

reviewed<sup>(33)</sup> and many of these have been used for mechanistic studies, e.g. the reactions of the specifically labelled thiosulfate ions  $^{35}\text{SSO}_3^{2-}$  and  $\text{S}^{35}\text{SO}_3^{2-}$ . Another ingenious application, which won Barbara B. Askins the US Inventor of the Year award for 1978, is the use of  $^{35}\text{S}$  for intensifying under-exposed photographic images: prints or films are immersed in dilute aqueous alkaline solutions of  $^{35}\text{S}$ -thiourea, which complexes all the silver in the image (including invisibly small amounts), and the alkaline medium converts this to immobile, insoluble  $\text{Ag}^{35}\text{S}$ ; the film so treated is then overlaid with unexposed film which reproduces the image with heightened intensity as a result of exposure to the  $\beta^-$  activity.

The isotope  $^{33}\text{S}$  has a nuclear spin quantum number  $I = \frac{3}{2}$  and so is potentially useful in nmr experiments (receptivity to nmr detection  $17 \times 10^{-6}$  that of the proton). The resonance was first observed in 1951 but the low natural abundance of  $^{33}\text{S}$  (0.75%) and the quadrupolar broadening of many of the signals has so far restricted the amount of chemically significant work appearing on this resonance.<sup>(34)</sup> However, more results are expected now that pulsed fourier-transform techniques have become generally available.

The S atom in the ground state has the electronic configuration  $[\text{Ne}]3s^23p^4$  with 2 unpaired p electrons ( $^3P_1$ ). Other atomic properties are: ionization energy  $999.30 \text{ kJ mol}^{-1}$ , electron affinities  $+200$  and  $-414 \text{ kJ mol}^{-1}$  for the addition of the first and second electrons respectively, electronegativity (Pauling) 2.5, covalent radius 103 pm and ionic radius of  $\text{S}^{2-}$  184 pm. These properties can be compared with those of the other elements in Group 16 on p. 754.

<sup>33</sup> R. H. HERBER, Sulfur-35, in R. H. HERBER (ed.), *Inorganic Isotopic Syntheses*, pp. 193–214, Benjamin, New York, 1962.

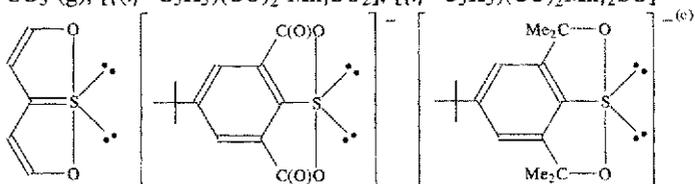
<sup>34</sup> C. RODGER, N. SHEPPARD, C. MCFARLANE and W. MCFARLANE, in R. H. HARRIS and B. E. MANN (eds.), *NMR and the Periodic Table*, pp. 401–2, Academic Press, London, 1978. H. C. E. MCFARLANE and W. MCFARLANE, in J. MASON (ed.) *Multinuclear NMR*, Plenum Press, New York, 1987, pp. 417–35.

### 15.1.6 Chemical reactivity

Sulfur is a very reactive element especially at slightly elevated temperatures (which presumably facilitates cleavage of S–S bonds). It unites directly with all elements except the noble gases, nitrogen, tellurium, iodine, iridium, platinum and gold, though even here compounds containing S bonded directly to N, Te, I, Ir, Pt and Au are known. Sulfur reacts slowly with  $\text{H}_2$  at  $120^\circ$ , more rapidly above  $200^\circ$ , and is in reversible thermodynamic equilibrium with  $\text{H}_2$  and  $\text{H}_2\text{S}$  at higher temperatures. It ignites in  $\text{F}_2$  and burns with a livid flame to give  $\text{SF}_6$ ; reaction with chlorine is more sedate at room temperature but rapidly accelerates above this to give (initially)  $\text{S}_2\text{Cl}_2$  (p. 689). Sulfur dissolves in liquid  $\text{Br}_2$  to form  $\text{S}_2\text{Br}_2$ , which readily dissociates into its elements; iodine has been used as a cryoscopic solvent for sulfur (p. 654) and no binary compound is formed (directly) even at elevated temperature (see, however, p. 691). Oxidation of sulfur by (moist?) air is very slow at room temperature though traces of  $\text{SO}_2$  are formed; the ignition temperature of S in air is  $250\text{--}260^\circ$ . Pure dry  $\text{O}_2$  does not react at room temperature though  $\text{O}_3$  does. Likewise direct reaction with  $\text{N}_2$  has not been observed but, in a discharge tube, activated N reacts. All other non-metals (B, C, Si, Ge; P, As, Sb; Se) react at elevated temperatures. Of the metals, sulfur reacts in the cold with all the main group representatives of Groups 1, 2, 13, Sn, Pb and Bi, and also Cu, Ag and Hg (which even tarnishes at liquid-air temperatures). The transition metals (except Ir, Pt and Au) and the lanthanides and actinides react more or less vigorously on being heated with sulfur to form binary metal sulfides (p. 676).

The reactivity of sulfur clearly depends sensitively on the molecular complexity of the reacting species. Little systematic work has been done. *Cyclo-S*<sub>8</sub> is obviously less reactive than the diradical *catena-S*<sub>8</sub>, and smaller oligomers in the liquid or vapour phase also complicate the picture. In the limit atomic sulfur, which can readily be generated photolytically, is an extremely reactive species. As with atomic oxygen and the various

Table 15.8 Coordination geometries of sulfur

CN	Examples
1	S <sub>2</sub> (g), CS <sub>2</sub> , HNCS, K[SCN] and "covalent" isothiocyanates, P <sub>4</sub> O <sub>6</sub> S <sub>4</sub> , P <sub>4</sub> S <sub>n</sub> (terminal S), SSF <sub>2</sub> , SSO <sub>3</sub> <sup>2-</sup> , Na <sub>3</sub> SbS <sub>4</sub> ·9H <sub>2</sub> O, Tl <sub>3</sub> VS <sub>4</sub> , M <sub>2</sub> MoS <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> WS <sub>4</sub> , S=WCl <sub>4</sub>
2 (linear)	[(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> Cr≡S≡Cr(CO) <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )] <sup>(a)</sup>
2 (bent)	S <sub>n</sub> , H <sub>2</sub> S, H <sub>2</sub> S <sub>n</sub> , Me <sub>2</sub> S <sub>n</sub> , S <sub>n</sub> X <sub>2</sub> (Cl, Br), SO <sub>2</sub> , P <sub>4</sub> S <sub>n</sub> (bridging S), Se(SCN) <sub>2</sub> and "covalent" thiocyanates
3 (planar, D <sub>3h</sub> )	SO <sub>3</sub> (g), [(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> Mn]SO <sub>2</sub> , [(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> Mn] <sub>2</sub> SO] <sup>(b)</sup>
3 (T-shaped planar)	
3 (pyramidal)	SSF <sub>2</sub> , OSOCl <sub>2</sub> , S <sub>8</sub> O(1 S), SO <sub>3</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>5</sub> <sup>2-</sup> (1 S), Me <sub>3</sub> S <sup>+</sup> , SF <sub>3</sub> <sup>+</sup>
4 (tetrahedral)	SO <sub>3</sub> (s) [i.e. cyclic S <sub>3</sub> O <sub>9</sub> or fibrous (SO <sub>3</sub> ) <sub>∞</sub> ], SO <sub>2</sub> Cl <sub>2</sub> , SO <sub>4</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> (O <sub>3</sub> SSO <sub>3</sub> <sup>2-</sup> ), S <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (O <sub>3</sub> SOSO <sub>3</sub> <sup>2-</sup> ), S <sub>3</sub> O <sub>10</sub> <sup>2-</sup> , S <sub>5</sub> O <sub>16</sub> <sup>2-</sup> , ZnS (blende, and M = Be, Cd, Hg), ZnS(wurtzite, and M = Cd, Mn)
4 (seesaw) (ψ-tpb)	SF <sub>4</sub>
4 (pyramidal)	[(μ <sub>4</sub> -S)(OsL <sub>n</sub> ) <sub>4</sub> ] pyramidal clusters, <sup>(d)</sup> [(μ <sub>4</sub> -S) <sub>2</sub> Ru <sub>8</sub> L <sub>n</sub> ] bioctahedral cluster <sup>(e)</sup> , [(μ <sub>4</sub> -S) <sub>2</sub> Nb <sub>4</sub> (SPh) <sub>12</sub> ] <sup>4-</sup> octahedral {S <sub>2</sub> Nb <sub>4</sub> } cluster <sup>(f)</sup>
5 (square pyramidal) (ψ-octahedral)	SF <sub>5</sub> <sup>-</sup> , SOF <sub>4</sub> , NiS (millerite structure)
6 (octahedral)	SF <sub>6</sub> , S <sub>2</sub> F <sub>10</sub> , MS(NaCl-type, M = Mg, Ca, Sr, Ba, Mn, Pb, Ln, Th, U, Pu)
6 (trigonal prismatic)	MS(NiAs-type), (M = Ti, V, Fe, Co, Ni), Hf <sub>2</sub> S
7 (mono-capped trigonal prismatic)	Ta <sub>6</sub> S, <sup>(g)</sup> Ti <sub>2</sub> S <sup>(h)</sup>
8 (cubic)	M <sub>2</sub> S (antifluorite-type, M = Li, Na, K, Rb)
9 (mono-capped square antiprismatic)	[Rh <sub>17</sub> (CO) <sub>32</sub> (S) <sub>2</sub> ] <sup>3-</sup> (encapsulated S) <sup>(i)</sup>
10 (bicapped square antiprismatic)	[Rh <sub>10</sub> (CO) <sub>10</sub> (μ-CO) <sub>12</sub> S] <sup>2-</sup> (encapsulated S) <sup>(j)</sup>

