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Table 8.5 Some physical properties and molecular dimensions of COX_2

Property	COF_2	$COCl_2$	$COBr_2$
MP/°C	−114°	−127.8°	—
BP/°C	−83.1°	7.6°	64.5°
Density (T°C)/g cm^{-3}	1.139(−144°)	1.392(19°)	—
Distance (C–O)/pm	117.4	116.6	113
Distance (C–X)/pm	131.2	174.6	(205)
Angle X–C–X	108.0°	111.3°	$110 \pm 5°$
Angle X–C–O	126.0°	124.3°	~125°

parent species, e.g. COFCl (bp −42°), COFBr (bp −20.6°). COI_2 is unknown but COFI has been prepared (mp −90°, bp 23.4°). Synthetic routes are as follows: COFCl from $COCl_2$/HF; COFBr from CO/BrF_3; COFI from CO/IF_3; and COClBr from CCl_3Br/H_2SO_4.

COF_2 can be made by fluorinating $COCl_2$ with standard fluorinating agents such as NaF/MeCN or SbF_5/SbF_3; direct fluorination of CO with AgF_2 affords an alternative route. COF_2 is rapidly hydrolysed by water to CO_2 and HX, as are all the other COX_2. It is a useful laboratory reagent for producing a wide range of fluoroorganic compounds and the heavier alkali metal fluorides react in MeCN to give trifluoromethoxides $MOCF_3$.

$COCl_2$ (phosgene) is highly toxic and should be handled with great caution. It was first made in 1812 by John Davy (Sir Humphry Davy's brother) by the action of sunlight on $CO + Cl_2$, whence its otherwise surprising name (Greek φως *phos*, light; -γενη'ς, *-genes*, born of). It is now a major industrial chemical and is made on the kilotonne scale by combining the two gases catalytically over activated C (p. 274). It was used briefly and rather ineffectively as a chemical warfare gas in 1916 but is now principally used to prepare isocyanates as intermediates to polyurethanes. It also acts as a ligand (Lewis base) towards $AlCl_3$, $SnCl_4$, $SbCl_5$, etc., forming adducts $Cl_2CO{\rightarrow}MCl_n$, and is a useful chlorinating agent, converting metal oxides into highly pure chlorides. It reacts with NH_3 to form mainly urea, $CO(NH_2)_2$, together with more highly condensed products such as guanidine, $C(NH)(NH_2)_2$; biuret, $NH_2CONHCONH_2$; and cyanuric acid, i.e. *cyclo*-$[CO(NH)]_3$ (p. 323).

$COBr_2$ has recently been shown to be a useful general brominating reagent for the preparation of d- and f-block bromides and oxide bromides.$^{(101)}$ Thus, when V_2O_5 is heated with an excess of $COBr_2$ in a sealed Carius tube at 125°C for 10 days, a quantitative yield of $VOBr_2$ is obtained by a reaction that is driven thermodynamically by the formation of CO_2: $[V_2O_5 + 3COBr_2 \longrightarrow 2VOBr_2 + 3CO_2 + Br_2]$. Similarly, MoO_2, Re_2O_7, Sm_2O_3 and UO_3 were smoothly converted to MoO_2Br_2, $ReOBr_4$, $SmBr_3$ and $UOBr_3$, respectively.

8.6 Oxides and Carbonates

Carbon forms 2 extremely stable oxides, CO and CO_2, 3 oxides of considerably lower stability, C_3O_2, C_5O_2 and $C_{12}O_9$, and a number of unstable or poorly characterized oxides including C_2O, C_2O_3 and the nonstoichiometric graphite oxide (p. 289). Of these, CO and CO_2 are of outstanding importance and their chemistry will be discussed in subsequent paragraphs after a few brief remarks about some of the others.

Tricarbon dioxide, C_3O_2, often called "carbon suboxide" and ponderously referred to in *Chemical Abstracts* as 1,2-propadiene-1,3-dione, is a foul-smelling gas obtained by dehydrating malonic acid, $CH_2(CO_2H)_2$, at

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(101) J. S. YADAV and V. R. GADGIL, *J. Chem. Soc., Chem. Commun.*, 1824–5 (1989).

Table 8.6 Some properties of CO, CO_2 and C_3O_2

Property	CO	CO_2	C_3O_2
MP/°C	−205.1	−56.6(5.2 atm)	−112.5
BP/°C	−191.5	−78.5 (subl)	6.7
ΔH_f°/kJ mol^{-1}	−110.5	−393.7	+97.8
Distance (C−O)/pm	112.8	116.3	116
Distance (C−C)/pm	—	—	128
D(C−O)/kJ mol^{-1}	1070.3	531.4	—

reduced pressure over P_4O_{10} at 140°, or by thermolysis of bis(trimethylsilyl) malonate, $CH_2(CO_2SiMe_3)_2$.[102] It has mp −112.5°, bp 6.7°, is stable at −78°, and polymerizes at room temperature to a yellow solid. C_3O_2 forms linear molecules ($D_{\infty h}$ symmetry) which can be written as O=C=C=C=O, consistent with the short interatomic distances C−C 128 pm and C−O 116 pm. Above 100°, polymerization yields a ruby-red solid; at 400° the product is violet and at 500° the polymer decomposes to C. The basic structure of all the polymers appears to be a polycyclic 6-membered lactone. C_3O_2 readily rehydrates to malonic acid, and reacts with NH_3 and HCl to give respectively the corresponding amide and acid chloride: $CH_2(CONH_2)_2$ and $CH_2(COCl)_2$. Thermolysis of C_3O_2 in a flow system has been reported to give a liquid product C_5O_2 though a better preparation is the photolysis or thermolysis of the tris(diazo)ketone, cyclo-1,3,5-$C_6O_3(N_2)_3$.[103] C_5O_2 is a yellow solid which decomposes above −90°; in solution it apparently remains unchanged for several days even at room temperature. Note that C_5O_2 is the next member after CO_2 and C_3O_2 of the linear catenated series OC_nO with n odd as required by simple π-bond theory. The other moderately stable lower oxide is $C_{12}O_9$, a white sublimable solid which is the anhydride of mellitic acid, $C_6(COOH)_6$.

Direct oxidation of C in a limited supply of oxygen or air yields CO; in a free supply CO_2 results. Some properties of these familiar gases and of C_3O_2 are in Table 8.6. The great strength of the C−O bond confers considerable thermal stability on these molecules but the compounds are also quite reactive chemically, and many of the reactions are of major industrial importance. Some of these are discussed more fully in the Panel.

The nature of the bonding, particularly in CO, has excited much attention because of the unusual coordination number (1) and oxidation state (+2) of carbon: it is discussed on p. 926 in connection with the formation of metal−carbonyl complexes.

Pure CO can be made on a laboratory scale by dehydrating formic acid (HCOOH) with conc H_2SO_4 at ~140°. CO is a colourless, odourless, flammable gas; it has a relatively high toxicity due to its ability to form a complex with haemoglobin that is some 300 times more stable than the oxygen−haemoglobin complex (p. 1099): the oxygen-transport function of the red corpuscles in the blood is thereby impeded. This can result in unconsciousness or death, though recovery from mild poisoning is rapid and complete in fresh air and the effects are not cumulative. CO can be detected by its ability to reduce an aqueous solution of $PdCl_2$ to metallic Pd:

$$CO + PdCl_2 + H_2O \longrightarrow Pd + CO_2 + 2HCl$$

Quantitative estimation relies on the liberation of I_2 from I_2O_5 or (in the absence of C_2H_2) on absorption in an acid solution of CuCl to form the adduct $[Cu(CO)Cl(H_2O)_2]$.

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[102] L. Birkofer and P. Sommer, *Chem. Ber.* **109**, 1701−7 (1976).

[103] G. Maier, H. P. Reisenauer, U. Schäfer and H. Balli, *Angew. Chem. Int. Edn. Engl.* **27**, 566−8 (1988).

Industrially Important Reactions of Oxygen and Oxides with Carbon

Carbon monoxide is widely used as a fuel in the form of producer gas or water gas and is also formed during the isolation of many metals from their oxides by reduction with coke. Producer gas is obtained by blowing air through incandescent coke and consists of about 25% CO, 4% CO_2 and 70% N_2, together with traces of H_2, CH_4 and O_2. The reactions occurring during production are:

$$2C + O_2 \longrightarrow 2CO\text{: } \Delta H^\circ = -221.0 \text{ kJ/mol } O_2\text{; } \Delta S^\circ + 179.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C + O_2 \longrightarrow CO_2\text{; } \Delta H^\circ = -393.5 \text{ kJ mol}^{-1}\text{; } \Delta S^\circ + 2.89 \text{ J K}^{-1} \text{ mol}^{-1}$$

Water gas is made by blowing steam through incandescent coke: it consists of about 50% H_2, 40% CO, 5% CO_2 and 5% $N_2 + CH_4$. The oxidation of C by H_2O is strongly endothermic:

$$C + H_2O \longrightarrow CO + H_2\text{; } \quad \Delta H^\circ = +131.3 \text{ kJ mol}^{-1}\text{; } \quad \Delta S^\circ + 133.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

Consequently, the coke cools down and the steam must be intermittently replaced by a flow of air to reheat the coke.

At high temperatures, particularly in the presence of metal catalysts, CO undergoes reversible disproportionation:[†]

$$2CO \rightleftharpoons C + CO_2\text{; } \quad \Delta H^\circ = -172.5 \text{ kJ/mol } CO_2\text{; } \quad \Delta S^\circ = -176.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

The equilibrium concentration of CO is 10% at 550°C and 99% at 1000°. As the forward reaction involves a reduction in the number of gaseous molecules it is accompanied by a large decrease in entropy. Remembering that $\Delta G = \Delta H - T\Delta S$ this implies that the reverse reaction becomes progressively more favoured at higher temperatures. The thermodynamic data for the formation of CO and CO_2 can be represented diagramatically on an Ellingham diagram (Fig. 19) which plots standard free energy changes per mol of O_2 as a function of the absolute temperature. The oxidation of C to CO results in an increase in the number of gaseous molecules; it is therefore accompanied by a large increase in entropy and is favoured at high temperature. By contrast, oxidation to CO_2 leaves the number of gaseous molecules unchanged; there is little change in entropy (ΔS° 2.93 J K^{-1} mol^{-1}), and the free energy is almost independent of temperature. The two lines (and that for the oxidation of CO to CO_2) intersect at 983 K; it follows that ΔG for the disproportionation reaction is zero at this temperature. The diagram also includes the plots of ΔG (per mole of O_2) for the oxidation of several representative metals. On the left of the diagram (at $T = 0$ K) $\Delta G = \Delta H$ and the sequence of elements is approximately that of the electrochemical series. The slope of most of the lines is similar and corresponds to the loss of 1 mol of gaseous O_2; small changes of slope occur at the temperature of phase changes or the mp of the metal, and a more dramatic increase in slope signals the bp of the metal. For example, for MgO(s), the slope increases about three-fold at the bp of Mg since, above this temperature, reaction removes three gaseous species ($2Mg + O_2$) rather than one (O_2).

Such diagrams are of great value in codefying a mass of information of use in extractive metallurgy.(105) For example, it is clear that below 710°C (983 K) carbon is a stronger reducing agent when it is converted into CO_2 rather than CO, whereas above this temperature the reverse is true. Again, as reduction of metal oxides with C will occur when the accompanying ΔG is negative, such reduction becomes progressively more feasible the higher the temperature: Zn (and Cd) can be reduced at relatively low temperatures but MgO can only be reduced at temperatures approaching 2000 K. Caution should be exercised, however, in predicting the outcome of such reactions since a number of otherwise reasonable reductions cannot be used because the metal forms a carbide (e.g. Cr, Ti). The temperature at which the oxygen dissociation pressure of the various metal oxides reaches a given value can also be obtained from the diagram: as $-\Delta G = RT \ln K_p [= 2.303RT \log\{p(O_2)/\text{atm}\}$ for the reactions considered] it follows that the line drawn from the point $\odot(\Delta G = 0, T = 0)$ to the appropriate scale mark on the right-hand side of the diagram intercepts the free-energy line for the element concerned at the required temperature. (Establish to your own satisfaction that this statement is approximately true — what assumptions does it embody?)

