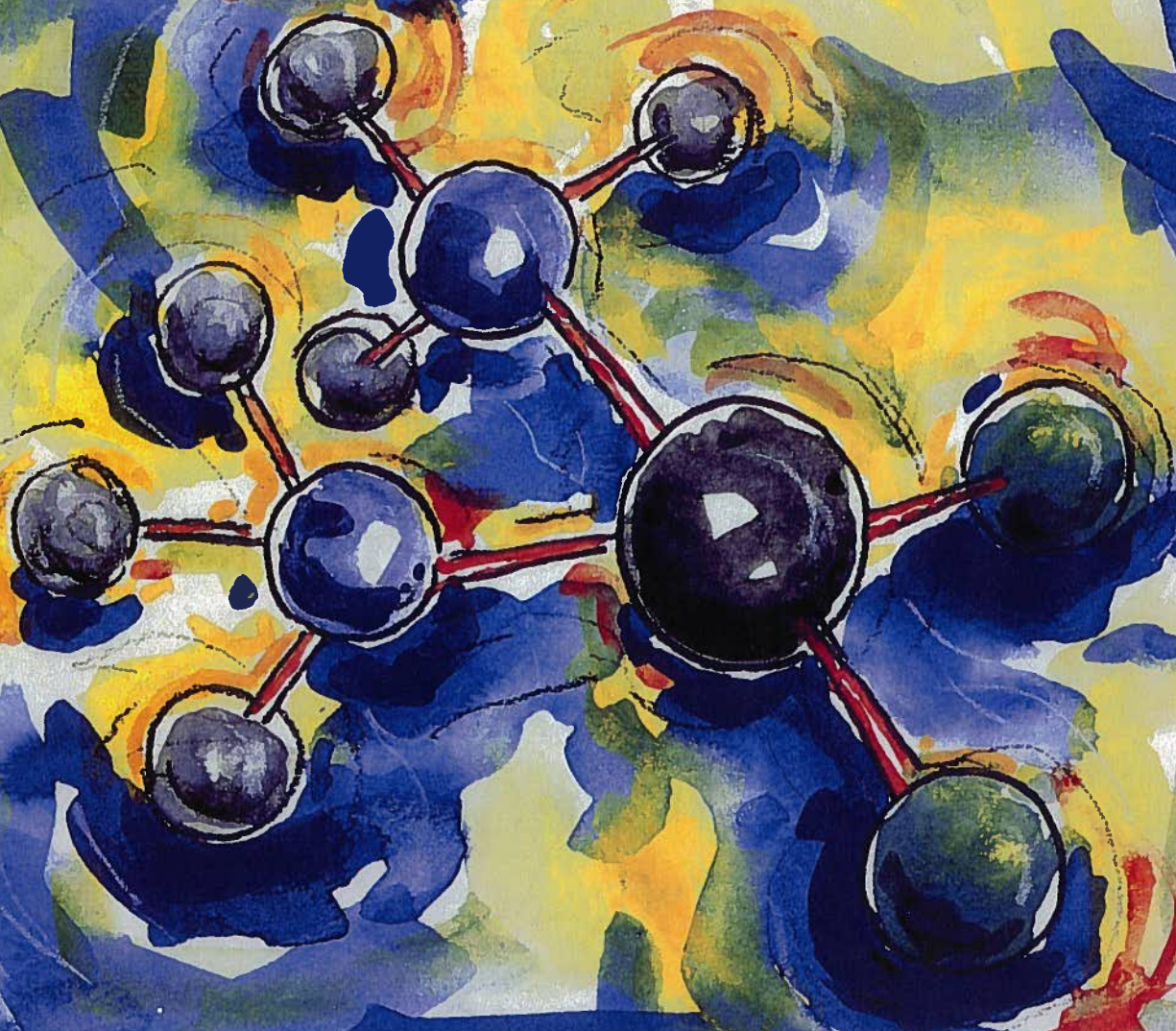


INORGANIC CHEMISTRY

DUWARD SHRIVER

PETER ATKINS

THIRD EDITION



7

d-Metal complexes

Structures and symmetries

- 7.1 Constitution
- 7.2 Representative ligands and nomenclature
- 7.3 Isomerism and chirality