(a)Ref. 35. (b)Ref. 36. (c)Ref. 37. (d)Ref. 38. (e)Ref. 39. (f)Ref. 40. (g)Ref. 41. (h)Ref. 42. (i)Ref. 43. (j)Ref. 44.

<sup>35</sup>T. J. GREENHOUGH, B. W. S. KOLTHAMMER, P. LEGZDINS and J. TROTTER, *Inorg. Chem.* **18**, 3543–8 (1979). See also L. Y. GOH and T. C. W. MAK, *J. Chem. Soc., Chem. Commun.*, 1474–5 (1986).

<sup>36</sup>I. P. LORENZ, J. MESSELHÄUSER, W. HILLER and K. HAUG, *Angew. Chem. Int. Edn. Engl.* **24**, 228–9 (1985).

<sup>37</sup>P. H. W. LAU and J. C. MARTIN, *J. Am. Chem. Soc.* **100**, 7077–9 (1978).

<sup>38</sup>R. D. ADAMS, *Polyhedron* **4**, 2003–25 (1985).

<sup>39</sup>R. D. ADAMS, J. E. BABIN and M. TASI, *Inorg. Chem.* **25**, 4460–1 (1986).

<sup>40</sup>J. L. SEELA, J. C. HUFFMAN and G. CHRISTOU, *J. Chem. Soc., Chem. Commun.*, 1258–60 (1987).

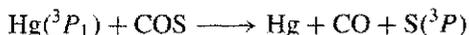
<sup>41</sup>H. F. FRANZEN and J. G. SMEGGL, *Acta Cryst.* **B26**, 125–9 (1970).

<sup>42</sup>J. P. OWENS, B. R. CONARD and H. F. FRANZEN, *Acta Cryst.* **23**, 77–82 (1967).

<sup>43</sup>J. L. VIDAL, R. A. FIATO, L. A. CROSBY and R. L. PRUEY, *Inorg. Chem.* **17**, 2574–82 (1978).

<sup>44</sup>G. CIANI, L. GARLASCHELLI, A. SIRONI and S. MARTINENGO, *J. Chem. Soc., Chem. Commun.*, 563–5 (1981).

methylenes, both singlet and triplet states are possible and these have different reactivities. The ground state is  $^3P_2$ , and the singlet state  $^1D_2$  lies  $110.52 \text{ kJ mol}^{-1}$  above this. Triplet state S atoms (with 2 unpaired electrons) can be generated by the Hg-photosensitized irradiation of COS:



Triplet S can also be generated by direct photolysis of  $\text{CS}_2$  ( $h\nu < 210 \text{ nm}$ ) or ethylene episulfide  $\overline{\text{CH}_2\text{CH}_2\text{S}}$  ( $h\nu 220\text{--}260 \text{ nm}$ ). Photolysis of  $\text{SPF}_3$  ( $h\nu 210\text{--}230 \text{ pm}$ ) generates singlet state S atoms (with no unpaired electrons) but the best syntheses of these is the direct primary photolysis of COS in the absence of Hg; this generates mainly singlet S (75%) with the rest being in the triplet state ( $^3P$ ):



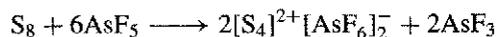
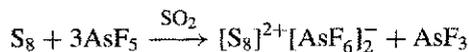
Generation of (excited state) singlet S in the presence of paraffins yields the corresponding mercaptan by a concerted single-step insertion:  $\text{RH} + \text{S}(^1D_2) \longrightarrow \text{RSH}$ . By contrast, paraffins are inert to triplet (ground state) S atoms. Singlet S undergoes analogous insertion reactions with  $\text{MeSiH}_3$ ,  $\text{SiMe}_4$  and  $\text{B}_2\text{H}_6$ . Olefins can undergo insertion of singlet S atoms on stereospecific addition of triplet S atoms; according to experimental conditions, the products are alkenyl mercaptans, vinylic mercaptans or episulfides. Analogous reactions with inorganic compounds appear to be a very promising field for future research. Generation of the reactive diatomic species  $\text{S}_2$  for synthetic purposes is also currently an active field.<sup>(45,46)</sup>

Sulfur compounds exhibit a rich and multifarious variety which derives not only from the numerous possible oxidation states of the element (from  $-2$  to  $+6$ ) but also from the range of bond types utilized (covalent, coordinate,

ionic and even metallic) and the multiplicity of coordination geometries adopted by the element. Oxidation states and their interrelationships as codified by oxidation state diagrams are dealt with more fully in the section on oxoacids of sulfur (p. 706) though the existence of several other series of compounds, notably the halides, also illustrates the element's versatility. The range of bond types, as reflected in the physical and chemical properties of the various compounds of the element, will become increasingly apparent throughout the rest of the chapter. The multiplicity of coordination geometries is amply demonstrated by the examples in Table 15.8. Most of these can be readily rationalized by the numerous variants of elementary bonding theory. See ref. 47 for a VSEPR treatment.

### Polyatomic sulfur cations

As long ago as 1804 C. F. Bucholz observed that sulfur dissolves in oleum to give clear, brightly coloured solutions which could be yellow, deep blue or red (or intermediate colours) depending on the strength of the oleum and the time of the reaction. These solutions are now known to contain  $\text{S}_n^{2+}$  cations, the structure of which has been elucidated during the past two decades mainly by elegant synthetic, Raman spectroscopic and crystallographic studies.<sup>(48–50)</sup> Selenium and tellurium behave similarly (p. 759). Sulfur can most conveniently be quantitatively oxidized using  $\text{SbF}_5$  or  $\text{AsF}_5$  in an inert solvent such as  $\text{SO}_2$ , e.g.:



<sup>47</sup> I. HARGITTAI, *The Structure of Volatile Sulfur Compounds*, D. Reidel Publ. Co., (Kluwer Academic Publ.), Dordrecht, 1985. 301 pp.

<sup>48</sup> R. J. GILLESPIE, *Chem. Soc. Rev.* **8**, 315–52 (1979).

<sup>49</sup> T. A. O'DONNELL, *Chem. Soc. Rev.* **16**, 1–43 (1987).

<sup>50</sup> N. BURFORD, J. PASSMORE and J. C. P. SANDERS, Chap. 2 in J. F. LIEBMAN and A. GREENBERG (eds.), *From Atoms to Polymers: Isoelectronic Analogies*, 1989, pp. 53–108.