[†] Note however that, at all pressures, there is a fairly wide range of temperatures in which CO_2 dissociates directly into CO and O_2 without precipitation of carbon:(104)

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2$$

For example, the temperature range is 250–370°C at 10^{-2} atm, 320–480°C at 1 atm, and 405–630°C at 100 atm. At higher temperatures in each case, C is also formed, but always in the presence of some O_2.

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[104] M. H. Lietzke and C. Mullins, *J. Inorg. Nucl. Chem.* **43**, 1769–71 (1981).

[105] C. B. Alcock, *Principles of Pyrometallurgy*, Academic Press, London, 1976, 348 pp.

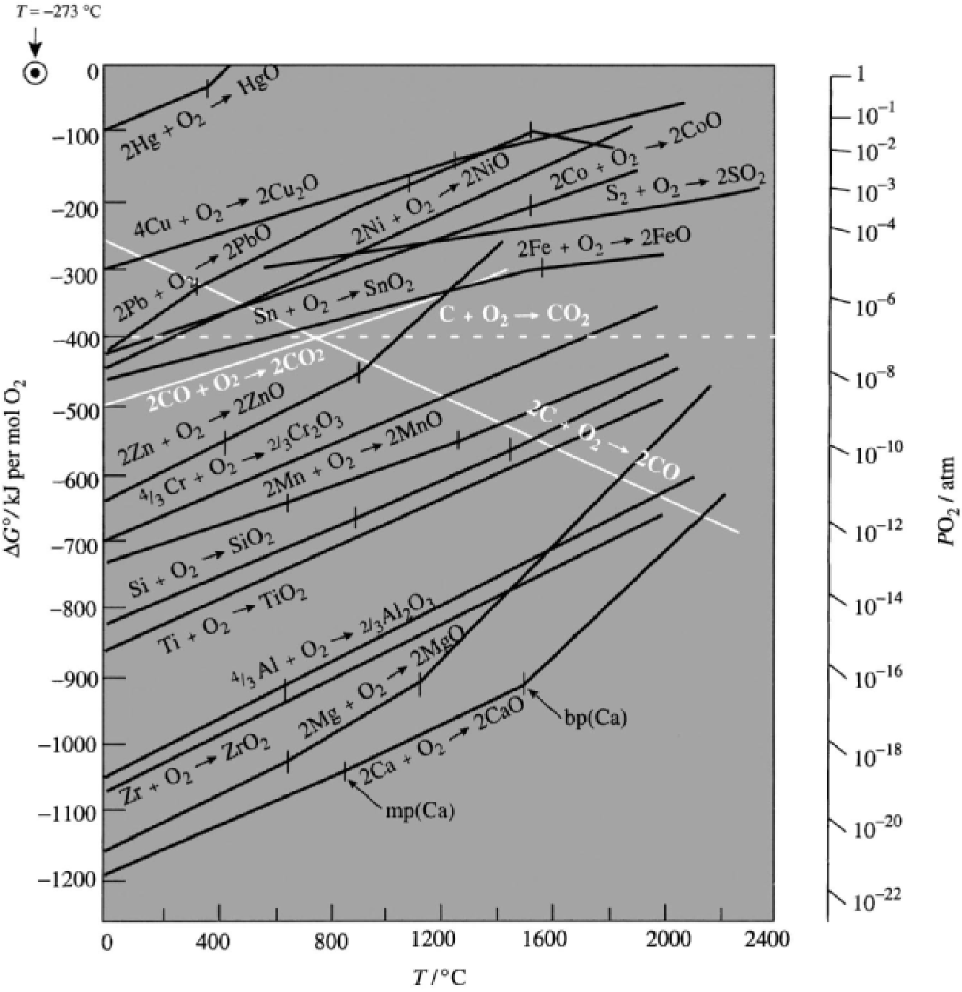

Figure 8.19 Ellingham diagram for the free energy of formation of metallic oxides. (After F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst.* **160**, 261 (1948).) The oxygen dissociation pressure of a given M–MO system at a given temperature is obtained by joining ⊙ on the top left hand to the appropriate point on the M–MO free-energy line, and extrapolating to the scale on the right hand ordinate for p_{O_2} (atm).

CO reacts at elevated temperatures to give formates with alkali hydroxides, and acetates with methoxides:

$$CO + NaOH \longrightarrow HCO_2Na;$$

$$CO + MeONa \longrightarrow MeCO_2Na$$

Reaction with alkali metals in liquid NH_3 leads to reductive coupling to give colourless crystals of the salt $Na_2C_2O_2$ which contains linear groups $NaOC{\equiv}CONa$ packed in chains. CO reacts with Cl_2 and Br_2 to give COX_2 (p. 305) and with liquid S to give COS. It cleaves B_2H_6 at high pressures to give the "symmetrical" adduct BH_3CO (p. 165), but in the presence of $NaBH_4$/thf the reaction takes a different course to yield the cyclic *B*-trimethylboroxine:

$$\tfrac{3}{2}B_2H_6 + 3CO \xrightarrow[\text{thf}]{NaBH_4/} \mathrm{Me\overline{BOB(Me)OB(Me)O}}$$

With BR_3, CO inserts in successive stages to give, ultimately, the corresponding trialkylmethylboroxine $(R_3CBO)_3$. Alternative products are obtained in the presence of other reagents, e.g. aqueous alkali yields R_3COH; water followed by alkaline peroxide yields R_2CO; and alkaline $NaBH_4$ yields RCH_2OH (p. 167). CO can also insert into M–C bonds (M = Mo, W; Mn, Fe, Co; Ni, Pd, Pt):

$$MeMn(CO)_5 + CO \longrightarrow MeC(O)Mn(CO)_5$$

A detailed discussion of CO as a ligand and the chemistry of metal carbonyls is on pp. 926–9. CO is a key intermediate in the catalytic production of a wide variety of organic compounds on an industrial scale. These include:(106,107)

1. Catalytic reduction to methanol (230–400°C, 50–100 atm):

$$CO + 2H_2 \longrightarrow CH_3OH$$

2. Homogeneous methanol carboxylation with I^-/Rh catalyst (175–195°C, 30 atm), this is now a leading route to acetic acid:

$$MeOH + CO \longrightarrow MeCO_2H$$

3. Hydroformylation of olefins to alcohols (the oxo process):(108)

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO \xrightarrow{H_2O} R(CH_2)_3OH$$

4. The Reppe synthesis of methyl acrylate and acrylic acid (100–190°C, 30 atm, Ni catalyst: **or** 40°C and 1 atm using $Ni(CO)_4$ as both the source of CO and the catalyst):

$$HC{\equiv}CH + MeOH + CO \longrightarrow CH_2{=}CHCO_2Me \xrightarrow{H_2O} CH_2{=}CHCO_2H$$

5. Sabatier methanation (230–450°C, 1–100 atm, Ni catalyst):

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

6. Fischer-Tropsch hydrogenation to a mixture of straight chain aliphatic, olefinic and oxygenated hydrocarbons.(109) Despite an enormous amount of research during the past two decades, this is still not an economically viable process except in special circumstances, such as in South Africa.(110)

Most industrial CO is produced and used on site. Prices for commercial supplies vary enormously depending on volume and purity required.(106) For large volumes (~28 000 m^3/day), "over the fence" prices can be as low as \$0.30/m^3 whereas for tube-trailer loads (1500–3000 m^3) prices are nearer \$1.40/m^3. For CO supplied in high-pressure cylinders current prices (1993) are \$15.00–35.00/m^3 for commercial grade (98–99% purity), \$63/m^3 for ultra high purity grade (99.8%) and \$68–1580/m^3 for research grades (99.97–99.98%).

Further reactions of CO of potential industrial or research significance are continually being explored. Recent examples include:

1. Amination with ammonia over zeolite catalysts at 350–400°C to give methylamine (and some dimethylamine):(111)

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[106] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., Wiley, New York, **5**, 97–122 (1993).

[107] W. KEIM, in H. GRÜNEWALD (ed.), *Chemistry for the Future* (Proc. 29th IUPAC Congress, Cologne, Germany, 5–10 June 1983) Pergamon Press, Oxford, 1984, pp. 53–62.

[108] R. L. PRUETT, *Adv. Organometallic Chem.* **17**, 1–60 (1979). See also G. P. COOLES and R. DAVIS, *Educ. in Chem.*, 48–50, March 1982.

[109] C. MASTERS, *Adv. Organometallic Chem.* **17**, 61–103 (1979). R. B. ANDERSON, *The Fischer-Tropsch Synthesis*, Academic Press, London, 1984, 320 pp.

[110] R. C. EVERSON and D. T. THOMPSON, *Platinum Metals Review* **25**, 50–6 (1981).

[111] M. SUBRAHMANYAM, S. J. KULKARNI and A. V. RAMA RAO, *J. Chem. Soc., Chem. Commun.*, 607–8 (1992).

$$CO + 3NH_3 \xrightarrow{\text{HZSM-5}} CH_3NH_2 + H_2O + N_2 + H_2$$

2. Reductive coupling of two CO ligands to form a coordinated alkyne derivative, e.g. treatment of the Ta^I complex $[Ta(CO)_2(dmpe)_2Cl]$ with activated Zn dust in thf and then with Me_3SiCl gave a 25% yield of $[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl]$ which can in turn be hydrolysed to the corresponding complex of the novel dihydroxyacetylene, HOC=COH.[112]

CO_2 is much less volatile than CO (p. 306). It is a major industrial chemical but its uses, though occasionally chemical, more frequently depend on its properties as a refrigerant, as an inert atmosphere, or as a carbonating (gasifying) agent in drinks and foam plastic (see Panel).[113] Of more chemical interest is the synthesis of radioactive ^{14}C compounds from $^{14}CO_2$ which is conveniently stored as a carbonate. ^{14}C is generated by an (n,p) reaction on a nitride or nitrate in a nuclear reactor (see p. 1256). More than 500 compounds specifically labelled with ^{14}C are now available commercially, the starting point of many of the syntheses being one of the following reactions:

1. $NaH^{14}CO_3 + H_2/Pd/C \longrightarrow H^{14}CO_2H$
2. $^{14}CO_2 + RMgX \longrightarrow R^{14}CO_2H$
3. $^{14}CO_2 + LiAlH_4 \longrightarrow {}^{14}CH_3OH$
4. $Ba^{14}CO_3 + Ba \longrightarrow Ba^{14}C_2 \xrightarrow{H_2O} {}^{14}C_2H_2$
5. $Ba^{14}CO_3 + NH_3 \longrightarrow Ba^{14}CN_2 \longrightarrow {}^{14}C/N$ compounds

When CO_2 dissolves in water at 25° it is only partly hydrated to carbonic acid according to the equilibrium

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O;$$

$$K = [CO_2]/[H_2CO_3] \approx 600$$

Interpretation of acid–base behaviour in this system is further complicated by the slowness of some of the reactions and their dependence on pH. The main reactions are:

$$\left.\begin{array}{r} CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (slow)} \\[1em] H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \text{ (fast)} \end{array}\right\} \text{pH} < 8$$

$$\left.\begin{array}{r} CO_2 + OH^- \rightleftharpoons HCO_3^- \text{ (slow)} \\[1em] HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \text{ (fast)} \end{array}\right\} \text{pH} > 10$$

In the range pH 8–10 both sets of equilibria are important. The apparent dissociation constant of carbonic acid is

$$K_1 = [H^+][HCO_3^-]/[CO_2 + H_2CO_3]$$
$$= 4.45 \times 10^{-7} \text{ mol l}^{-1}$$

As $[CO_2]/[H_2CO_3] = K \approx 600$, it follows that the true dissociation constant is:

$$K_a = [H^+][HCO_3^-]/[H_2CO_3]$$
$$= K_1(1 + K) \approx 2.5 \times 10^{-4} \text{ mol l}^{-1}$$

This value is in the range expected from an acid of structure $(HO)_2CO$ (p. 50). The second dissociation constant is given by

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$$
$$= 4.84 \times 10^{-11} \text{ mol l}^{-1}$$

A hydrate $CO_2.8H_2O$ can be crystallized from aqueous solutions at 0° and $p(CO_2) \sim 45$ atm. There is also evidence for a hydrogen-bonded sesquicarbonate ion, $H_3C_2O_6^-$; this was originally suggested to have the sandwich

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[112] P. A. Bianconi, I. D. Williams, M. P. Engeler and S. J. Lippard, *J. Am. Chem. Soc.* **108**, 311–3 (1986). R. N. Vrtis, C. P. Rao, S. G. Bott and S. J. Lippard, *J. Am. Chem. Soc.* **110**, 7564–6 (1988).