Bonding and electronic structure

- 7.4 Crystal-field theory
- 7.5 The electronic structures of four-coordinate complexes
- 7.6 Ligand-field theory

Reactions of complexes

- 7.7 Coordination equilibria
- 7.8 Rates and mechanisms of ligand substitution

Further reading

Exercises

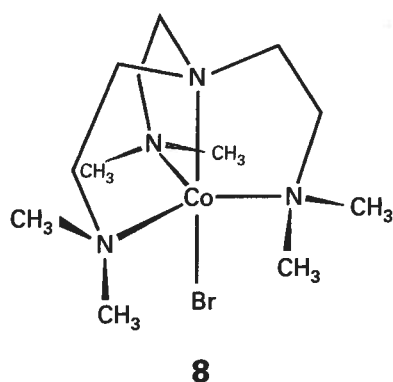
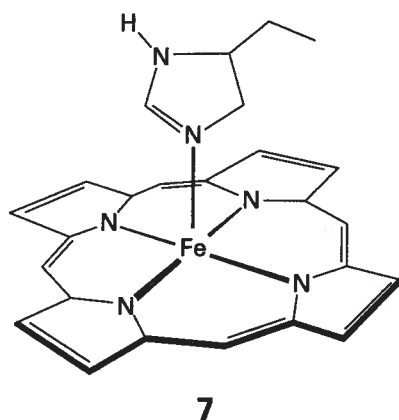
Problems

*Metal complexes, in which a single central metal atom or ion is surrounded by several atoms or ions, play an important role in inorganic chemistry, especially for elements of the *d*-block. In this chapter, we introduce the common structural arrangements for ligands around a central metal atom. We then discuss the nature of the ligand–metal bonding in terms of two theoretical models. We start with the simple but useful crystal-field theory, which is based on an electrostatic model of the bonding, and then progress to the more sophisticated ligand-field theory. Both theories invoke a parameter, the ligand-field splitting parameter, to correlate spectroscopic and magnetic properties. The same parameter also helps to systematize the discussion of the stabilities of complexes and their rates of reaction.*

In the context of *d*-metal chemistry, the term **complex** means a central metal atom or ion surrounded by a set of ligands. A **ligand** is an ion or molecule that can have an independent existence. An example of a complex is $[\text{Co}(\text{NH}_3)_6]^{3+}$, in which the Co^{3+} ion is surrounded by six NH_3 ligands. We shall use the term **coordination compound** to mean a neutral complex or an ionic compound in which at least one of the ions is a complex. Thus, $[\text{Ni}(\text{CO})_4]$ and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are both coordination compounds. A complex is a combination of a Lewis acid (the central metal atom) with a number of Lewis bases (the ligands). The atom in the Lewis base ligand that forms the bond to the central atom is called the **donor atom**, because it donates the electrons used in bond formation. Thus, O is the donor atom when H_2O acts as a ligand. The metal atom or ion, the Lewis acid in the complex, is the **acceptor atom**. This chapter focusses on complexes that contain *d*-metal atoms or ions, but *s*- and *p*-metal ions also form complexes (see Chapter 9).

The principal features of the geometrical structures of *d*-metal complexes were identified by the Swiss chemist Alfred Werner (1866–1919), whose training was in organic stereochemistry. Werner combined the interpretation of optical and geometrical isomerism, patterns of reactions, and conductance data in work that remains a model of how to use physical and chemical evidence effectively and imaginatively.¹ The striking colors of

¹ G.B. Kauffman gives a fascinating account of the history of structural coordination chemistry in *Inorganic coordination compounds*. Wiley, New York (1981). Translations of Werner's key papers are available in G.B. Kauffman, *Classics in coordination chemistry; I Selected papers of Alfred Werner*. Dover, New York (1968).