<sup>45</sup> M. SCHMIDT and U. GÖRL, *Angew. Chem. Int. Edn. Engl.* **26** 887–8 (1987).

<sup>46</sup> T. L. GILCHRIST and J. E. WOOD, *J. Chem. Soc., Chem. Commun.*, 1460–1 (1992).

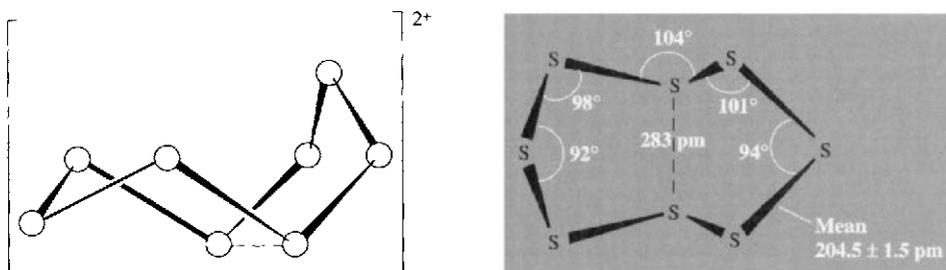


Figure 15.10 The structure and dimensions of the  $S_8^{2+}$  cation in  $[S_8]^{2+}[AsF_6]_2$ .

The bright-yellow solutions contain  $S_4^{2+}$ , a square-planar ring whose structure has been confirmed by an X-ray study on the unusual crystalline compound  $As_6F_{36}I_4S_{32}$ , i.e.  $[S_4]^{2+}[S_7I]_4[AsF_6]_6$  (p. 692). The S-S interatomic distance is 198 pm compared with 204 pm for a single-bonded species. Note also that  $S_4^{2+}$  is isoelectronic with the known heterocyclic compound  $S_2N_2$  (p. 725). The pale-yellow compound  $[S_4]^{2+}[SbF_6]_2$  has also been isolated.

The deep-blue solutions contain  $S_8^{2+}$ , and the X-ray structure of  $[S_8]^{2+}[AsF_6]_2$  reveals that the cation has an *exo-endo* cyclic structure with a long transannular bond as shown in Fig. 15.10 (see also p. 724). The bright-red solutions were originally thought to contain the  $S_{16}^{2+}$  cation and a compound thought to be  $S_{16}(AsF_6)_2$  was isolated; however, crystallographic study has shown<sup>(51)</sup> that the compound has the totally unexpected formulation  $[S_{19}]^{2+}[AsF_6]_2$  which could not have been distinguished from the earlier stoichiometry on the basis of the original analytical data. This astonishing cation consists of two 7-membered rings joined by a 5-atom chain. As shown in Fig. 15.11, one of the rings has a boat conformation whilst the other is disordered, existing as a 4:1 mixture of chair and boat conformations. S-S distances vary greatly from 187 to 239 pm and S-S-S angles vary from  $91.9^\circ$  to  $127.6^\circ$ . See also p. 692 for  $[S_7X]^+$  cations.

Solutions of sulfur in oleum also give rise to paramagnetic species, probably  $S_n^+$ , but the

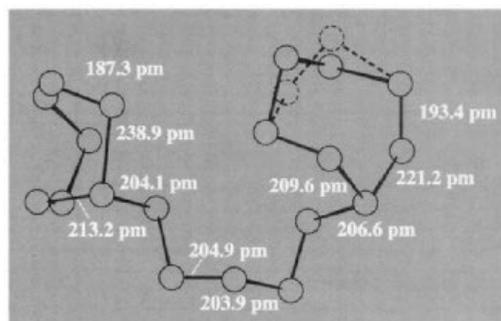


Figure 15.11 The structure and some of the dimensions of the disordered cation  $S_{19}^{2+}$  (see text).

nature of these has not yet been fully established. For polysulfur anions  $S_n^{2-}$ , see p. 681.

### Sulfur as a ligand

The S atom can act either as a terminal or a bridging ligand. The dianion  $S_2^{2-}$  is also an effective ligand, and chelating polysulfides  $-S_n-$  are well established. These various sulfur ligands will be briefly considered before dealing with the broad range of compounds in which S acts as the donor atom, e.g.  $H_2S$ ,  $R_2S$ , dithiocarbamates and related anions, 1,2-dithiolenes etc. Ligands in which S acts as a donor atom are usually classified as class-b ligands ("soft" Lewis bases), in contrast to oxygen donor-atom ligands which tend to be class-a or hard (p. 909). The larger size of the S atom and the consequent greater deformability of its electron cloud give a qualitative rationalization of this difference and the possible participation

<sup>51</sup> R. C. BURNS, R. J. GILLESPIE and J. F. SAWYER, *Inorg. Chem.* **19**, 1423-32 (1980).

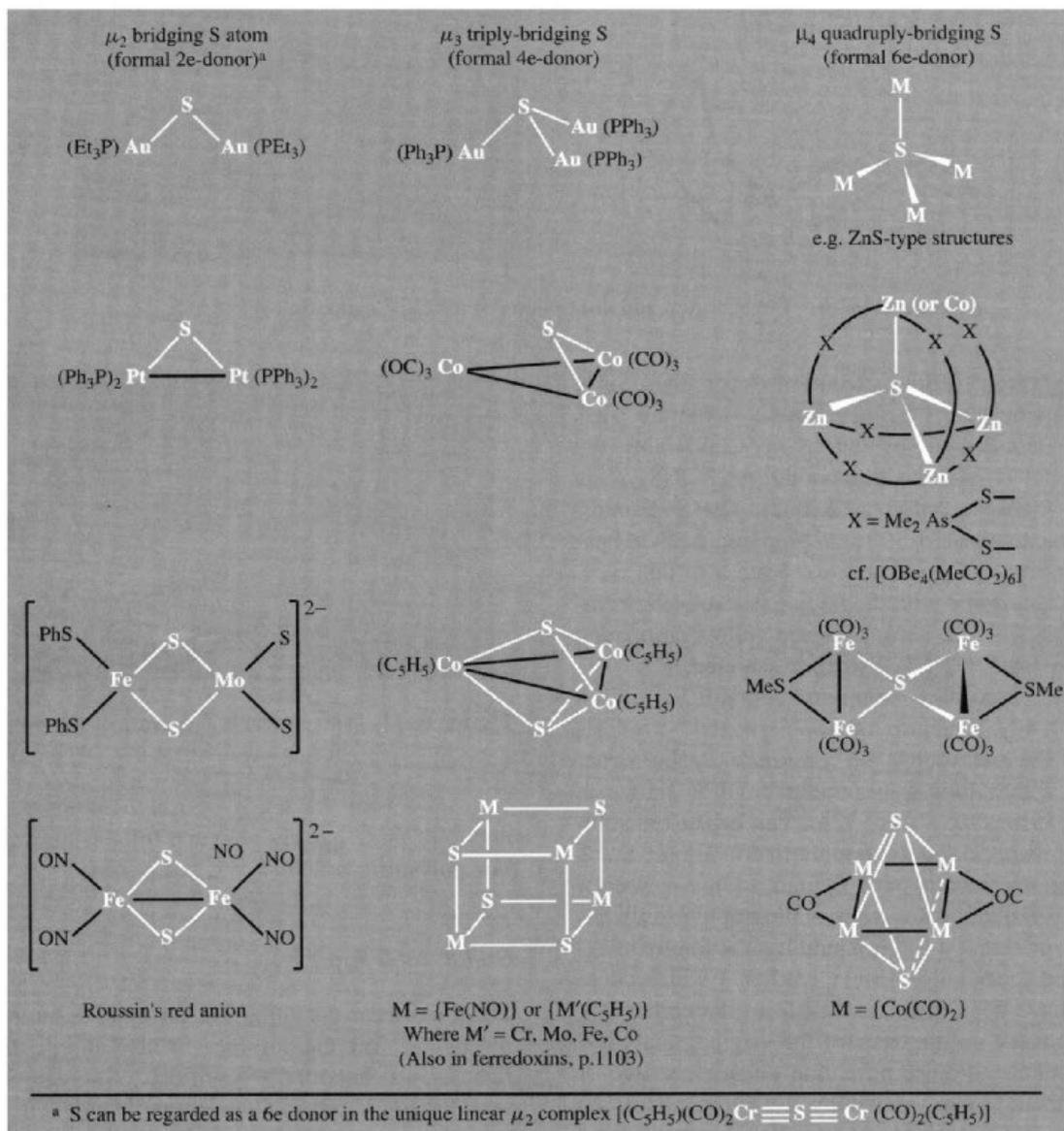


Figure 15.12 The S atom as a bridging ligand.

of  $d_{\pi}$  orbitals in bonding to sulfur has also been invoked (see comparison of N and P, p. 416).