[113] Ref. 106, pp. 35–53. See also W. M. Ayers, (ed.) *Catalytic Activation of Carbon Dioxide*, ACS Symposium 363, Washington, DC (1988), 212 pp.

Production and Uses of CO_2

CO_2 can be readily obtained in small amounts by the action of acids on carbonates. On an industrial scale the main source is as a byproduct of the synthetic ammonia process in which the H_2 required is generated either by the catalytic reaction (a) or by the water-gas shift reaction (b):

$$\text{(a) } CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2; \quad \text{(b) } CO + H_2O \rightleftharpoons CO_2 + H_2$$

CO_2 is also recovered economically from the flue gases resulting from combustion of carbonaceous fuels, from fermentation of sugars and from the calcination of limestone: recovery is by reversible absorption either in aqueous Na_2CO_3 or aqueous ethanolamine (Girbotol process).

$$Na_2CO_3 + H_2O + CO_2 \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} 2NaHCO_3$$

$$2HOC_2H_4NH_2 + H_2O + CO_2 \underset{100-150^\circ}{\overset{25-65^\circ}{\rightleftharpoons}} (HOC_2H_4NH_3)_2CO_3$$

In certain places CO_2 can be obtained from natural gas wells. H_2S impurity is removed by oxidation using a buffered alkaline solution saturated with $KMnO_4$:

$$3H_2S + 2KMnO_4 + 2CO_2 \longrightarrow 3S + 2MnO_2 + 2KHCO_3 + 2H_2O$$

The scale of production has increased rapidly in recent years and in 1980 exceeded 33 million tonnes in the USA alone though much of this is used in integrated plants, on site.

The most extensive application of CO_2 is as a refrigerant, some 52% of production being consumed in this way. CO_2 can be liquefied at any temperature between its triple point -56.6° (5.11 atm) and its critical point $+31.1^\circ$ (72.9 atm). The gas can either be pressurized to 75 atm and then water-cooled to room temperature, or precooled to about -15° ($\pm 5^\circ$) and then pressurized to 15.25 atm. Solid CO_2 is obtained by expanding liquid CO_2 from cylinders to give a "snow" which is then mechanically compressed into blocks of convenient size. Until about 40 y ago the bulk of CO_2 refrigerant was in the form of solid CO_2, but since 1960 production of liquid CO_2 has overtaken the solid form because of lower production costs and ease of transporting and metering the material. Some typical production figures are shown in the Table. Supercritical CO_2 is also finding increasing use as a versatile solvent for chemical reactions.[113a]

USA production of CO_2

CO_2 production/kilotonnes	1955	1960	1962	1977	1987
Solid	520	426	406	340	310
Liquid and gas	185	432	522	1660	7310
Total	705	858	928	2000	7620

Solid CO_2 is used as a refrigerant for ice-cream, meat and frozen foods, and as a convenient laboratory cooling agent and refrigerant. Liquid CO_2 is extensively used to improve the grindability of low-melting metals (and hamburger meat), and for the rapid cooling of loaded trucks and rail cars; it is also used for inflating life rafts, in fire extinguishers, and in blasting shells for coal mining. A related application of growing importance is as a replacement for chlorofluorocarbon aerosol propellants (p. 304) though this application will never consume large amounts of the gas since the amount in each tin is extremely small.

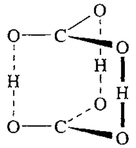
Gaseous CO_2 is extensively used to carbonate soft drinks and this use alone accounts for 20% of production. Other quasi-chemical applications are its use as a gas purge, as an inert protective gas for welding, and for the neutralization of caustic and alkaline waste waters. Small amounts are also used in the manufacture of sodium salicylate, basic lead carbonate ("white lead"), and various carbonates such as $M^I_2CO_3$ and M^IHCO_3 (M^I = Na, K, NH_4, etc.). One of the most important uses of CO_2 is to manufacture urea via ammonium carbamate:

$$CO_2 + 2NH_3 \xrightarrow[200\text{ atm}]{185^\circ} NH_2CO_2NH_4 \xrightarrow{-H_2O} CO(NH_2)_2$$

Urea is used to make urea-formaldehyde plastics and resins and, increasingly, as a nitrogenous fertilizer (46.7% N). World production of urea was 23 million tonnes in 1984.

[113a] M. POLIAKOFF and S. HOWDLE, *Chem in Brit.*, February 1995, pp. 118–21, and references cited therein.

structure (1)[114] though later *ab initio* calculations favour the all-planar structure (2).[115] Solid alkali-metal peroxocarbonates Li_2CO_4, $MHCO_4$ and $M_2C_2O_6$ (M = Na, K, Rb, Cs) are known and the anion HCO_4^- (CO_4^{2-} at high pH) can be prepared in solution by reaction of HCO_3^- with aqueous H_2O_2.[116] The peroxodianion, $C_2O_6^{2-}$ (3), can be prepared in aprotic solvents such as MeCN, dmf and dmso, via nucleophilic oxidation of CO_2 by the superoxide ion $O_2^{\cdot-}$: [$2CO_2 + 2O_2^{\cdot-} \rightarrow C_2O_6^{2-} + O_2$].[117] The amusing all-planar squarate ion, $C_4O_4^{2-}$ (4), although chemically unrelated to the preceding species, may be mentioned here as a further well-characterized binary C/O anion.[118,119] The short C–C and C–O distances have been interpreted in terms of π-electron delocalization.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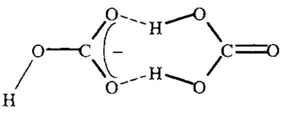
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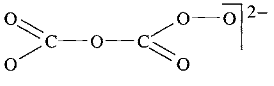
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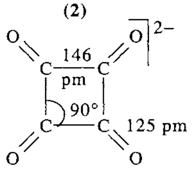
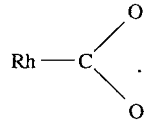


(4)

The coordination chemistry of CO_2 is by no means as extensive as that of CO (p. 926) but some exciting developments have recently been published.[120] The first transition metal complexes with CO_2 were claimed by M. E. Volpin's group in 1969: tertiary phosphine or N_2 ligands were displaced from Rh and Ni complexes to give binuclear products whose definitive structure has not yet been established. CO_2 also displaced N_2 from $[Co(N_2)(PPh_3)_3]$ to give $[Co(CO_2)(PPh_3)_3]$. The Ni^0 complexes $[Ni(PEt_3)_4]$ (violet) and $[Ni(PBu^n_3)_4]$ (red) react in toluene at room temperature with CO_2 (1 atm) to give the yellow complexes $[Ni(CO_2)L_3]$. The structure of the analogous complex with $P(C_6H_{11})_3$ was established by X-ray diffraction analysis; it features a pseudo-3-coordinate Ni atom μ-bonded to a bent CO_2 ligand as in Fig. 8.20a. The isoelectronic Rh^I appears to form two types of complex: an orange-red series $[Rh(CO_2)ClL_2]$ (L = tertiary phosphine) with a μ-bonded bent CO_2 as in Fig. 8.20a and a somewhat less-stable yellow series $[Rh(CO_2)ClL_3]$ which is thought to contain the ligand configuration  . A Pt compound which had earlier (1965) been thought to contain CO_2 as a ligand was subsequently found to require the presence of O_2 for its formation and to be, in fact, a novel bidentate carbonato complex (Fig. 8.20b).

$$[Pt(PPh_3)_3] + CO_2 + O_2 \xrightarrow{C_6H_6/25^\circ} [Pt(CO_3)(PPh_3)_2] + Ph_3PO$$

If the starting material contains M–H or M–C bonds a further complication can arise due to the possibility of a CO_2 insertion reaction. Thus, both $[Ru(H)_2(N_2)(PPh_3)_3]$ and $[Ru(H)_2(PPh_3)_4]$ react to give the formate $[Ru(H)(OOCH)(PPh_3)_3]$, and similar CO_2 insertions into M–H are known for M = Co, Fe, Os, Ir, Pt. These "normal" insertion reactions are consistent with the expected bond polarities $M^{\delta+}-H^{\delta-}$ and $O^{\delta-}=C^{\delta+}=O$, but occasionally "abnormal" insertion occurs to give metal carboxylic acids

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[114] A. K. COVINGTON, *Chem. Soc. Rev.* **14**, 265–81 (1985).

[115] N. V. RIGGS, *J. Chem. Soc., Chem. Commun.*, 137–8 (1987).

[116] J. FLANAGAN, D. P. JONES, W. P. GRIFFITH, A. C. SKAPSKI and A. P. WEST, *J. Chem. Soc., Chem. Commun.*, 20–1 (1986).

[117] J. L. ROBERTS, T. S. CALDERWOOD and D. T. SAWYER, *J. Am. Chem. Soc.* **106**, 4667–70 (1984).

[118] C. ROBL, V. GNUTZMANN and A. WEISS, *Z. anorg. allg. Chem.* **549**, 187–94 (1987), and references cited therein.

[119] R. SOULIS, F. DAHAN, J.-P. LAURENT and P. CASTAN, *J. Chem. Soc., Dalton Trans.*, 587–90 (1988).

[120] M. E. VOLPIN and I. S. KOLOMNIKOV, *Organometallic Reactions* **5**, 313–86 (1975). Further references to isolable CO_2-transition metal adducts are given in R. L. HARLOW, J. B. KINNEY, and T. HERSKOVITZ, *J. Chem. Soc., Chem. Commun.*, 813–4. (1980). G. S. BRISTOW, P. B. HITCHCOCK and M. F. LAPPERT, *J. Chem. Soc., Chem. Commun.*, 1145–6 (1981).

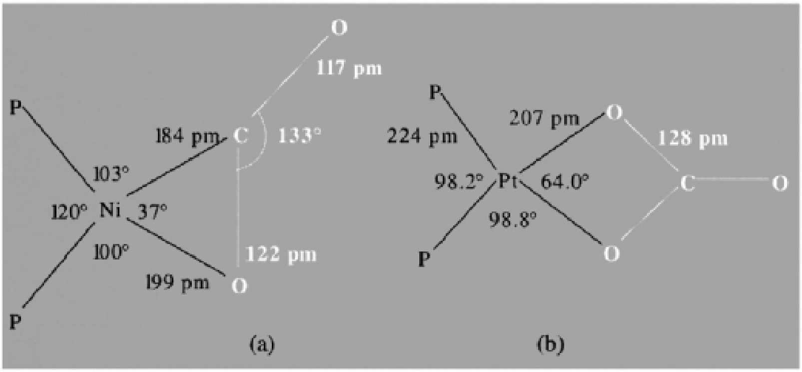

Figure 8.20 (a) Coordination about the Ni atom in the complex $[\mathrm{Ni(CO_2)\{P(C_6H_{11})_3\}_2}].0.75\mathrm{C_6H_5Me}$. (b) Coordination about the Pt atom in the complex $[\mathrm{Pt(CO_3)(PPh_3)_2}].\mathrm{C_6H_6}$.