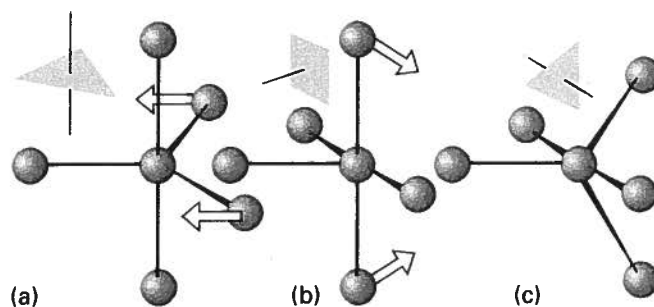
important porphyrins, where the ligand ring enforces a square-planar structure and a fifth ligand attaches above the plane. Structure (7) shows the active center of myoglobin, the oxygen transport protein; the location of the Fe atom above the plane of the ring is important to its function, as we shall see in Section 19.3. In some cases, five-coordination is induced by a polydentate ligand containing a donor atom that can bind to an axial location of a trigonal bipyramid, with its remaining donor atoms reaching down to the three equatorial positions (8).

The energies of the various geometries of five-coordinate complexes often differ little from one another. The delicacy of this balance is underlined by the fact that $[\text{Ni}(\text{CN})_5]^{3-}$ can exist as both square-pyramidal (9a) and trigonal-bipyramidal (9b) conformations in the same crystal. In solution, trigonal-bipyramidal complexes with monodentate ligands are often highly fluxional, so a ligand that is axial at one moment becomes equatorial at the next moment: the conversion from one stereochemistry to another may occur by a **Berry pseudorotation** (Fig. 7.3). The neutral complex $[\text{Fe}(\text{CO})_5]$, for instance, is trigonal-bipyramidal in the crystal; however, in solution the ligands exchange their axial and equatorial positions at a rate that is fast on an NMR timescale but slow on an IR timescale.

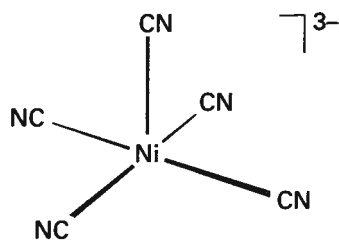
In the absence of polydentate ligands that enforce the geometry, the energies of the various geometries of five-coordinate complexes differ little from one another and such complexes are often fluxional.

(d) Six-coordination

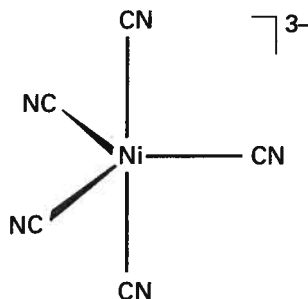
Six-coordination is the most common arrangement for electronic configurations ranging from d^0 to d^9 . For example, complexes formed by M^{3+} ions of the 3d series are usually octahedral (10). A few examples representative of the wide range of six-coordinate complexes



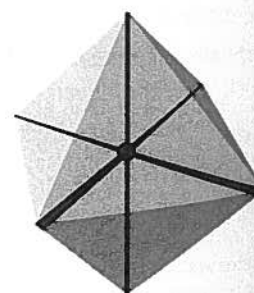
7.3 A Berry pseudorotation in which (a) a trigonal-bipyramidal $[\text{Fe}(\text{CO})_5]$ distorts into (b) a square-pyramidal isomer and then (c) becomes trigonal-bipyramidal again, but with two initially equatorial carbonyls now axial. An example of a complex of this kind is $[\text{Fe}(\text{CO})_5]$.



9a $[\text{Ni}(\text{CN})_5]^{3-}$ (square-pyramidal conformation)



9b $[\text{Ni}(\text{CN})_5]^{3-}$ (trigonal-bipyramidal conformation)



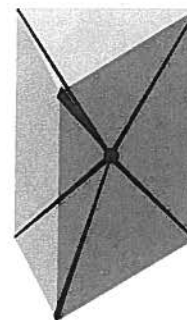
10 Octahedral complex, O_h

that can occur are $[\text{Sc}(\text{OH}_2)_6]^{3+}$ (d^0), $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (d^3), $[\text{Mo}(\text{CO})_6]$ (d^6), $[\text{Fe}(\text{CN})_6]^{3-}$ (d^5), and $[\text{RhCl}_6]^{3-}$ (d^6). Even some halides of the f -block elements can display six-coordination, but higher coordination numbers, especially 8 and 9, are more common with these large cations.