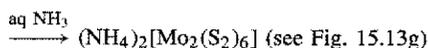
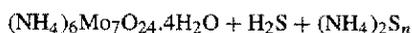
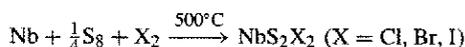
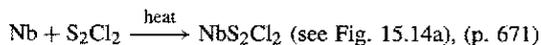
Some examples of the S atom as a bridging ligand are given in Fig. 15.12. In the  $\mu_2$  bridging mode S is usually regarded as a 2-electron donor, though in the linear bridge [(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Cr]<sub>2</sub>S] it is probably best regarded

as a 6-electron donor.<sup>(35)</sup> In the  $\mu_3$  triply bridging mode S can be regarded as a 4-electron donor, using both its unpaired electrons and one lone-pair.<sup>(52)</sup> If the 3 bridged metal atoms

<sup>52</sup> H. VAHRENKAMP, *Angew. Chem. Int. Edn. Engl.* **14**, 322-9 (1975).

are different then a chiral tetrahedrane molecule results and this has permitted the recent (1980) resolution of the enantiomers of the first optically active metal cluster compound, the red complex  $[\{\text{Co}(\text{CO})_3\}\{\text{Fe}(\text{CO})_3\}\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}\text{S}]$ .<sup>(53)</sup> The pseudo-cubane structure adopted by some of the  $\mu_3\text{-S}$  compounds is assuming added significance as a crucial structural unit in many biologically important systems, e.g. the  $\{(\text{RS})\text{FeS}\}_4$  units which cross-link the polypeptide chains in ferredoxins (p. 1103). In the  $\mu_4$ -mode 6-electrons are involved, if the bonding is considered to be predominantly covalent, though metal-sulfides are sometimes treated as compounds of  $\text{S}^{2-}$ . No molecular compounds are known in which S bridges 6 or 8 metal atoms though, again, these coordinations are prevalent in solid-state compounds, many of which have interatomic bonding which is far from being purely ionic.

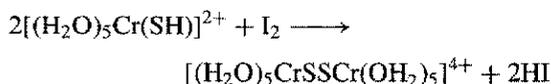
The disulfur ligand  $\text{S}_2$  (sometimes more helpfully considered as  $\text{S}_2^{2-}$ ) is attracting increasing attention since no other simple ligand is as versatile in the variety of its modes of coordination. Moreover, in one particular mode (see Type III, p. 669) it is particularly effective in stabilizing metal clusters. Many of the complexes of  $\text{S}_2$  were first obtained accidentally, and their seemingly bizarre stoichiometries only became intelligible after structural elucidation by X-ray crystallography. The complexes can be prepared by reacting metals or their compounds with: (a) a positive  $\text{S}_2$  group as in  $\text{S}_2\text{Cl}_2$ ,<sup>(54)</sup> (b) a neutral  $\text{S}_2$  group, usually derived from  $\text{S}_8$ ; (c) a negative  $\text{S}_2^{2-}$  group such as an alkaline polysulfide solution. Examples are:



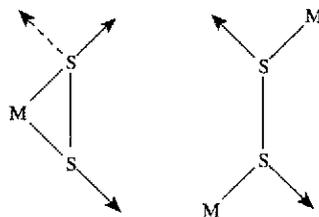
<sup>53</sup> F. RICHTER and H. VAHRENKAMP, *Angew. Chem. Int. Edn. Engl.* **19**, 65 (1980).

<sup>54</sup> M. J. ATHERTON and J. H. HOLLOWAY, *Adv. Inorg. Chem. Radiochem.* **22**, 171–98 (1979).

The S–S bond can also be formed by a direct coupling reaction, e.g.:



At least 8 modes of coordination are known (Table 15.9);<sup>(55)</sup> they are all based on either side-on  $\text{S}_2$  or bridging  $-\text{S}-\text{S}-$  with possible further ligation via one or two lone-pairs as shown schematically below:



Frequently, more than one type of coordination occurs in a given complex, e.g. Figs. 15.13b, c and g. Interestingly, there appear to be no known example of terminal “end-on” coordination,  $\text{M}-\text{S}-\text{S}$  (see dioxygen complexes, p. 615). Detailed descriptions of all the structures and their bonding are beyond the scope of this treatment but it will be noted from Table 15.9 that the S–S interatomic distances in disulfide complexes range from 201 to 209 pm. The following specific points of interest may also be mentioned. The orange-red anion  $[\text{Mo}_4(\text{NO})_4\text{S}_{13}]^{4-}$  (Fig. 15.13b) features two triangular arrays of Mo atoms joined by a common edge and with an angle of  $127.6^\circ$  between the two  $\text{Mo}_3$  planes; each plane has a  $\mu_3$ -bonded S atom above it ( $\text{Mo}-\text{S}$  250.1 pm) and there is a further unique  $\mu_4$ -bonded S atom which is 261.6 pm from each of the 4 Mo atoms. Four of the 5  $\text{S}_2^{2-}$  ligands are simultaneously bonded both end on ( $\text{Mo}-\text{S}$  246.5 pm) and side on ( $\text{Mo}-\text{S}$  249.2 pm) whilst the fifth is side-on only. The complex therefore has sulfur in five different bonding states. In the red complex  $[\text{Mn}_4(\text{CO})_{15}(\text{S}_2)_2]$  (Fig. 15.13c) the 2  $\text{S}_2^{2-}$  ligands are different (Types Ic and Id); the 4 Mn

<sup>55</sup> A. MULLER and W. JAEGERMANN, *Inorg. Chem.* **18**, 2631–3 (1979).