M–COOH. Likewise, normal insertion into M–C yields alkyl carboxylates M–OOCR, though metalloacid esters M–COOR are sometimes obtained. The reactions have obvious catalytic implications and are being actively studied at the present time by several groups.$^{(121)}$

CO_2 insertion into M–C bonds has, of course, been known since the first papers of V. Grignard in 1901 (p. 134). Organo-Li (and other M^I and M^{II}) also react extremely vigorously to give salts of carboxylic acids, RCO_2Li, $(RCO_2)_2Be$, etc. Zinc dialkyls are much less reactive towards CO_2, e.g.

$$\mathrm{ZnEt_2 + 2CO_2 \xrightarrow{150^\circ} (EtCOO)_2Zn},$$

and organo-Cd and -Hg compounds are even less reactive. With AlR_3, one CO_2 inserts at room temperature and a second at 220° under pressure to give $R_2Al(OOCR)$ and $RAl(OOCR)_2$ respectively. B–C, Si–C, Ge–C, and Sn–C are rather inert to CO_2 but insertion readily occurs into bonds between these elements and N. A few examples are:

$$\mathrm{PhB(NHEt)_2 + CO_2 \xrightarrow{25^\circ} PhB(OCONHEt)_2}$$

$$\mathrm{Me_3SiNEt_2 + CO_2 \xrightarrow{Et_2NH/25^\circ} Me_3SiOCONEt_2}$$

$$\mathrm{Me_3SnNMe_2 + CO_2 \xrightarrow{20^\circ} Me_3SnOCONMe_2}$$

$$\mathrm{As(NMe_2)_3 + 1(3)CO_2 \xrightarrow{20^\circ - 40^\circ}}$$
$$\mathrm{(Me_2N)_2AsOCONMe_2,\ As(OCONMe_2)_3}$$

$$\mathrm{Ti(NMe_2)_4 + CO_2 \xrightarrow{20^\circ} Ti(OCONMe_2)_4,\ etc.}$$

Returning briefly to CO_2 as a ligand: in addition to the various mono-CO_2 complexes referred to above, several bis(η^2-CO_2) transition-metal adducts are known, e.g. *trans*-$[\mathrm{Mo}(\eta^2\text{-}\mathrm{CO_2})_2(\mathrm{PMe_3})_4]$ (5) and *trans,mer*-$[\mathrm{Mo}(\eta^2\text{-}\mathrm{CO_2})_2(\mathrm{PMe_3})_3(\mathrm{CNPr}^i)]$.$^{(122)}$ The first homo-bimetallic bridging-CO_2 complex has also been structurally characterized by X-ray analysis, *viz.* $[(\mathrm{dppp})(\mathrm{CO})_2\mathrm{Re}(\mu,\eta^2\text{-O,O}'\text{:}\eta'\text{-C})\mathrm{Re(CO)_3(dppp)}]$ (6) [dppp = 1,3-bis(diphenylphosphino)propane].$^{(123)}$

The carbonate ion, CO_3^{2-}, by contrast, is a classic Werner ligand which forms innumerable complexes as a monohapto, dihapto or bridging donor. Examples of this latter mode

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[121] A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, 1988, 161 pp. See also J. D. Miller in P. S. Braterman (ed.), *Reactions of Coordinated Ligands*, Vol. 2., Plenum Press, New York, pp. 1–52 (1989) and J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos and M. Calvin, *J. Chem. Soc., Dalton Trans.*, 2105–9 (1987) and references cited therein.

[122] R. Alvarez, E. Carmona, M. L. Poveda and R. Sánchez-Delgardo, *J. Am. Chem. Soc.* **106**, 2731–2 (1984). R. Alvarez, E. Carmona, E. Gutierrez-Puebla, J. M. Marin, A. Monge and M. L. Poveda, *J. Chem. Soc., Chem. Commun.*, 1326–7 (1984).

[123] S. K. Mandal, J. A. Krause and M. Orchin, *Polyhedron* **12**, 1423–5 (1993).

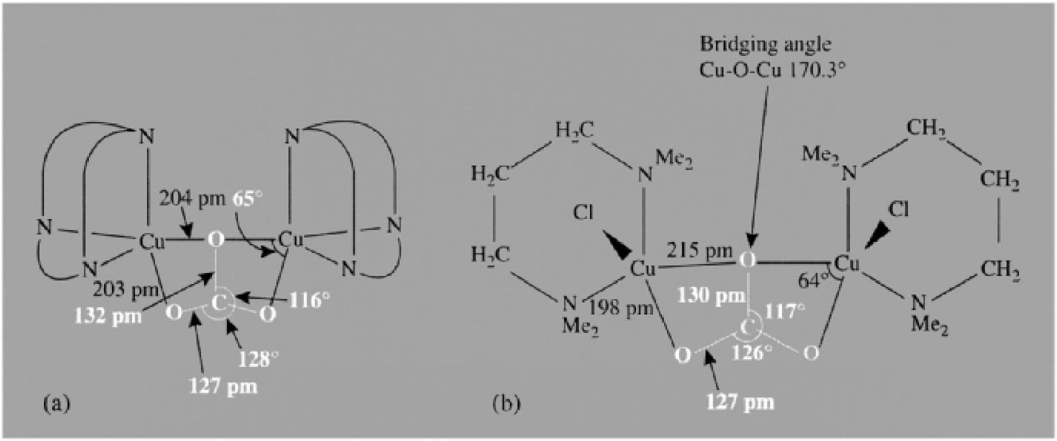
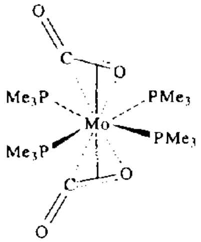


Figure 8.21 (a) The complex cation $[Cu(L_2)_2(\mu\text{-}\eta^2,\eta^2\text{-}CO_3)]^{2+}$. (b) The binuclear complex $[\{CuCl(Me_2N\text{-}CH_2CH_2CH_2NMe_2)\}_2(\mu\text{-}\eta^2,\eta^2\text{-}CO_3)]$.



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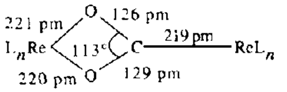

(6)

are the complex cation $[(CuL_2)_2(\mu\text{-}CO_3)]^{2+}$, where L is a tridentate macrocylic triaza ligand (Fig. 8.21a),$^{(124)}$ and in the binuclear molecular complex molecule $[\{CuCl(Me_2NCH_2CH_2-CH_2NMe_2\}_2(\mu\text{-}CO_3)]$ (Fig. 8.21b).$^{(125)}$ This mode of coordination confers some unusual properties including diamagnetism on these Cu^{II} complexes. Even more extensive ligation occurs in the deep violet hexanuclear vanadium (IV) complex $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9].10H_2O$ which was made by reacting $VOCl_2$ with aqueous NH_4HCO_3 under CO_2.$^{(126)}$ The novel anion (Fig. 8.22) features a unique tris(bidentate) sextuply bridging carbonato ligand as well as three bidentate μ_2-carbonato ligands. Other chelating and bridging coordination modes are also known.$^{(126a)}$

8.7 Chalcogenides and Related Compounds

Carbon forms a great many sulfides in addition to the well known CS_2. CS (unlike CO) is an unstable reactive radical even at −196°: it reacts with the other chalcogens and with halogens to give CSSe, CSTe, and CSX_2. It is formed by action of a high-frequency discharge on CS_2 vapour. (See p. 319 for complexes of CS.) Passage of an electric discharge or arc through liquid or gaseous CS_2 yields C_3S_2, a red liquid mp −5°; it has a linear molecular structure, S=C=C=C=S, which polymerizes slowly at room temperature (cf. C_3O_2).$^{(127)}$

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[124] A. R. Davis, F. W. P. Einstein, N. F. Curtis and J. W. L. Martin, *J. Am. Chem. Soc.* **100**, 6258–60 (1978).

[125] M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, M. Rupich and K. O. Watkins, *Inorg. Chem.* **18**, 2296–300 (1979).

[126] T. C. W. Mak, P. Li, C. Zheng and K. Huang, *J. Chem. Soc., Chem. Commun.*, 1597–8 (1986).

[126a] F. W. B. Einstein and A. C. Willis, *Inorg. Chem.* **20**, 609–14 (1981). A. J. Lindsay, M. Motevalli, M. B. Hursthouse and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 433–4 (1986).

[127] M. T. Bech and G. B. Kauffman, *Polyhedron* **5**, 775–81 (1985) and references cited therein. (This paper also gives an accessible account of the history of the discovery and applications of COS, i.e. O=C=S.)

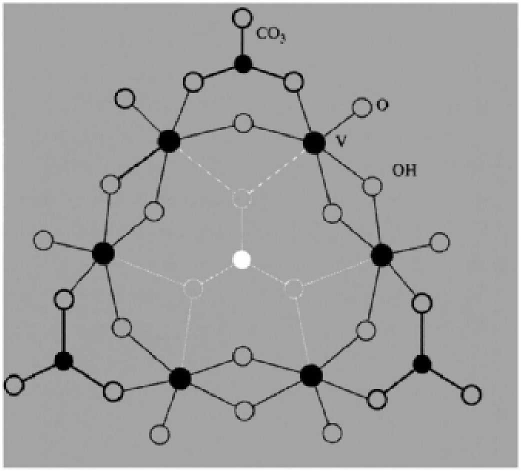
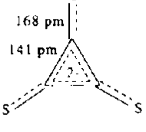
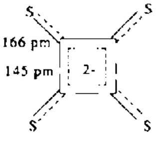


Figure 8.22 Perspective view of the hexanuclear anion $[(VO)_6(\mu_6\text{-}\eta^2,\eta^2,\eta^2\text{-}CO_3)(\mu\text{-}CO_3)_3\text{-}(\mu\text{-}OH)_9]^{5-}$. Averaged interatomic distances: vanadyl V=O 161.6 pm, V-OH(*syn*) 195.6 pm, V-OH(*anti*) 201.2 pm, V-O (μ_2-CO_3) 200.2 pm, V-O (μ_6-CO_3) 228.7 pm, C-Oμ) 129.1 pm, C-O(*exo*) 126.6 pm.[126]

During the past decade there has been an astonishing proliferation of further binary carbon-sulfur species, both anionic and neutral.[128] Of the anions, the beige coloured dianion $C_3S_3^{2-}$ (made from tetrachlorocyclopropene) has the D_{3h} structure (1) and the yellow $C_4S_4^{2-}$ (made from squaric acid, p. 312) has the D_{4h} structure (2). The off-white $C_6S_6^{6-}$, (3), (made from C_6Cl_6) is air-sensitive but can readily be protonated to give the more stable hexathiol $C_6(SH)_6$. Reduction of CS_2 either electrochemically or by alkali metals yields $C_3S_5^{2-}$ which can exist in two isomeric forms, (4) and (5):



(1)



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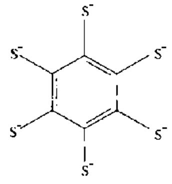

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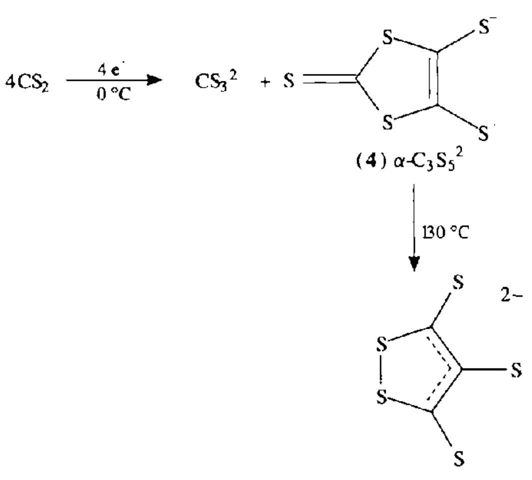
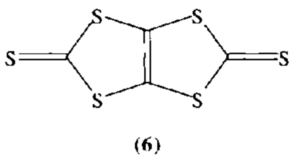


(4) α-$C_3S_5^{2-}$

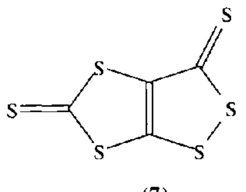
(5) β-$C_3S_5^{2-}$

Treatment of the primary product with a zinc salt leads to separation of α-$C_3S_5^{2-}$ from its coproduct CS_3^{2-}, and multigram amounts of its complexes $[NR_4]_2[Zn(\alpha\text{-}C_3S_5)_2]$ and of the corresponding β-isomer's complexes afford convenient starting points for the synthesis of *molecular* binary sulfides as indicated below.