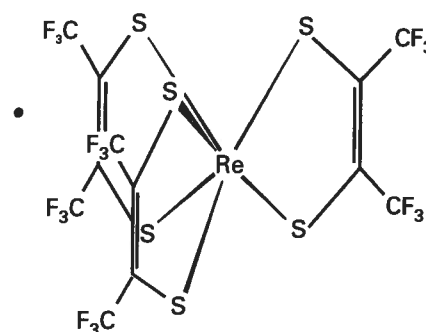
Almost all six-coordinate complexes are octahedral, at least in the colloquial sense of the term. A regular octahedral (O_h) arrangement of ligands is especially important in six-coordination not only because it is found for many complexes of formula ML_6 but also because it is the starting point for discussions of complexes of lower symmetry, such as those shown in Fig. 7.4. The simplest distortion from O_h symmetry is tetragonal (D_{4h}), and occurs when two ligands along one axis differ from the other four. For the d^9 configuration (particularly for Cu^{2+} complexes) a tetragonal (D_{4h}) distortion may occur even when all ligands are identical. Rhombic (D_{2h}) and trigonal (D_{3d}) distortions also occur. Trigonal distortion gives rise to a large family of structures that are intermediate between regular octahedral and trigonal-prismatic (D_{3h}).

Trigonal-prismatic complexes (11) are rare, but have been found in solid MoS_2 and WS_2 ; the trigonal prism is also the shape of several complexes of formula $[\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3]$ ((12), see Summary chart 4). Trigonal-prismatic d^0 complexes such as $[\text{Zr}(\text{CH}_3)_6]^{2-}$, have also been isolated. Such structures require either very small σ -donor ligands or favorable ligand-ligand interactions that can constrain the complex into a trigonal-prismatic shape; such ligand-ligand interactions are often provided by ligands that contain sulfur atoms, which can form covalent bonds to each other.⁵

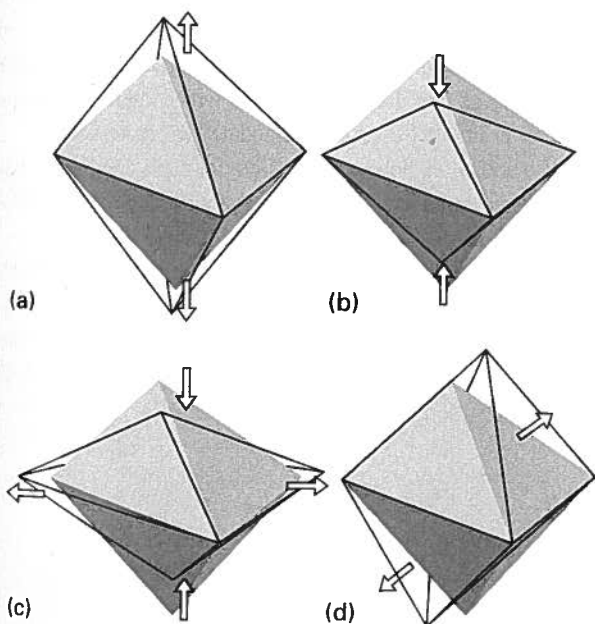
The overwhelming majority of six-coordinate complexes are octahedral or have shapes that are small distortions of octahedral.



11 Trigonal-prismatic complex, D_{3h}



12 $[\text{Re}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3]$



7.4 (a) and (b) Tetragonal (D_{4h}) distortions of a regular octahedron, (c) rhombic (D_{2h}), and (d) trigonal (D_{3d}) distortions. The last can lead to a trigonal prism (D_{3h}) by a further 60° rotation of the faces containing the arrows.

⁵ The structures of six-coordinate trigonal-prismatic zirconium and hafnium complexes are described and interpreted in P.M. Morse and G.S. Girolami, *J. Am. Chem. Soc.* **111**, 4114 (1989).