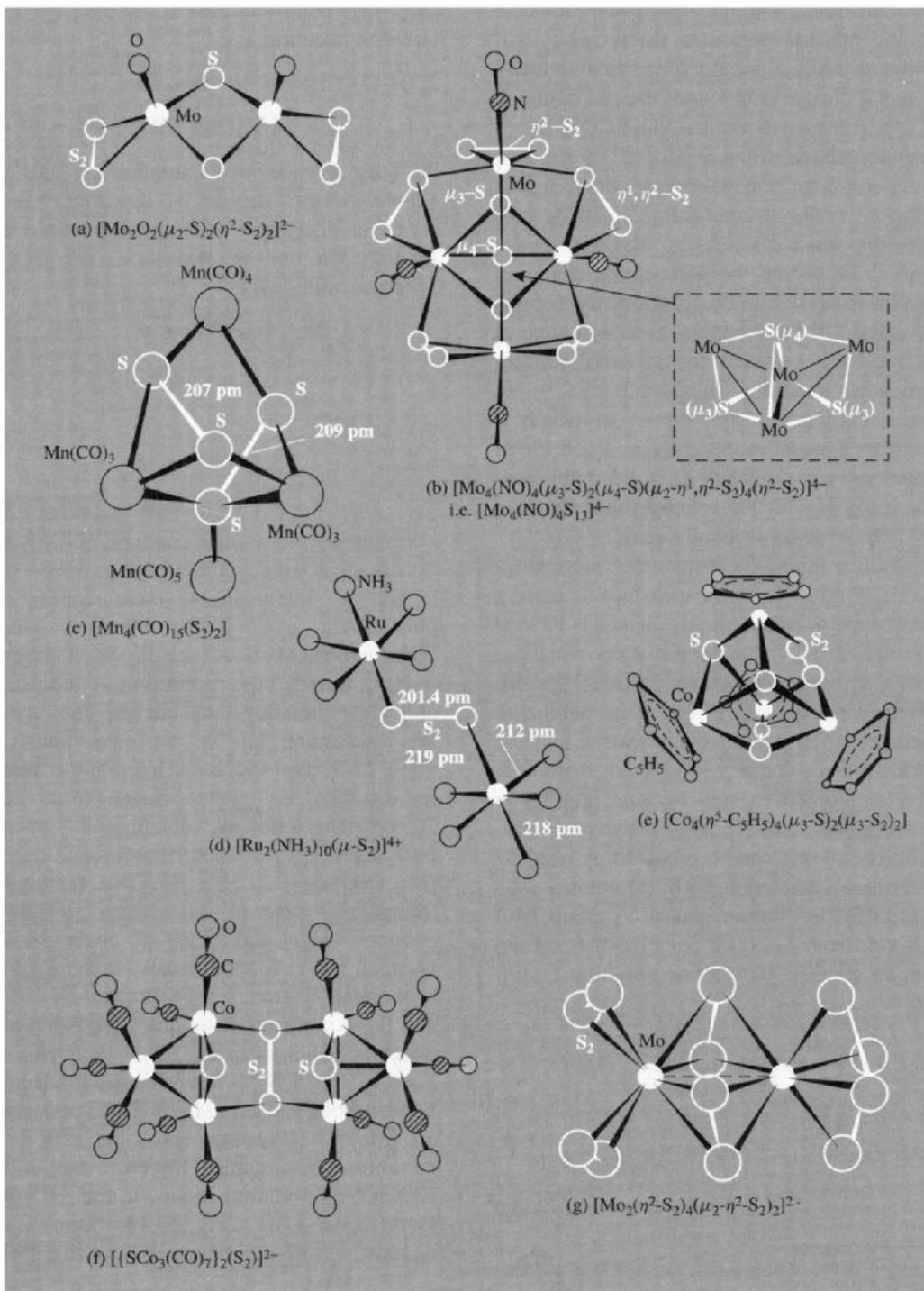
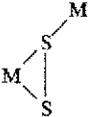
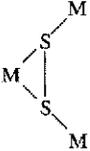
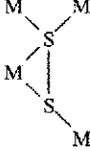
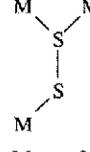
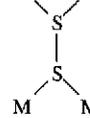
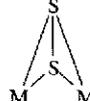


Figure 15.13 Structures of some disulfide complexes.

Table 15.9 Types of metal-disulfide complex

Type	Example	$d(S-S)/\text{pm}$	Structure
Ia 	$[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2)_2]^{2-}$	208(1)	Figure 15.13a <sup>(56)</sup>
Ib 	$\{\text{Mo}_4(\text{NO})_4\text{S}_{13}\}^{4-}$	204.8(7)	Figure 15.13b <sup>(57)</sup>
Ic 	$[\text{Mn}_4(\text{CO})_{15}(\text{S}_2)_2]$	207	Figure 15.13c <sup>(58)</sup>
Id 	$[\text{Mn}_4(\text{CO})_{15}(\text{S}_2)_2]$	209	Figure 15.13c <sup>(58)</sup>
IIa 	$[\text{Ru}_2(\text{NH}_3)_{10}\text{S}_2]^{4+}$	201.4(1)	Figure 15.13d <sup>(59)</sup>
IIb 	$[\text{Co}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-S})_2(\mu_3\text{-S}_2)_2]$	201(3)	Figure 15.13e <sup>(60)</sup>
IIc 	$[\{\text{SCo}_3(\text{CO})_7\}_2\text{S}_2]$	204.2(14)	Figure 15.13f <sup>(61)</sup>
III 	$[\text{Mo}_2(\text{S}_2)_6]^{2-}$	204.3(5)	Figure 15.13g <sup>(62)</sup>

<sup>56</sup>W. CLEGG, N. MOHAN, A. MÜLLER, A. NEUMAN, W. RITTNER and G. M. SHELDRIK, *Inorg. Chem.* **19**, 2066-9 (1980).

<sup>57</sup>A. MÜLLER, W. ELTZNER and N. MOHAN, *Angew. Chem. Int. Edn. Engl.* **18**, 168-9 (1979).

<sup>58</sup>V. KÜLLMER, E. RÖTTINGER and H. VAHRENKAMP, *J. Chem. Soc., Chem. Commun.*, 782-3 (1977).

<sup>59</sup>R. C. ELDER and M. TRKULA, *Inorg. Chem.* **16**, 1048-51 (1977).

<sup>60</sup>V. A. UCHTMAN and L. F. DAHL, *J. Am. Chem. Soc.* **91**, 3756-63 (1969).

<sup>61</sup>D. L. STEVENSON, V. R. MAGNUSON and L. F. DAHL, *J. Am. Chem. Soc.* **89**, 3727-32 (1967).

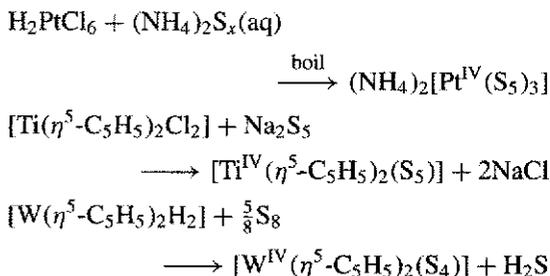
<sup>62</sup>A. MÜLLER, W.-O. NOLTE and B. KREBS, *Angew. Chem. Int. Edn. Engl.* **17**, 279 (1978); A. MÜLLER, W.-O. NOLTE and B. KREBS, *Inorg. Chem.* **19**, 2835-6 (1980).

atoms are bonded, respectively, to 3, 3, 4 and 5 carbonyl ligands, but each achieves a distorted octahedral coordination by being bonded also to 3, 3, 2 and 1 S atoms respectively. There seems no reason to suppose that the diamagnetic bridged dinuclear anion  $[(\text{NC})_5\text{Co}^{\text{III}}\text{SSCo}^{\text{III}}(\text{CN})_5]^{6-}$  is not a formal Type IIa disulfido  $\text{S}_2^{2-}$  complex, but there is evidence<sup>(59)</sup> that the superficially analogous paramagnetic dinuclear ruthenium cation in Fig. 15.13d is, in fact, a mixed-valence supersulfido  $\text{S}_2^-$  complex:  $[(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}\text{SSRu}^{\text{III}}(\text{NH}_3)_5]^{4+}$ . The bridged dinuclear cobalt anion undergoes a remarkable aerial oxidation in aqueous ethanol solutions at  $-15^\circ\text{C}$ ; one of the bridging S atoms only is oxidized and this results in the formation of a bridging thiosulfito group  $[(\text{NC})_5\text{CoSSO}_2\text{Co}(\text{CN})_5]^{6-}$  coordinated through the two S atoms to the two Co atoms.<sup>(63)</sup> Other recent examples of  $\text{S}_2$ -complexes include  $[\text{V}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-S}_2)]$ ,<sup>(64)</sup>  $[\text{W}_2(\text{S})_2(\text{SH})(\mu\text{-}\eta^2\text{-S}_2)(\eta^2\text{-S}_2)_3]^-$ ,<sup>(65)</sup>  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-}\eta^2, \eta^2\text{-S}_2)]^{(66)}$  and  $[\text{Ru}_2\{\text{P}(\text{OMe})_3\}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-}\eta^1, \eta^1\text{-S}_2)_2]$ .<sup>(67)</sup>

Not all disulfide complexes are discrete molecular or ionic species and several solid-state compounds of  $\text{S}_2^{2-}$  are known in addition to the familiar pyrites and marcasite-type disulfides (p. 680). Examples are the chlorine-bridged polymeric  $\text{NbS}_2\text{Cl}_2$  mentioned on p. 667 (Fig. 15.14a) and the curious series of brown and red compounds formed by heating Mo or  $\text{MoS}_3$  with  $\text{S}_2\text{Cl}_2$ , e.g.<sup>(54)</sup>  $\text{MoS}_2\text{Cl}_2$ ,  $\text{MoS}_2\text{Cl}_3$  (Fig. 15.14b),  $\text{Mo}_2\text{S}_4\text{Cl}_5$  (Fig. 15.14c),  $\text{Mo}_2\text{S}_5\text{Cl}_3$  and  $\text{Mo}_3\text{S}_7\text{Cl}_4$ .