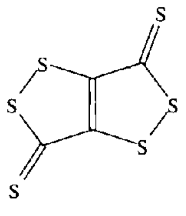
The sulfide C_4S_6 is known in three isomeric forms (6), (7) and (8).[128] The yellow-orange D_{2h} isomer (6) is readily prepared



(6)



(7)



(8)

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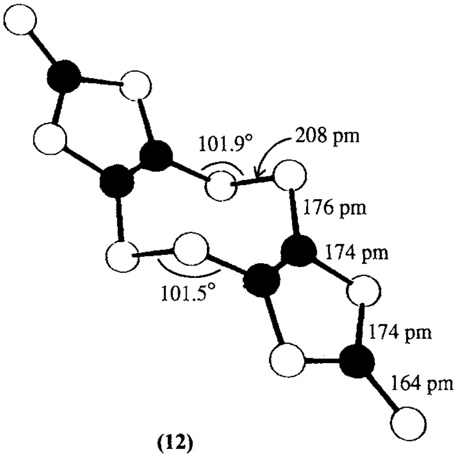
[128] C. P. GALLOWAY, T. B. RAUCHFUSS and X. YANG, in R. STEUDEL (ed.) *The Chemistry of Inorganic Ring Systems*, Studiees in Inorganic Chemistry, Vol. 14, Elsevier, Amsterdam, 1992, pp. 25-34. See also X. YANG, T. B. RAUCHFUSS and S. R. WILSON, *J. Am. Chem. Soc.* **111**, 3465-6 (1989) and *J. Chem. Soc., Chem. Commun.*, 34-5 (1990).

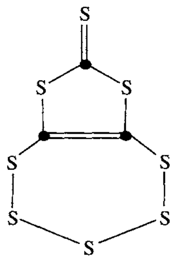
by the reaction of $CSCl_2$ with α-$C_3S_5{}^{2-}$, whilst the C_1 isomer (7) results from the corresponding reaction with β-$C_3S_5{}^{2-}$. The C_{2h} isomer (8) is less well characterized but is said to result from the reaction of hexachlorobutadiene, $CCl_2{=}CCl{-}CCl{=}CCl_2$, with polysulfide anions. The treatment of S_2Cl_2 with $[NBu_4]_2[Zn(\alpha\text{-}C_3S_5)_2]$ yields a mixture of C_3S_8 and C_6S_{12} which can be separated by fractional crystallization from CS_2:

$$[Zn(C_3S_5)_2]^{2-} + 2S_2Cl_2 \longrightarrow [ZnCl_4]^{2-} + 0.5C_6S_{12} + C_3S_8$$

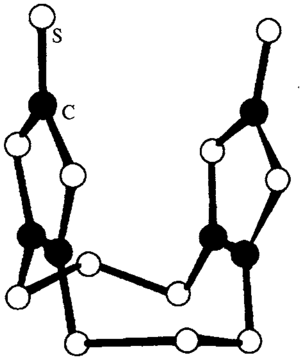
C_3S_8 is a bicyclic species composed of the α-C_3S_5 unit capped by a polysulfide linkage (9), whereas C_6S_{12} features two cisoid eclipsed planar α-C_3S_5 units conjoined by further sulfur linkages to form a third ring (10); note that, if each of the two C_2 groups in this 10-membered ring are notionally replaced by an S atom, the conformation of the resulting S_8 ring is reminiscent of the familiar crown configuration for this species (p. 655). Oxidation of $[NEt_4]_2[Zn(\beta\text{-}C_3S_5)_2]$ with $SOCl_2$ affords small amounts of the yellow C_6S_8 (11) which features an almost planar molecule with S···S fold angles <3.8°. By contrast, oxidation of $[NBu_4]_2[Zn(\alpha\text{-}C_3S_8)_2]$ with SO_2Cl_2 yields the orange dimer C_6S_{10} (12) in which the two planar C_3S_5 groups are interconnected by a pair of transoid S_2 linkages to give an overall chair configuration. Finally we should mention the two known isomers of C_9S_9. The simpler, formed by the reaction of $C_6S_6{}^{6-}$ (3) with $CSCl_2$, is the tris(trithiocarbonate) (13) which sublimes at 310° and can be recrystallized from 1,2-$C_6H_4Cl_2$. The second C_9S_9 isomer is synthesized by



(12)



(9)



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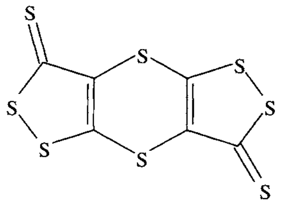

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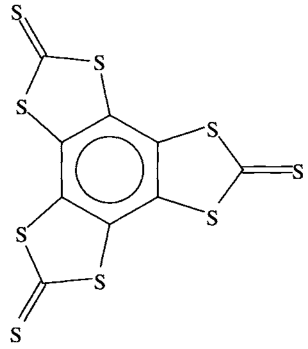
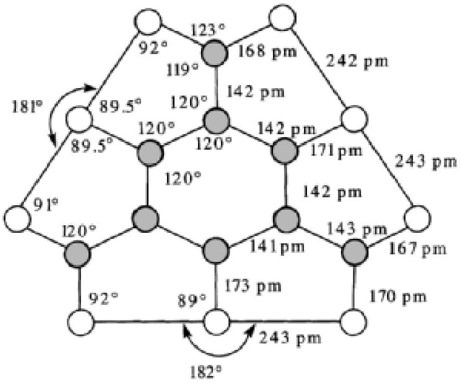


(13)

reaction of the benzene derivative 1,3,5-C_6Cl_3-2,4,6-$(CH_2NMe_2)_3$ with sulfur and H_2S in boiling quinoline; it forms red crystals of the planar D_{3h} molecule (14) which has a non-classical structure with three 3-coordinate S atoms. Both isomers are formally also oligomeric isomers of the diatomic monomer CS (p. 314).



(14)

By far the most important sulfide is CS_2, a colourless, volatile, flammable liquid (mp −111.6°, bp 46.25°, flash point −30°, auto-ignition temperature 100°, explosion limits in air 1.25–50%). Impure samples have a fetid almost nauseating stench due to organic impurities but the purified liquid has a rather pleasant ethereal smell; it is very poisonous and can have disastrous effects on the nervous system and brain. CS_2 was formerly manufactured by direct reaction of S vapour and coke in Fe or steel retorts at 750–1000°C but, since the early 1950s, the preferred synthesis has been the catalysed reaction between sulfur and natural gas:

$$CH_4 + 4S \xrightarrow[\text{SiO}_2\text{ gel or Al}_2\text{O}_3]{\sim 600^\circ} CS_2 + 2H_2S$$

World production in 1991 was about 1 million tonnes the principal industrial uses being in the manufacture of viscose rayon (35–50%), cellophane films (15%) (see below), and CCl_4 (15–30%) depending on country. Indeed the CCl_4 application dropped to zero in USA in 1991 because of environmental concerns (p. 304).

CS_2 reacts with aqueous alkali to give a mixture of M_2CO_3 and the trithiocarbonate M_2CS_3. NH_3 gives ammonium dithiocarbamate $NH_4[H_2NCS_2]$; under more forcing conditions in the presence of Al_2O_3 the product is NH_4CNS and this can be isomerized at 160° to thiourea, $(NH_2)_2CS$. Water itself reacts only reluctantly, yielding COS at 200° and $H_2S + CO_2$ at higher temperatures; many other oxocompounds also convert CS_2 to COS, e.g. MgO, SO_3, HSO_3Cl and urea. With aqueous NaOH/EtOH carbon disulfide yields sodium ethyl dithiocarbonate (xanthate):

$$CS_2 + NaOH + EtOH \longrightarrow Na[SC(S)OEt]$$

When ethanol is replaced by cellulose, sodium cellulose xanthate is obtained; this dissolves in aqueous alkali to give a viscous solution (viscose) from which either viscose rayon or cellophane can be obtained by adding acid to regenerate the (reconstituted) cellulose. Trithiocarbonates (CS_3^{2-}), dithiocarbonates (COS_2^{2-}), xanthates (CS_2OR^-), dithiocarbamates ($CS_2NR_2^-$) and 1,2-dithiolates have an extensive coordination chemistry which has been reviewed.(129)

Chlorination of CS_2, when catalysed by $Fe/FeCl_3$, proceeds in two steps:

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

With I_2 as catalyst the main product is perchloromethylthiol (Cl_3CSCl). Reaction products with F_2 depend on the conditions used, typical products being SF_4, SF_6, S_2F_{10}, $F_2C(SF_3)_2$, $F_2C(SF_5)_2$, F_3CSF_5 and $F_3SCF_2SF_5$.

CS_2 is rather more reactive than CO_2 in forming complexes and in undergoing insertion reactions. The field was opened up by G. Wilkinson and his group in 1966 when they showed that $[Pt(PPh_3)_3]$ reacts rapidly and

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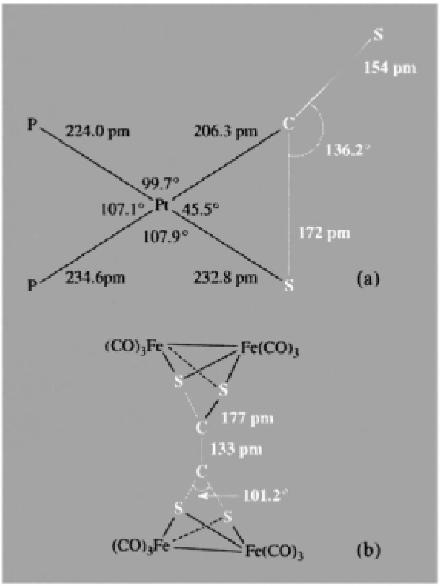
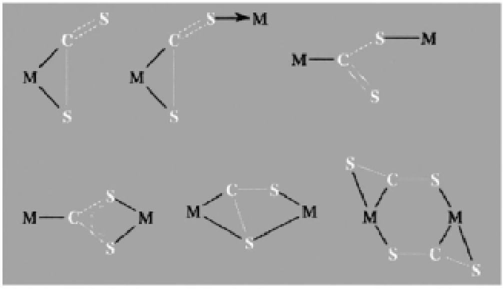
[129] G. D. Thorn and R. A. Ludwig, *The Dithiocarbamates and Related Compounds*, Elsevier 1962, 298 pp. J. A. McCleverty, *Prog. Inorg. Chem.* **10**, 49–221 (1968) (188 refs.). D. Coucouvanis, *Prog. Inorg. Chem.* **11**, 233–71 (1970) (516 refs.). R. E. Eisenberg, *Prog. Inorg. Chem.* **12**, 295–369 (1971) (173 refs.).

quantitatively with CS_2 at room temperature to give orange needles of $[Pt(CS_2)(PPh_3)_2]$, mp 170°. X-ray crystal diffraction analysis revealed the structure shown diagramatically in Fig. 8.23(a). The geometry of the bent CS_2 ligand is similar to that in the first excited state of the molecule and the CS_2 is almost coplanar with PtP_2 (dihedral angle 6°). Bonding is considered to involve a 1-electron transfer via the intermediary of Pt from the highest filled π MO of the ligand to its lowest antibonding MO, and the Pt can be thought of as being oxidized from Pt^0 to Pt^{II}. However, the substantial difference between the two Pt–P distances and the wide deviation of the angles of Pt from 90° emphasize the inadequacy of describing the bonding of such complicated species in terms of simple localized bonding theory. The orange complex $[Pd(CS_2)(PPh_3)_2]$ is isostructural and further work yielded deep-green $[V(\eta^5\text{-}C_5H_5)_2(CS_2)]$, dimeric $[(Ph_3P)Ni(\mu\text{-}CS_2)_2Ni(PPh_3)]$ and various CS_2 complexes of Fe, Ru, Rh and Ir. The deep-red complex $[Rh(CS_2)_2Cl(PPh_3)_2]$ probably involves pseudo-octahedral Rh^{III} with one of the CS_2 ligands η^2-bonded as above and the other one σ-bonded via a single S atom. By contrast, reaction of $[Fe_3(CO)_{12}]$ with an excess of CS_2 in hexane for several hours at 80°C under a 10 atm pressure of CO/Ar gave the orange complex $[\{Fe_2(CO)_6\}_2(\mu_4\text{-}C_2S_4)]$ as one of the products (1–2%). As can be seen from Fig. 8.23(b), the structure has two $\{Fe_2(CO)_6\}$ units bridged by a planar $\{S_2C=CS_2\}$ group, which can in turn be regarded as an ethenetetrathiol moiety formed by the C–C coupling of two CS_2 molecules.(130)

The numerous η^1,η^2, and bridging modes of coordination now known for CS_2 are indicated schematically below:(131)





Insertion reactions of CS_2 are known for all the elements which undergo CO_2 insertion

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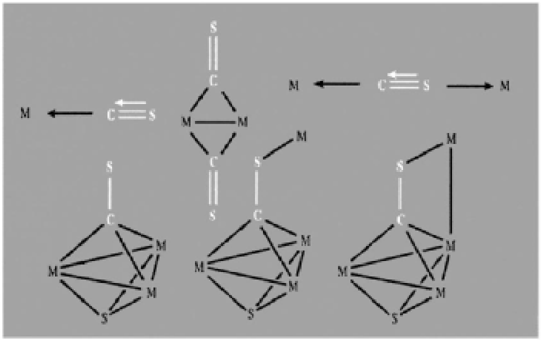
(130) P. V. Broadhurst, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 140–1 (1982).