Bonding and electronic structure

An early theory of the electronic structure of complexes was developed to account for the properties of d -metal ions in ionic crystals. In this **crystal-field theory**, a ligand lone pair is modeled as a point negative charge (or as the partial negative charge of an electric dipole) that repels electrons in the d orbitals of the central metal ion. This approach concentrates on the resulting splitting of the d orbitals into groups of different energies. It then uses that splitting to account for the number of unpaired electrons on the ion and for the spectra, stability, and magnetic properties of complexes. The crystal-field approach is simple and readily visualized; however, it ignores covalent interactions between the ligand and the central metal ion, and the approach has been superseded by **ligand-field theory**. This theory focusses on the overlap of d orbitals with ligand orbitals to form molecular orbitals. The qualitative variation in the separation of orbitals associated primarily with the metal atom is the same as that of crystal-field theory, but ligand-field theory provides a better understanding of the origin of the energy separation.

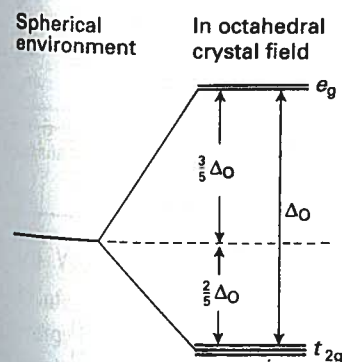
7.4 Crystal-field theory

In the model of an octahedral complex used in crystal-field theory, six ligands are placed on the cartesian axes centered on the metal ion. The ligands interact strongly with the central metal ion, and the stability of the complex stems in large part from this interaction. There is a much smaller secondary effect arising from the fact that electrons in different d orbitals interact with the ligands to different extents. Although this differential interaction is little more than about 10 per cent of the overall metal-ligand interaction, it has major consequences for the properties of the complex and is the principal focus of this section.

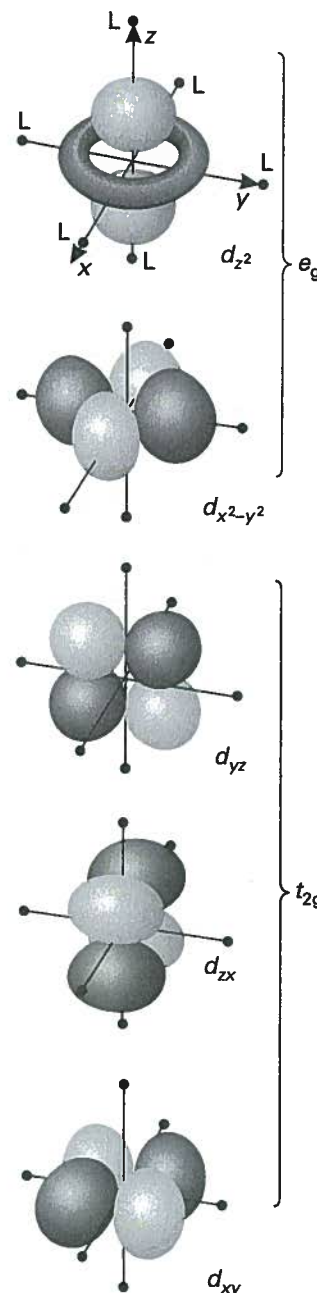
(a) Ligand-field splitting parameters

Electrons in the two d orbitals pointing directly along the cartesian axes and directly at the ligands, namely d_{z^2} and $d_{x^2-y^2}$ (which are jointly of symmetry type e_g in O_h), are repelled more strongly by negative charge on ligands than electrons in the three d orbitals that point between the ligands, namely, d_{xy} , d_{yz} , and d_{zx} (symmetry type, t_{2g}). Group theory shows that the e_g orbitals are doubly degenerate (although this is not readily apparent from drawings), and that the t_{2g} orbitals are triply degenerate (Fig. 7.8). This simple model leads to an energy level diagram in which the t_{2g} orbitals lie below the e_g orbitals (Fig. 7.9). The separation of the orbitals is called the **ligand-field splitting parameter**, Δ_O (where the subscript O signifies an octahedral crystal field).¹⁰

The simplest property that can be interpreted by crystal-field theory is the absorption

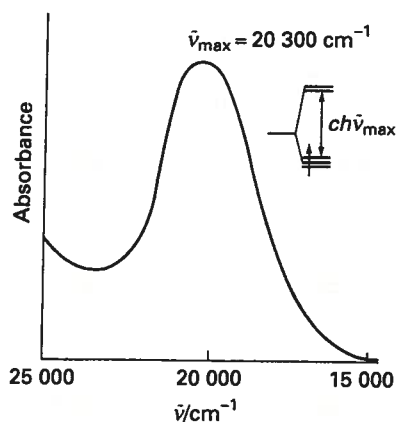


7.9 The energies of the d orbitals in an octahedral crystal field. Note that the mean energy remains unchanged relative to the energy of the d orbitals in a spherically symmetric environment (such as in a free atom).