Complexes with chelating polysulfide ligands can be made either by reacting complex metal halides with solutions of polysulfides or by reacting hydrido complexes with elemental

sulfur, e.g.:



The red dianion  $[\text{PtS}_{15}]^{2-}$  was first made in 1903 but its structure as a chiral tris chelating pentasulfido complex (Fig. 15.15a) was not established until 1969.<sup>(68)</sup> It is a rare example of a "purely inorganic" (carbon-free) optically active species.<sup>(69)</sup> [Other examples are S. Heřmánek and J. Plešek's resolution of the main group element cluster compound  $i\text{-B}_{18}\text{H}_{22}$ ,<sup>(70)</sup> A. Werner's first-row transition-metal complex cation  $[\text{Co}\{(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4\}_3]^{6+}$ ,<sup>(71)</sup> and F. G. Mann's second-row complex anion  $\text{cis-}[\text{Rh}(\eta^2\text{-}(\text{NH})_2\text{-SO}_2)_2(\text{OH}_2)_2]^-$ .<sup>(72)</sup> The structure of the complex  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{S}_5)]$  is in Fig. 15.15b; it has previously been mentioned in connection with the synthesis of *cyclo*-polysulfur allotropes (p. 657). The chair conformation of the 6-membered  $\text{TiS}_5$  ring undergoes chair-to-chair inversion above room temperature with an activation energy of about  $69\text{ kJ mol}^{-1}$ .<sup>(73)</sup> A similar ring inversion in  $[\text{Pt}(\text{S}_5)_3]^{2-}$  is even more facile and  $^{195}\text{Pt}$  n.m.r. studies lead to a value of  $50.5 \pm 1.3\text{ kJ mol}^{-1}$  for  $\Delta G^\ddagger$  at  $0^\circ\text{C}$ .<sup>(74)</sup> Other recent examples of chelating  $\text{S}_n^{2-}$  ligands occur in the dark red-brown dianion<sup>(75)</sup>  $[(\eta^2\text{-S}_5)\text{Fe}(\mu\text{-S})_2\text{Fe}(\eta^2\text{-S}_5)]^{2-}$  and in the intriguing black

<sup>63</sup> F. R. FRONCZEK, R. E. MARSH and W. P. SCHAEFER, *J. Am. Chem. Soc.* **104**, 3382–5 (1982).

<sup>64</sup> C. FLORIANO, S. GAMBAROTTA, A. CHIESI-VILLA and C. GUASTINI, *J. Chem. Soc., Dalton Trans.*, 2099–103 (1987).

<sup>65</sup> F. SÉCHERESSE, J. M. MANOLI and C. POTVIN, *Inorg. Chem.* **25**, 3967–71 (1986).

<sup>66</sup> H. OGINO, H. TOBITA, S. INOMATA, and M. SHIMOI, *J. Chem. Soc., Chem. Commun.*, 586–7 (1988).

<sup>67</sup> P. M. TREICHEL, R. A. CRANE and K. J. HALLER, *Polyhedron* **9**, 1893–9 (1990).

<sup>68</sup> P. E. JONES and L. KATZ, *Acta Cryst.* **B25**, 745–52 (1969).

<sup>69</sup> R. D. GILLARD and F. L. WIMMER, *J. Chem. Soc., Chem. Commun.*, 936–7 (1978).

<sup>70</sup> S. HEŘMÁNEK and J. PLEŠEK, *Coll. Czech. Chem. Comm.* **35**, 2488–93 (1970).

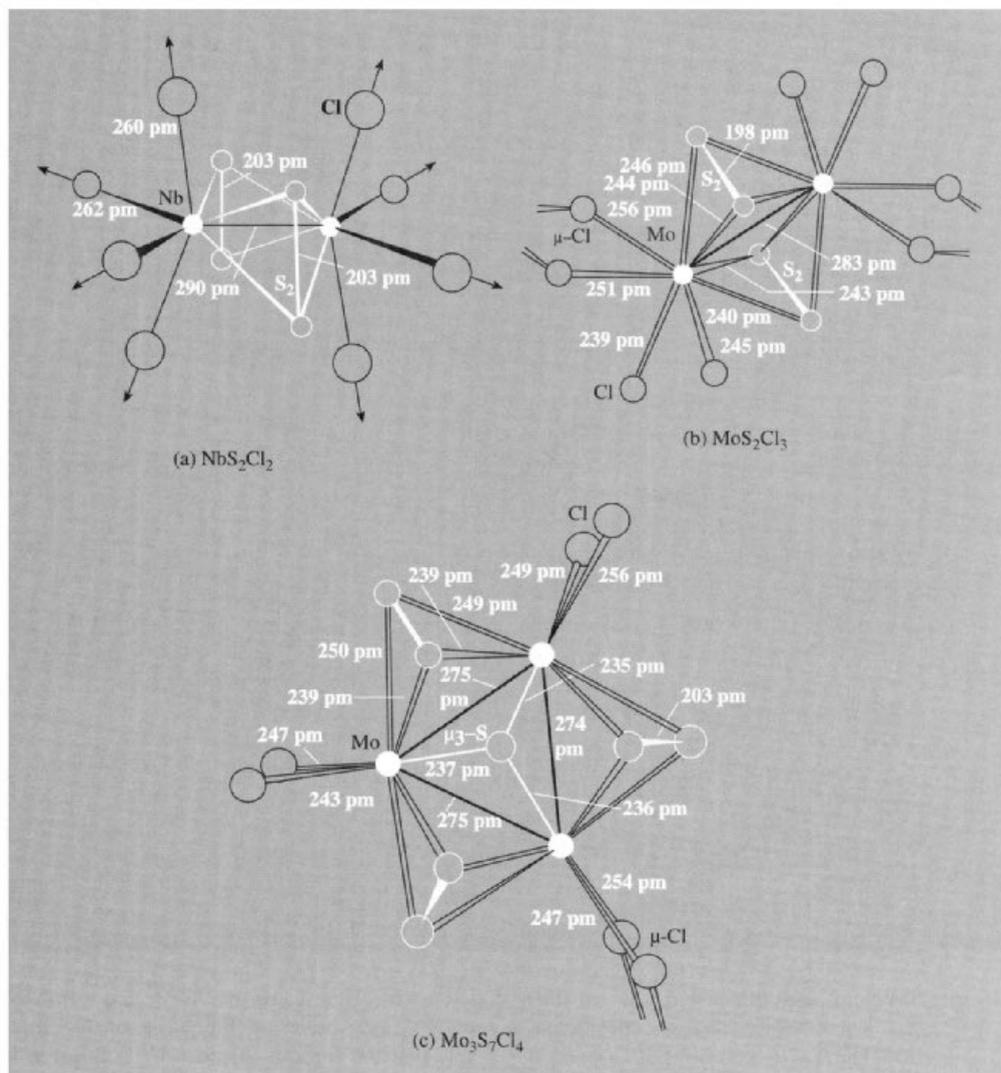
<sup>71</sup> A. WERNER, *Ber.* **47**, 3057–94 (1914).

<sup>72</sup> F. G. MANN, *J. Chem. Soc.* 412–19 (1933).

<sup>73</sup> E. W. ABEL, M. BOOTH and K. G. ORRELL, *J. Organometall. Chem.* **160**, 75–9 (1978).

<sup>74</sup> F. G. RIDDELL, R. D. GILLARD and F. L. WIMMER, *J. Chem. Soc., Chem. Commun.*, 332–3 (1982).

<sup>75</sup> D. COUCOUVANIS, D. SWENSON, P. STREMPLE and N. C. BAENZIGER, *J. Am. Chem. Soc.* **101**, 3392–4 (1979).