(131) T. G. Southern, U. Oehmichen, J. Y. le Marouille, H. le Bozec, D. Grandjean and P. H. Dixneuf, *Inorg. Chem.* **19**, 2976–80 (1980). Other key papers in this burgeoning field are: G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guestini, *J. Chem. Soc., Dalton Trans.*, 1612–17 (1979). P. Conway, S. M. Grant and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1920–4 (1979). P. J. Vergamini and P. G. Eller, *Inorg. Chim. Acta* **34**, L291–2 (1979). C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, *Inorg. Chim. Acta* **35**, L375–6 (1979). C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, *Angew. Chem. Int. Edn. Engl.*, **18**, 673–4 (1979). C. Bianchini, C. Mealli, A. Melli, A. Orlandini and L. Sacconi, *Inorg. Chem.* **19**, 2968–75 (1980). W. P. Fehlhammer and H. Stolzenberg, *Inorg. Chim. Acta* **44**, L151–2 (1980). C. Bianchini, C. A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, *J. Chem. Soc., Chem. Commun.*, 753–4 (1983). D. H. Farrar, R. R. Gukathasan and S. A. Morris, *Inorg. Chem.* **23**, 3258–61 (1984).

(p. 312) and also for M–N bonds involving Sb^{III}, Zr^{IV}, Nb^{V}, Ta^{V}, etc. Reaction of CS_2 with Au_2Cl_6 results in its novel insertion into Au–Cl bonds to form orange crystals of the chlorodithioformate complex $[AuCl_2(\eta^2\text{-}S_2CCl)]$.[132] The parent dithioformate ligand, HCS_2^-, has been prepared by insertion of CS_2 into the Ru–H bond of $[RuH(CO)Cl(PPh_3)_2(4\text{-vinyl pyridine})]$ to form the yellow complex $[Ru(CO)Cl(PPh_3)_2(\eta^2\text{-}S_2CH)]$.thf.[133] Perhaps even more intriguingly, treatment of the orange *nido* 11-vertex metallathiaborane cluster $[8,8\text{-}(PPh_3)_2\text{-}8,7\text{-}nido\text{-}RhSB_9H_{10}]$ (cf. structure (42), p. 178) with CS_2 under reflux gives a 37% yield of the pale orange *nido* cluster $[8,8\text{-}(PPh_3)_2\text{-}\mu\text{-}8,9\text{-}(\eta^2\text{-}S_2CH)\text{-}8,7\text{-}RhSB_9H_9]$ which features a unique dithioformate bridge between Rh(8)-B(9), perhaps by addition of $B\text{–}H_t(9)$ across a C–S bond.[134]

Stable thiocarbonyl complexes containing the elusive CS ligand are also now well established and known coordination modes, which include terminal, bridging and polyhapto, are as shown at the top of the next column.[135]



Likewise complexes of CSe and CTe have been characterized.[136] The structure and reactivity of CS complexes has been well reviewed[137] and exciting work in this area continues.[138]

8.8 Cyanides and Other Carbon–Nitrogen Compounds

The chemistry of compounds containing the CN group is both extensive and varied. The types of compound to be discussed are listed in Table 8.7, which also summarizes some basic structural information. The names cyanide, cyanogen, etc., refer to the property of forming deep-blue pigments such as Prussian blue (p. 1094) with iron salts (Greek κύανος, *cyanos*, dark blue).

A useful theme for cohering much of the chemistry of compounds containing the CN group is the concept of pseudohalogens, a term introduced in 1925 for certain strongly bound, univalent radicals such as CN, OCN, SCN, SeCN, (and N_3, etc.). These groups can form anions X^-, hydracids HX, and sometimes neutral species X_2,

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[132] D. Jentsch, P. G. Jones, C. Thöne and E. Schwarzmann, *J. Chem. Soc., Chem. Commun.*, 1495–6 (1989).

[133] V. G. Puranik, S. S. Tavale and T. N. G. Row, *Polyhedron* **6**, 1859–61 (1987).

[134] G. Ferguson, M. C. Jennings, A. L. Lough, S. Coughlan, T. R. Spalding, J. D. Kennedy, X. L. R. Fontaine and B. Štíbr, *J. Chem. Soc., Chem. Commun.*, 891–4 (1990).

[135] I. S. Butler, *Acc. Chem. Res.* **10**, 359–65 (1977). P. V. Yaneff, *Coord. Chem. Rev.* **23**, 183–220 (1977) (includes CS_2 complexes also). H. Werner and K. Leonhard, *Angew. Chem. Int. Edn. Engl.* **18**, 627–8 (1979). H Herberhold and P. H. Smith, *Angew. Chem. Int. Edn. Engl.* **18**, 631–2 (1979). W. W. Greaves, R. J. Angelici, B. J. Helland, R. Klima and R. A. Jacobson, *J. Am. Chem. Soc.* **101**, 7618–20 (1979). F. Farone, G. Tresoldi, and G. A. Loprete, *J. Chem. Soc., Dalton Trans.*, 933–7 (1979); *J. Chem. Soc., Dalton Trans.*, 1053–6 (1979). P. V. Broadhurst, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 812–13 (1980); *J. Am. Chem. Soc.* **103**, 3198–200 (1981).

[136] G. R. Clark, K. Marsden, W. R. Roper and L. J. Wright, *J. Am. Chem. Soc.* **102**, 1206–7 (1981). J.-P. Battioni, D. Mansuy and J.-C. Chottard, *Inorg. Chem.* **19**, 791–2 (1980).

[137] P. V. Broadhurst, *Polyhedron* **4**, 1801–46 (1985).

[138] K. J. Klabunde, M. P. Kramer, A. Senning and E. K. Moltzen, *J. Am. Chem. Soc.* **106**, 263–4 (1984). L. Busetto, V. Zanotti, V. G. Albano, D. Braga and M. Monari, *J. Chem. Soc., Dalton Trans.*, 1791–4 (1986) and 1133–3 (1987). S. Lotz, R. R. Pille and P. H. van Rooyen, *Inorg. Chem.* **25**, 3053–7 (1986). G. Gervasio, R. Rossetti, P. L. Stanghellini and G. Bor, *J. Chem. Soc., Dalton Trans.*, 1707–11 (1987). A. R. Manning, L. O'Dwyer, P. A. McArdle and D. Cunningham, *J. Chem. Soc., Chem. Commun.*, 897–8 (1992).

Table 8.7 Some compounds containing the CN group

Name	Conventional formula	r(C–N)/pm	Remarks(a)
Cyanogen	$N\equiv C-C\equiv N$	115	Linear; r(C–C) 138 pm (short)
Paracyanogen	$(CN)_x$	—	Involatile polymer, see text
diisocyanogen	CN–NC	118 (calc.)	Linear, symmetric, unstable(140)
isocyanogen	CN–CN	118&116 (calc.)	Zig-zag, unsymmetric, stable(140)
Hydrogen cyanide	$H-C\equiv N$	115.6	Linear; r(C–H) 106.5 pm
Cyanide ion	$(C\equiv N)^-$	116	r_{eff} 192 pm when "freely rotating" in MCN
Cyanides (nitriles)	$M-C\equiv N$ $(R-C\equiv N)$	115.8	Linear; r(C–C) 146.0 pm (for MeCN)
Isocyanides	$R-N\equiv C$	116.7	Linear, $r(H_3C-N)$ 142.6 pm (for MeNC). Coordinated isocyanides are slightly bent, e.g. $[M(\leftarrow C{=}N-C_6H_5)_6]$ angle CNC 173°. r(C=N) 117.6 pm: bridging modes are also known, e.g. structure (1), p. 321
Cyanogen halides (halogen cyanides)	$X-C\equiv N$	116	Linear
Cyanamide	$H_2N-C\equiv N$	115	Linear NCN; $r(C-NH_2)$ 131 pm
Dicyandiamide	$N\equiv C-N{=}C(NH_2)_2$	122–136	See structure (2), p. 321
Cyanuric compounds	$\{-C(X){=}N-\}_3$	134	Cyclic trimers; X = halogen, OH, NH_2
Cyanate ion	$(O-C\equiv N)^-$	~121	Linear
Isocyanates	$R-N{=}C{=}O$	120	Linear NCO; ∠RNC ~ 126°
Fulminate ion	$>(C{=}N-O)^-$	109	Linear; another form of AgCNO has r(C–N) 112 pm
Thiocyanate ion	$(S-C\equiv N)^-$	115	Linear
Thiocyanates	$R-S-C\equiv N$ $(M-S-C\equiv N)$	116	Linear NCS; ∠RSC 100° in MeSCN; ∠MSC variable (80–107°)
Isothiocyanates	$R-N{=}C{=}S$	122	Linear NCS; ∠HNC 135° in HNCS; ∠MNC variable (111–180°)
Selenocyanate ion	$(Se-C\equiv N)^-$	~112	Linear NCSe

(a)Several groups can also act as bridging ligands in metal complexes, e.g. –CN–, >NCO, –SCN–

XY, etc. It is also helpful to recognize that CN^- is isoelectronic with C_2^{2-} (p. 299) and with several notable ligands such as CO, N_2 and NO^+. Similarly, the cyanate ion OCN^- is isoelectronic with CO_2, N_3^-, fulminate (CNO^-), etc.(139)

Cyanogen, $(CN)_2$, is a colourless poisonous gas (like HCN) mp −27.9°, bp −21.2° (cf. Cl_2, Br_2). When pure it possesses considerable thermal stability (800°C) but trace impurities normally facilitate polymerization at 300–500° to paracyanogen a dark-coloured solid which may have a condensed polycyclic structure (3).

The polymer reverts to $(CN)_2$ above 800° and to CN radicals above 850°. $(CN)_2$ can be prepared in 80% yield by mild oxidation of CN^- with aqueous Cu^{II}; the reaction is complex but can be idealized as

$$2CuSO_4 + 4KCN \xrightarrow{H_2O/60^\circ} (CN)_2 + 2CuCN + 2K_2SO_4$$

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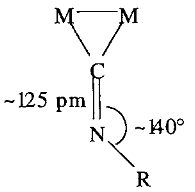
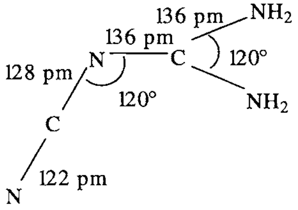
[139] A. M. Golub, H. Köhler and V. V. Skopenko (eds.), *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986, 479 pp., 4217 refs.

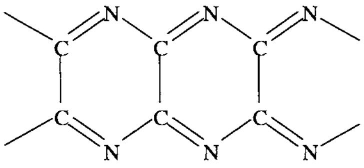
[140] L. S. Cederbaum, F. Tarantelli, H. G. Weikert, M. Scheller and H. Köppel, *Angew. Chem. Int. Edn. Engl.* **28**, 761–2 (1989).