7.8 The orientation of the five d orbitals with respect to the ligands of an octahedral complex.

¹⁰ Strictly, in the context of crystal-field theory, the ligand-field splitting parameter should be called the 'crystal-field splitting parameter', but we use the former name to avoid a proliferation of names.

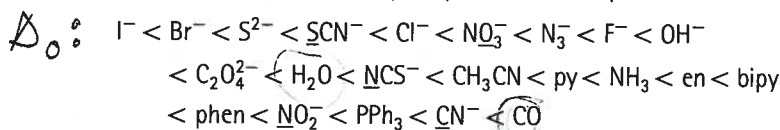


7.10 The optical absorption spectrum of $[\text{Ti}(\text{OH}_2)_6]^{3+}$.

spectrum of a one-electron complex. Figure 7.10 shows the optical absorption spectrum of the d^1 hexaaquatitanium(III) ion, $[\text{Ti}(\text{OH}_2)_6]^{3+}$. Crystal-field theory assigns the first absorptive maximum at $20\,300\text{ cm}^{-1}$ to the transition $e_g \leftarrow t_{2g}$. (In keeping with spectroscopic notation the higher-energy orbital is shown first.) We can identify $20\,300\text{ cm}^{-1}$ with Δ_0 for the complex. It is more complicated to obtain values of Δ_0 for complexes with more than one electron because the energy of a transition then depends not only on orbital energies (which we wish to know) but also on the repulsion energies between the several electrons present. This aspect is treated more fully in Chapter 13, and the results from the analyses described there have been used to obtain the values of Δ_0 in Table 7.3.

The ligand-field splitting parameter varies systematically with the identity of the ligand. The empirical evidence for this trend was the observation, by the Japanese chemist R. Tsuchida, that there are certain regularities in the absorption spectra as the ligands of a complex are varied. For instance, in the series of complexes $[\text{CoX}(\text{NH}_3)_5]^{n+}$ with $\text{X} = \text{I}^-$, Br^- , Cl^- , H_2O , and NH_3 , the colors range from deep purple (for $\text{X} = \text{I}^-$) through pink (for Cl^-) to yellow (with NH_3). This observation indicates that there is an increase in the energy of the lowest energy electronic transition (and therefore in Δ_0) as the ligands are varied along the series. Moreover, this variation is quite general, for the same order of ligands is followed regardless of the identity of the metal ion.

On the basis of these observations, Tsuchida proposed that ligands could be arranged in a **spectrochemical series**, in which the members are arranged in order of increasing energy of transitions that occur when they are present in a complex:



(The donor atom in an ambidentate ligand is underlined.) For example, the series indicates that the optical absorption of a hexacyano complex will occur at much higher energy than that of a hexachloro complex of the same metal.

The values of Δ_0 also depend in a systematic way on the metal ion, and it is not in general possible to say that a particular ligand exerts a strong or a weak ligand field without considering the metal ion too. In this connection, the most important trends to keep in mind are that

- 1 Δ_0 increases with increasing oxidation number.
- 2 Δ_0 increases down a group.