**Figure 15.14** Chlorine bridged polymeric structures of (a)  $\text{NbS}_2\text{Cl}_2$ , (b)  $\text{MoS}_2\text{Cl}_3$  and (c)  $\text{Mo}_3\text{S}_7\text{Cl}_4$ .

dianion  $[\text{Mo}_2\text{S}_{10}]^{2-}$  which features 4 different sorts of sulfur ligand and at least 6 different S-atom environments (Fig. 15.15c).<sup>(76)</sup> More complicated structures, including those featuring multidentate polymers or metal-sulfur clusters are continually being discovered in polysulfides whose apparently simple stoichiometry often

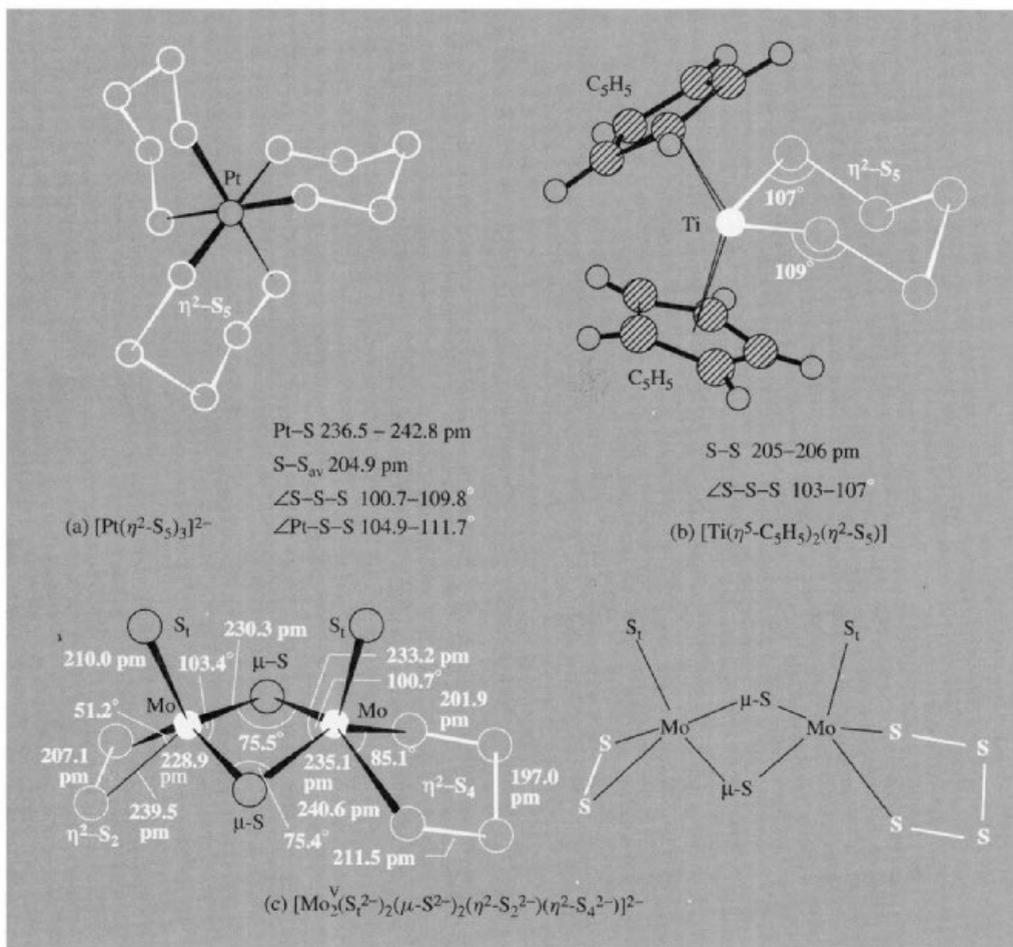
conceals an amazing structural complexity. Some recent examples are:  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^4\text{-S}_5)]$ ,<sup>(77)</sup>  $[\text{NMe}_4]^+[\text{Ag}(\text{S}_5)]_\infty$ ,<sup>(78)</sup>  $[\text{Cu}_4(\text{S}_5)_2(\text{py})_4]$ ,<sup>(79)</sup>

<sup>77</sup> D. A. WROBLESKI, D. T. CROMER, J. V. ORTIZ, T. B. RAUCHFUSS, R. R. RYAN and A. P. SATTELBERGER, *J. Am. Chem. Soc.* **108**, 174–5 (1986).

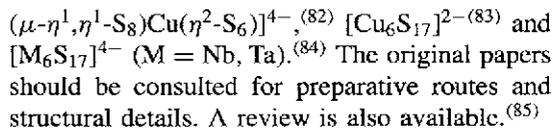
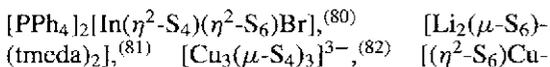
<sup>78</sup> R. M. H. BANDA, D. C. CRAIG, I. G. DANCE and M. L. SCUDDER, *Polyhedron* **8** 2379–83 (1989).

<sup>79</sup> E. RAMLI, T. B. RAUCHFUSS and C. L. STERN, *J. Am. Chem. Soc.* **112** 4043–4 (1990).

<sup>76</sup> W. CLEGG, G. CHRISTOU, C. D. GARNER and G. M. SHELDRICK, *Inorg. Chem.* **20**, 1562–6 (1981).



**Figure 15.15** Structure and dimensions of (a)  $[\text{Pt}(\eta^2\text{-S}_5)_3]^{2-}$ , (b)  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-S}_5)]$  and (c)  $[\text{Mo}_2\text{S}_{10}]^{2-}$ : this last complex can be considered as an  $\text{Mo}^{\text{V}}$  derivative on the basis of the formulation  $[\text{Mo}_2^{\text{V}}(\text{S}_4^{2-})_2(\mu\text{-S}^{2-})_2(\eta^2\text{-S}_2^{2-})(\eta^2\text{-S}_4^{2-})]^{2-}$ . Note that the angles subtended by S atoms at Mo vary from 51.2° through 85.1° to 100.7° and 103.4°, the M-S distances from 211 pm through 229 and 235 pm to 241 pm, and the S-S distances from 197 to 211.5 pm with the  $\text{S}_2^{2-}$  group being 207 pm.



<sup>80</sup> S. DHINGRA and M. G. KANATZIDS, *Polyhedron* **10**, 1069–73 (1991). See also W. BUBENHEIM and U. MÜLLER, *Z. anorg. allg. Chem.* **620**, 1607–12 (1994) for  $[\text{In}(\eta^2\text{-S}_4)(\eta^2\text{-S}_6)\text{Cl}]^-$ .

<sup>81</sup> A. J. BANISTER (and 12 others), *J. Chem. Soc., Chem. Commun.*, 105–7 (1990).

<sup>82</sup> A. MÜLLER, F.-W. BAUMANN, H. BÖGGE, M. RÖMER, E. KRICKEMEYER and K. SCHMITZ, *Angew. Chem. Int. Edn. Engl.* **23**, 632–3 (1984).

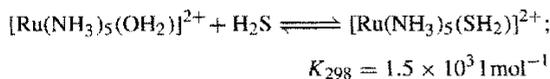
<sup>83</sup> A. MÜLLER, M. RÖMER, H. BÖGGE, E. KRICKEMEYER and D. BERGMANN, *J. Chem. Soc., Chem. Commun.*, 384–5 (1984).

<sup>84</sup> J. SOLA, Y. DO, J. M. BERG and R. H. HOLM, *J. Am. Chem. Soc.* **105**, 7784–6 (1983).

<sup>85</sup> M. DRAGANJAC and T. B. RAUCHFUSS, *Angew. Chem. Int. Edn. Engl.* **24** 742–57 (1985).