(1)



(2)



(3)

CO_2 which is also formed (20%) can be removed by passage of the product gas over solid NaOH and the byproduct CuCN can be further oxidized with hot aqueous Fe^{III} to complete the conversion:

$$2CuCN + 2FeCl_3 \xrightarrow{H_2O/heat} (CN)_2 + 2CuCl + 2FeCl_2$$

Industrially it is now made by direct gas-phase oxidation of HCN with O_2 (over a silver catalyst), or with Cl_2 (over activated charcoal), or NO_2 (over CaO glass). $(CN)_2$ is fairly stable in H_2O, EtOH and Et_2O but slowly decomposes in solution to give HCN, HNCO, $(H_2N)_2CO$ and $H_2NC(O)C(O)NH_2$ (oxamide). Alkaline solutions yield CN^- and $(OCN)^-$ (cf. halogens).

$$(CN)_2 + 2OH^- \longrightarrow CN^- + OCN^- + H_2O$$

Hydrogen cyanide, mp −13.3° bp 25.7°, is an extremely poisonous compound of very high dielectric constant (p. 55). It is miscible with H_2O, EtOH and Et_2O. In aqueous solution it is an even weaker acid than HF, the dissociation constant K_a being 7.2×10^{-10} at 25°C. It was formerly produced industrially by acidifying NaCN or $Ca(CN)_2$ but the most modern catalytic processes are based on direct reaction between CH_4 and NH_3, e.g.:$^{(141)}$

Andrussow process:

$$CH_4 + NH_3 + 1\tfrac{1}{2}O_2 \xrightarrow[2\ \text{atm}/1000-1200^\circ]{\text{Pt/Rh or Pt/Ir}} HCN + 3H_2O$$

Degussa process:

$$CH_4 + NH_3 \xrightarrow[1200-1300^\circ]{\text{Pt}} HCN + 3H_2$$

Both processes rely on a fast flow system and the rapid quenching of product gases; yields of up to 90% can be attained. It is salutory to note that US production of this highly toxic compound is 600 000 tonnes pa (1992) and world production exceeds one million tonnes pa. Of this, 41% is used to manufacture adiponitrile for nylon and 28% for acrylic plastics:

$$HCN + Me_2CO \longrightarrow \text{acetone cyanohydrin}$$
$$\xrightarrow{H_2SO_4} \text{methacrylamide sulfate} \xrightarrow{MeOH}$$
$$\text{methyl methacrylate}$$

HCN is now also used to make $(ClCN)_3$ for pesticides (9%), NaCN for gold recovery (13%), and chelating agents such as edta (4%), etc.

As noted above, $CN^-(aq)$ is fairly easily oxidized to $(CN)_2$ or OCN^-; E° values calculated from free energy data (p. 435) are:

$$\tfrac{1}{2}(CN)_2 + H^+ + e^- \rightleftharpoons HCN; \quad E^\circ\ +0.37\ V$$

$$OCN^- + 2H^+ + 2e^- \rightleftharpoons CN^- + H_2O; \quad E^\circ\ -0.14\ V$$

HCN can also be reduced to $MeNH_2$ by powerful reducing agents such as Pd/H_2 at 140°.

The alkali metal cyanides MCN are produced by direct neutralization of HCN; they crystallize

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[141] Ref. 2, Vol. 7 (1993), Cyanides (including HCN, M^ICN, and $M^{II}(CN)_2$, pp. 753–82; Cyanamides including CaNCN, H_2NCN, dicyandiamide, and melamine), pp. 736–52; cyanuric and isocyanuric acids, pp. 834–51.

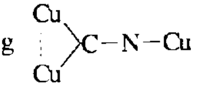
with the NaCl structure (M = Na, K, Rb) or the CsCl structure (M = Cs, Tl) consistent with "free" rotation of the CN$^-$ group. The effective radius is ~190 pm, intermediate between those of Cl$^-$ and Br$^-$. At lower temperatures the structures transform to lower symmetries as a result of alignment of the CN$^-$ ions. LiCN differs in having a loosely packed 4-coordinate arrangement and this explains its low density (1.025 g cm^{-3}) and unusually low mp (160°, cf. NaCN 564°, KCN 634°C). World production of alkali metal cyanides was ~340 000 tonnes in 1989. NaCN readily complexes metallic Ag and Au under mildly oxidizing conditions and is much used in the extraction of these metals from their low-grade ores (first patented in 1888 by R. W. Forrest, W. Forrest and J. S. McArthur):

$$8NaCN + 4M + 2H_2O + O_2 \longrightarrow 4Na[M(CN)_2] + 4NaOH$$

Until the 1960s, when HCN became widely available, NaCN was made by the Castner process via sodamide and sodium cyanamide:

$$2Na + C + 2NH_3 \xrightarrow{750^\circ} 2NaCN + 3H_2$$

The CN$^-$ ion can act either as a monodentate or bidentate ligand.$^{(142)}$ Because of the similarity of electron density at C and N it is not usually possible to decide from X-ray data whether C or N is the donor atom in monodentate complexes, but in those cases where the matter has been established by neutron diffraction C is always found to be the donor atom (as with CO). Very frequently CN$^-$ acts as a bridging ligand -CN- as in AgCN, and AuCN (both of which are infinite linear chain polymers), and in Prussian-blue type compounds (p. 1094). The same tendency for a coordinated M–CN group to form a further donor–acceptor bond using the lone-pair of electrons on the N atom is illustrated by the mononuclear BF$_3$ complexes with tetracyanonickelates and hexacyanoferrates, e.g. $K_2[Ni(CN.BF_3)_4]$ and $K_4[Fe(CN.BF_3)_6]$.

The complex CuCN.NH$_3$ provides an unusual example of CN acting as a bridging ligand at C, a mode which is common in μ-CO complexes (p. 928); indeed, the complex is unique in featuring tridentate CN groups which link the metal atoms into plane nets via the grouping  $\begin{matrix}Cu\\ \vdots\\ Cu\end{matrix}\!>\!C{-}N{-}Cu$ as shown in Fig. 8.24. Other cyanide complexes are discussed under the appropriate metals. In organic chemistry, both nitriles R–CN and isonitriles (isocyanides) R–NC are known. Isocyanides have been extensively studied as ligands (p. 926).$^{(143)}$ More

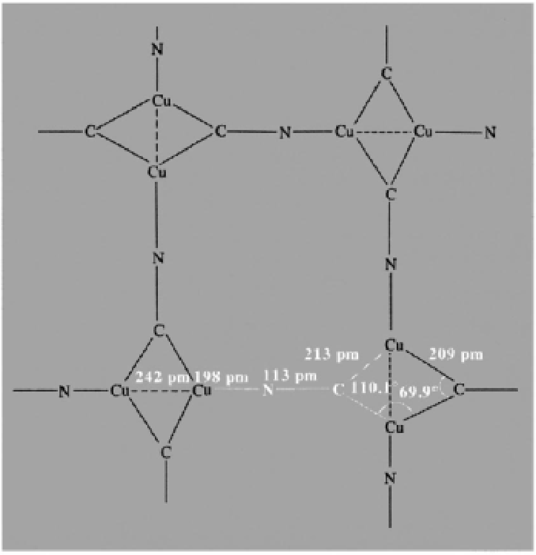


Figure 8.24 Schematic diagram of the layer structure of CuCN.NH$_3$ showing the tridentate CN groups; each Cu is also bonded to 1 NH$_3$ molecule at 207 pm. Note also the unusual 5-coordination of Cu including one near neighbour Cu at 242 pm (13 pm closer than Cu–Cu in the metal). The lines in the diagram delineate the geometry and do not represent pairs of electrons.

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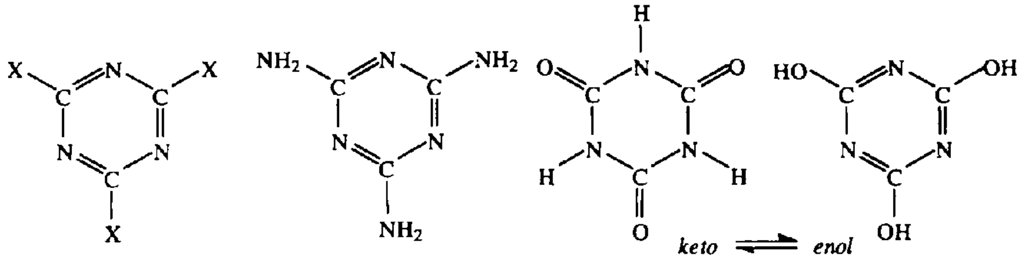
[142] A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, London, 1976, 302 pp.

[143] L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, London, 1969, 199 pp.



Cyanuric halides Cyanuric amide (melamine) Cyanuric acid

Figure 8.25 The planar structure of various cyanuric compounds: all 6 C–N distances within the ring are equal.

complex coordination modes are now also well documented for CN$^-$, RCN and RNC.[144]

Cyanogen halides, X–CN, are colourless, volatile, reactive compounds which can be regarded as pseudohalogen analogues of the interhalogen compounds, XY (p. 824) (Table 8.8). All tend to trimerize to give cyclic cyanuric halides (Fig. 8.25) especially in the presence of free HX. FCN is prepared by pyrolysis of $(FCN)_3$ which in turn is made by fluorinating $(ClCN)_3$ with NaF in tetramethylene sulfone. ClCN and BrCN are prepared by direct reaction of X_2 on MCN in water or CCl_4, and ICN is prepared by a dry route from $Hg(CN)_2$ and I_2. Similarly, colourless crystals of cyanamide (H_2NCN mp 46°) result from the reaction of NH_3 on ClCN and trimerize to melamine at 150° (Fig. 8.25). The industrial preparation is by acidifying CaNCN (see Panel). The "dimer", dicyandiamide, $CNC(NH_2)_2$, can be made by boiling calcium cyanamide with water: the colourless crystals are composed of nonlinear molecules which feature three different C–N distances (see Table 8.7).

The hydroxyl derivative of X–CN is cyanic acid HO–CN: it cannot be prepared pure due to rapid decomposition but it is probably present to the extent of about 3% when its tautomer, isocyanic acid (HNCO) is prepared from sodium cyanate and HCl. HNCO rapidly trimerizes to cyanuric acid (Fig. 8.25) from which it can be regenerated by pyrolysis. It is a fairly strong acid (K_a 1.2×10^{-4} at 0°) freezing at −86.8° and boiling at 23.5°C. Thermolysis of urea is an alternative route to HNCO and $(HNCO)_3$; the reverse reaction, involving the isomerization of ammonium cyanate, is the classic synthesis of urea by F. Wöhler (1828):[145]

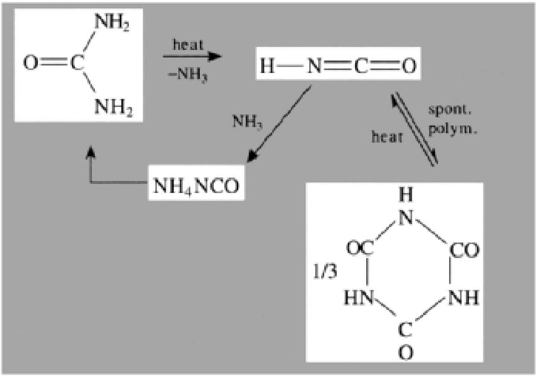


Table 8.8 Cyanogen halides

Property	FCN	ClCN	BrCN	ICN
MP/°C	−82	−6.9	51.3	146
BP/°C	−46	13.0	61.3	146 (subl)

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[144] Some typical examples will be found in the following references. M. A. ANDREWS, C. B. KNOBLER and H. D. KAESZ, *J. Am. Chem. Soc.* **101**, 7260–4 (1979). M. I. BRUCE, T. W. HAMBLEY and B. K. NICHOLSON, *J. Chem. Soc., Chem. Commun.*, 353–5 (1982). V. CHEBOLU, R. R. WHITTLE and A. SEN, *Inorg. Chem.* **24**, 3082–5 (1985). T. C. WRIGHT, G. WILKINSON, M. MOTEVALLI and M. B. HURSTHOUSE, *J. Chem. Soc., Dalton Trans.*, 2017–9 (1986). K. S. RATLIFF, P. E. FANWICK and C. P. KUBIAK, *Polyhedron* **9**, 1487–9 (1990).