The variation with oxidation number reflects the smaller size of more highly charged ions and the consequent smaller metal-ligand distances. The second factor reflects the improved

NO_3^- low Δ_0
 Co^{2+} low Δ_0

Table 7.3 Ligand-field splitting parameters Δ_0 of ML_6 complexes*

	Ions	Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13.7	17.4	21.5	21.9	26.6
d^5	Mn^{2+}	7.5	8.5		10.1	30
	Fe^{3+}	11.0	14.3			(35)
d^6	Fe^{2+}		10.4			(32.8)
	Co^{3+}		(20.7)	(22.9)	(23.2)	(34.8)
	Rh^{3+}	(20.4)	(27.0)	(34.0)	(34.6)	(45.5)
d^8	Ni^{2+}	7.5	8.5	10.8	11.5	

*Values are in multiples of 1000 cm^{-1} ; entries in parentheses are for low-spin complexes.
 Source: H.B. Gray, *Electrons and chemical bonding*. Benjamin, Menlo Park (1965).

very high charge/radius ratio and so it is not surprising to find that it is a very strong Lewis acid. In the gas phase it readily attaches to other molecules and atoms; for example, it attaches to He to form HeH^+ . In condensed phases, H^+ is always found in combination with a Lewis base, and its ability to transfer between Lewis bases gives it the special role in chemistry that we explored in detail in Chapter 5.

The molecular cations H_2^+ and H_3^+ have only a transitory existence in the gas phase and are unknown in solution. As remarked in Section 3.11, H_3^+ has been detected in the interstellar medium and in the auroras of Uranus, Jupiter, and Saturn. Their electronic structures were described in Section 3.11, where we saw that spectroscopic data indicate that $\text{H}_3^+(\text{g})$ is an equilateral triangle. The H_3^+ ion is the simplest example of a three-center, two-electron bond (a 3c,2e-bond) in which three nuclei are bonded by only two electrons.

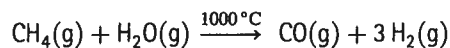
In combination with metals hydrogen is often regarded as a hydride; hydrogen compounds with elements of similar electronegativity have low polarity.

8.3 Properties and reactions of dihydrogen

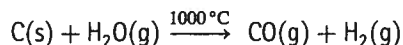
The stable form of elemental hydrogen under normal conditions is *dihydrogen*, H_2 , more informally and henceforth plain 'hydrogen'. The H_2 molecule has a high bond enthalpy (436 kJ mol^{-1}) and a short bond length (0.74 \AA). Because it has so few electrons, the forces between neighboring H_2 molecules are weak, and at 1 atm the gas condenses to a liquid only when cooled to 20 K.

(a) Production

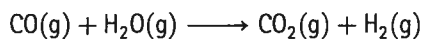
Molecular hydrogen is not present in significant quantities in the Earth's atmosphere or in underground gas deposits, but it is produced in huge quantities to satisfy the needs of industry. The main commercial process for the production of hydrogen is currently *steam reforming*, the catalyzed reaction of water and hydrocarbons (typically methane from natural gas) at high temperatures:



A similar reaction, but with coke as the reducing agent, is sometimes called the *water-gas reaction*:



This reaction was once a primary source of H_2 and it may become important again when natural hydrocarbons are depleted. Both reactions are generally followed by a second reaction, often called the *shift reaction*, in which water is reduced to hydrogen by reaction with carbon monoxide:



Hydrogen production is often integrated with chemical processes that require H_2 as a feed-stock. As shown in Chart 8.1, a major use of hydrogen is direct combination with N_2 to produce NH_3 , the primary source of nitrogen-containing chemicals, plastics, and fertilizers. Another major chemical, methanol, is produced from the catalytic combination of H_2 and CO.

Because of its high specific enthalpy,³ hydrogen is an excellent fuel for large rockets. The more general use of hydrogen as a fuel has been analyzed seriously since the early 1970s when petroleum prices rose sharply. Strategies have been devised for a 'hydrogen economy' in

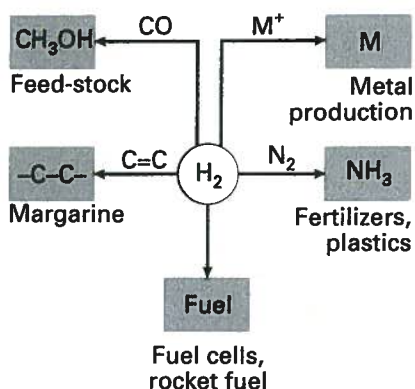


Chart 8.1

³ Specific enthalpy is the enthalpy of combustion of a sample divided by the mass of the sample; the specific enthalpy of hydrogen is 142 kJ g^{-1} ; that of a typical hydrocarbon is 50 kJ g^{-1} .