[145] J. SHORTER, *Chem. Soc. Revs.* **7**, 1–14 (1978).

The Cyanamide Industry(141)

The basic chemical of the cyanamide industry is calcium cyanamide CaNCN, mp 1340°, obtained by nitrogenation of CaC_2.

$$CaC_2 + N_2 \xrightarrow{1000^\circ} CaNCN + C$$

CaNCN is used as a direct application fertilizer, weed killer, and cotton defoliant; it is also used for producing cyanamide, dicyandiamide and melamine plastics. Production formerly exceeded 1.3 million tonnes pa, but this has fallen considerably in the last few years, particularly in the USA where the use of CaNCN as a nitrogenous fertilizer has been replaced by other materials. In 1990 most of the world's supply was made in Japan, Germany and Canada.

Acidification of CaNCN yields free cyanamide, H_2NCN, which reacts further to give differing products depending on pH: at pH ≤ 2 or >12 urea is formed, but at pH 7–9 dimerization to dicyandiamide $NCNC(NH_2)_2$ occurs. Solutions are most stable at pH ~ 5; accordingly commercial preparation of H_2NCN is by continuous carbonation of an aqueous slurry of CaNCN in the presence of graphite: the overall reaction can be represented

$$CaNCN + CO_2 + H_2O \longrightarrow H_2NCN + CaCO_3$$

Reaction of H_2NCN with H_2S gives thiourea, $SC(NH_2)_2$.

Dicyandiamide forms white, non-hygroscopic crystals which melt with decomposition at 209°. Its most important reaction is conversion to melamine (Fig. 8.25) by pyrolysis above the mp under a pressure of NH_3 to counteract the tendency to deammonation. Melamine is mainly used for melamine-formaldehyde plastics. Total annual production of both H_2NCN and $NCNC(NH_2)_2$ is on the 30 000 tonne scale.

Several of these compounds and their derivatives are commercially and industrially important. Urea has already been mentioned on p. 311. Again, world production of chloroisocyanurates, $(ClNC{=}O)_3$, in 1987 was ca. 80 000 tonnes (50 000 tonnes in USA alone, of which 75% went for swimming pool disinfection and most of the rest for scouring powders, household bleaches and dishwashing powder formulations).(141)

Alkali metal cyanates are stable and readily obtained by mild oxidation of aqueous cyanide solutions using oxides of Pb^{II} or Pb^{IV}. The commercial preparation of NaNCO is by reaction of urea with Na_2CO_3.

$$Na_2CO_3 + 2OC(NH_2)_2 \xrightarrow[\text{(dry)}]{\text{heat}} 2NaNCO + CO_2 + 2NH_3 + H_2O$$

The pseudohalogen concept (p. 319) might lead one to expect the existence of a cyanate analogue of cyanogen but there is little evidence for NCO–OCN, consistent with the known reluctance of oxygen to catenate. By contrast, thiocyanogen $(SCN)_2$ is moderately stable; it can be prepared as white crystals by suspending AgSCN in Et_2O or SO_2 and oxidizing the anion at low temperatures with Br_2 or I_2. $(SCN)_2$ melts at $\sim -7^\circ$ to an unstable orange suspension which rapidly polymerizes to the brick-red solid parathiocyanogen $(SCN)_x$.(146) This ready polymerization hampers structural studies but it is probable that the molecular structure is $N{\equiv}C{-}S{-}S{-}C{\equiv}N$ with a nonlinear central C–S–S–C group. $(SeCN)_2$ can be prepared similarly as a yellow powder which polymerizes to a red solid.

Thiocyanates and selenocyanates can be made by fusing the corresponding cyanide with S or Se. The SCN^- and $SeCN^-$ ions are both linear, like OCN^-. (See p. 779 for $TeCN^-$) Treatment of KSCN with dry $KHSO_4$ produces free isothiocyanic acid HNCS, a white crystalline solid which is stable below 0° but which decomposes rapidly at room temperatures to HCN and a yellow solid $H_2C_2N_2S_3$. Thiocyanic acid, HSCN, (like HOCN) has not been prepared

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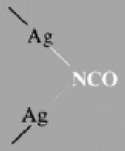
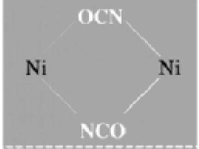
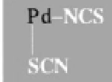
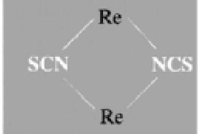
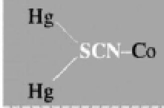
[146] F. Cataldo, *Polyhedron* **11**, 79–83 (1992).

Table 8.9 Modes of bonding established by X-ray crystallography

Mode	Example	Comment
Ag–NCO	$[AsPh_4][Ag(NCO)_2]$	Linear anion
Mo–OCN	$[Mo(OCN)_6]^{3-}$, $[Rh(OCN)(PPh_3)_3]$	Based on infrared data only
	AgNCO	Cf. fulminate in Table 8.7
	$[Ni_2(NCO)_2\{N(CH_2CH_2NH_2)_3\}_2][BPh_4]_2$	Note bent Ni–N–C
Co–NCS	$[Co(NH_3)_5(NCS)]Cl_2$	Linkage isomerism
Co–SCN	$[Co(NH_3)_5(SCN)]Cl_2$	
	$[Pd(NCS)(SCN)\{Ph_2P(CH_2)_3PPh_2\}]$	Both *N* and *S* monodentate in a single crystal
	$K_2[Pd(SCN)_4]$	Weak *S* bridging to a second Pd
	$[NBu^n_4]_3[Re_2(NCS)_{10}]$	*N*-bonded bridging (and terminal)(154)
Co–NCS–Hg	$[Co(NCS)_4Hg]$	Bidentate, different metals
	$[Pt_2(Cl)_2(PPr_3)_2(SCN)_2]$	Bidentate, same metal
	Ph_2SbSCN	Spiral chain polymer(149)
	$[Co(NCS)_6Hg_2]\cdot C_6H_6$	Tridentate
Ni–NCSe	$[Ni(HCONMe_2)_4(NCSe)_2]$	*N* donor
Co–SeCN	$K[Co(Me_2glyoxime)_2(SeCN)_2]$	*Se* donor

pure but compounds such as MeSCN and $Se(SCN)_2$ are known.

The thiocyanate ion has been much studied as an ambidentate ligand (in which either S or N is the donor atom); it can also act as a bidentate bridging ligand –SCN–, and even as a tridentate ligand >SCN–.(147,148,149) The ligands OCN^- and $SeCN^-$ have been less studied but appear to be generally similar. A preliminary indication of the mode of coordination can sometimes be obtained from vibrational spectroscopy since *N* coordination raises both ν(CN) and ν(CS) relative to the values of the uncoordinated ion, whereas *S* coordination leaves ν(CN) unchanged and increases ν(CS) only somewhat. The bridging mode tends to increase both ν(CN) and ν(CS). Similar trends are noted for OCN^- and $SeCN^-$ complexes. However, these "group vibrations" are in reality appreciably mixed with other modes both in the ligand itself and in the complex as a whole, and vibrational spectroscopy is therefore not always a reliable criterion. Increasing use is being made of ^{14}N and ^{13}C nmr data(150) but the most reliable data, at least for crystalline complexes, come from X-ray diffraction studies.(151) The variety of coordination modes so revealed is illustrated in Table 8.9, which is based on one by A. H. Norbury.(147) Phenomenologically it is observed that class a metals tend to be *N*-bonded whereas class b tend to be *S*-bonded (see below), though it should be stressed that kinetic and solubility factors as well as relative thermodynamic stability are sometimes implicated, and so-called 'linkage isomerism" is well established, e.g. $[Co(NH_3)_5(NCS)]Cl_2$ and $[Co(NH_3)_5(SCN)]Cl_2$. In terms of the a and b (or "hard" and "soft") classification of ligands and acceptors it is noted that metals in Groups 3–8 together with the lanthanoids and actinoids tend to form –NCS complexes; in the later transition groups Co, Ni, Cu and Zn also tend to form –NCS complexes whereas their heavier congeners Rh, Ir; Pd, Pt; Au; and Hg are predominantly *S*-bonded. Ag and Cd are intermediate and readily form both types of complex. See also refs. 152, 153. The interpretation to be placed on these observations is less certain. Steric influences have been mentioned (*N* bonding, which is usually linear, requires less space than the bent M–S–CN mode). Electronic factors also play a role, though the detailed nature of the bonding is still a matter of debate and devotees of the various types of electronic influence have numerous interpretations to select from. Solvent effects (dielectric constant ε, coordinating power, etc.) have also been invoked and it is clear that these various explanations are not mutually exclusive but simply tend to emphasize differing aspects of an extremely complicated and delicately balanced situation. The interrelation of these various interpretations is summarized in Table 8.10.

Table 8.10 Mode of bonding in thiocyanate complexes

Metal type[a]	σ-Donor ligand	High-ε solvent	Low-ε solvent	π-Acceptor ligand
Class a	–NCS	–NCS	–SCN	–SCN
Class b	–SCN	–SCN	–NCS	–NCS

[a] Sometimes discussed in terms of "hard" and "soft" acids and bases.

Fewer data are available for $SeCN^-$ complexes but similar generalizations seem to hold. By contrast, OCN^- complexes are not so readily discussed in these terms: in fact, very few cyanato

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[147] A. H. NORBURY, *Adv. Inorg. Chem. Radiochem.* **17**, 231–402 (1975) (825 refs.).

[148] A. A. NEWMAN (ed.), *Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives*, Academic Press, London, 1975, 351 pp.

[149] G. E. FORSTER, I. G. SOUTHERINGTON, M. J. BEGLEY and D. B. SOWERBY, *J. Chem. Soc., Chem. Commun.*, 54–5 (1991).

[150] J. A. KARGOL, R. W. CRECELY and J. L. BURMEISTER, *Inorg. Chim. Acta* **25**, L109–L110 (1977), and references therein.

[151] S. J. ANDERSON, D. S. BROWN and K. J. FINNEY, *J. Chem. Soc., Dalton Trans.*, 152–4 (1979). (The compounds, originally thought to be *O*-bonded on the basis of infrared and ^{14}N nmr spectroscopy, now shown by X-ray analysis to be *N*-bonded.) See also ref. 154.

[152] W. KELM and W. PREETZ, *Z. anorg. allg. Chem.* **568**, 106–16 (1989).

[153] M. KAKOTI, S. CHAUDHURY, A. K. DEB and S. GOSWAMI, *Polyhedron* **12**, 783–9 (1993).

(–OCN) complexes have been characterized and the ligand is usually *N*-bonded (isocyanato).(151)

8.9 Organometallic Compounds

Compounds which contain direct M–C bonds comprise a vast field which spans the traditional branches of inorganic and organic chemistry. A general overview is given in Section 19.7 (p. 924) and specific aspects are treated separately under the chemistry of each individual element, e.g. alkali metals (pp. 102–6), alkaline earth metals (pp. 127–38), Group 13 metals (pp. 257–67) etc. In addition to the references cited on p. 924, useful general accounts can be found in refs. 155–160.

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[154] F. A. Cotton, A. Davison, W. H. Isley and H. S. Trop, *Inorg. Chem.* **18**, 2719–23 (1979).

[155] A. W. Parkins and R. C. Poller, *An Introduction to Organometallic Chemistry*, Macmillan, Basingstoke, 1986, 252 pp.

[156] J. S. Thayer, *Organometallic Chemistry: An Overview*, VCH Publishers (UK), 1988, 250 pp.

[157] R. H. Crabtree *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 1988, 440 pp.

[158] Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH Publishers (NY), 1989, 479 pp.

[159] T. J. Marks (ed.) *Bonding Energetics in Organometallic Compounds*, ACS Symposium Series No. 428, Washington DC, 1990, 320 pp.

[160] E. W. Abel, F. G. A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry II:* A review of the literature 1982–1994 in 14 volumes, Pergamon, Oxford, 1995, approx 8750 pp.