### Other ligands containing sulfur as donor atom

$\text{H}_2\text{S}$ , the simplest compound of sulfur, differs markedly from its homologue  $\text{H}_2\text{O}$  in complex-forming ability: whereas aquo complexes are extremely numerous and frequently very stable (p. 625),  $\text{H}_2\text{S}$  rarely forms simple adducts due to its ready oxidation to sulfur or its facile deprotonation to  $\text{SH}^-$  or  $\text{S}^{2-}$ .  $[\text{AlBr}_3(\text{SH}_2)]$  has long been known as a stable compound of tetrahedral  $\text{Al}^{(86)}$  but the few transition metal complexes having some degree of stability at room temperature are of more recent vintage: examples include  $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SH}_2)]$ ,  $[\text{W}(\text{CO})_5(\text{SH}_2)]$ , and the *triangulo* cluster complexes  $[\text{Ru}_3(\text{CO})_9(\text{SH}_2)]$  and  $[\text{Os}_3(\text{CO})_9(\text{SH}_2)]$ .<sup>(52,87)</sup> Action of  $\text{H}_2\text{S}$  on acidic aqueous solutions frequently precipitates the metal sulfide (cf. qualitative analysis separation schemes) but, in the presence of a reducing agent such as  $\text{Eu}^{\text{II}}$ ,  $\text{H}_2\text{S}$  can displace  $\text{H}_2\text{O}$  from the pale-yellow aquopentammine ruthenium(II) ion:



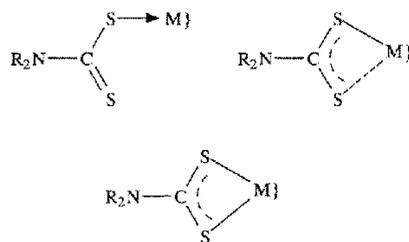
In the absence of  $\text{Eu}^{\text{II}}$ , oxidative deprotonation of the pale-yellow  $\text{H}_2\text{S}$  complex occurs to give the orange ruthenium(III) complex  $[\text{Ru}(\text{NH}_3)_5(\text{SH})]^{2+}$ . Other examples of complexes containing the  $\text{SH}^-$  ligand are  $[\text{Cr}(\text{OH}_2)_5(\text{SH})]^{2+}$ ,  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{SH})]$ ,  $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBU}_3)(\text{SH})]$ , *trans*- $[\text{PtH}(\text{PET}_3)_2(\text{SH})]$  and *trans*- $[\text{Pt}(\text{PET}_3)_2(\text{SH})_2]$ .<sup>(52,88,89)</sup>

The S-donor ligands  $\text{SO}$ ,  $\text{S}_2\text{O}_2$  and  $\text{SO}_2$  are mentioned in Section 15.2.5 and S-N ligands in Section 15.2.7. Thiocyanate ( $\text{SCN}^-$ ) is ambidentate, but towards heavier metals it

tends to be S-bonded rather than N-bonded. Bridging modes are also known (p. 324), including M-SCN-M and the rare S-only bridged  $\text{MS}(\text{CN})\text{M}$ .<sup>(90)</sup>

Organic thio ligands are well established, examples being the thiols  $\text{RSH}$  ( $\text{R} = \text{Et}$ ,  $\text{Pr}^n$ ,  $\text{Bu}'$ ,  $\text{Ph}$ ),<sup>(91)</sup> the thioethers  $\text{SMe}_2$ ,  $\text{SEt}_2$ , tetrahydrothiophene, etc., the chelating dithioethers, e.g.  $\text{MeS}(\text{CH}_2)_2\text{SMe}$ , and macro-cyclic ligands such as  $\{-(\text{CH}_2)_3\text{S}-\}_n$  with  $n = 3, 4$  etc.<sup>(92)</sup> Thiourea,  $(\text{H}_2\text{N})_2\text{C}=\text{S}$ , affords a further example. Factors affecting the stability of the resulting complexes have already been reviewed (p. 198). It is also notable that when  $\text{B}_{10}\text{H}_{14}$  reacts with solutions of thioethers in  $\text{OEt}_2$ , tetrahydrofuran, etc., it is the thio ligand rather than the oxygen-containing species which forms the stable *arachno*-bis adducts  $[\text{B}_{10}\text{H}_{12}(\text{SR}_2)_2]$  (p. 176).

Another large class of S-donor ligands comprises the dithiocarbamates  $\text{R}_2\text{NC}_2\text{S}_2^{2-}$  and related anions  $\text{YCS}_2^-$ , e.g. dithiocarbonylates  $\text{RCS}_2^-$ , xanthates  $\text{ROCS}_2^-$ , thioxanthates  $\text{RSCS}_2^-$ , dithiocarbonate  $\text{OCS}_2^{2-}$ , trithiocarbonate  $\text{SCS}_2^{2-}$  and dithiophosphinates  $\text{R}_2\text{PS}_2^-$  (see p. 509 for applications). Dithiocarbamates can function either as unidentate or bidentate (chelating) ligands:



<sup>90</sup> S. M. NELSON, F. S. ESHO and M. G. B. DREW, *J. Chem. Soc., Chem. Commun.*, 388-9 (1981).

<sup>91</sup> F. M. CONROY-LEWIS and S. J. SIMPSON, *J. Chem. Soc., Chem. Commun.*, 388-9 (1991) and references cited therein.

<sup>92</sup> S. CRAWLE, J. R. HARTMAN, D. J. WATKIN and S. R. COOPER, *J. Chem. Soc., Chem. Commun.*, 1083-4 (1986); C. M. THORNE, S. C. RAWLE, G. A. ADMANS and S. R. COOPER, *ibid.*, 306-7 (1987); S. C. RAWLE and S. R. COOPER, *ibid.*, 308-9 (1987); T. YOSHIDA, T. ADACHI, M. KAMINAKA and T. UEDA, *J. Am. Chem. Soc.* **110**, 4872-3 (1988). See also W. TREMEL, B. KREBS and G. HENKEL, *J. Chem. Soc., Chem. Commun.*, 1527-9 (1986).

<sup>86</sup> A. WEISS, R. PLASS, and AL. WEISS, *Z. anorg. allg. Chem.* **283**, 390-400 (1956).

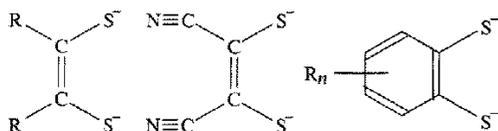
<sup>87</sup> C. G. KUEHN and H. TAUBE, *J. Am. Chem. Soc.* **98**, 689-702 (1976).

<sup>88</sup> T. RAMASAMI and A. G. SYKES, *Inorg. Chem.* **15**, 1010-14 (1976).

<sup>89</sup> I. M. BLACKLAWS, E. A. V. EBSWORTH, D. W. H. RANKIN and H. E. ROBERTSON, *J. Chem. Soc., Dalton Trans.*, 753-8 (1978).

In the chelating mode they frequently stabilize the metal centre in an unusually high apparent formal oxidation state, e.g.  $[\text{Fe}^{\text{IV}}(\text{S}_2\text{CNR}_2)_3]^+$  and  $[\text{Ni}^{\text{IV}}(\text{S}_2\text{CNR}_2)_3]^+$ . They also have a propensity for stabilizing novel stereochemical configurations, unusual mixed oxidation states (e.g. of Cu), intermediate spin states (e.g.  $\text{Fe}^{\text{III}}$ ,  $S = \frac{3}{2}$ ), and for forming a variety of tris chelated complexes of  $\text{Fe}^{\text{III}}$  which lie at the  ${}^2T_2 - {}^6A_1$  spin crossover (p. 1096).<sup>(93)</sup>

Dithiocarbamates and their analogues have 2 potential S-donor atoms joined to a single C atom and their complexes are sometimes called 1,1-dithiolato complexes. If the 2 S atoms are joined to adjacent C atoms then the equally numerous class of 1,2-dithiolato complexes results. Examples of chelating dithiolene ligands (drawn for convenience with localized valence bonds and ionic charges) are:



R = alkyl, aryl,  $\text{CF}_3$ , H

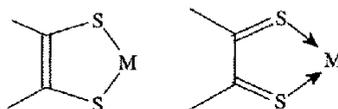
R = Me, F, Cl, H

Complexes of these ligands have been extensively studied during the past few decades not only because of the intrinsically interesting structural and bonding problems that they pose but also because of their varied industrial applications.<sup>(94-96)</sup> These include their use as highly specific analytical reagents, chromatographic supports, polarizers in sunglasses, mode-locking additives in neodymium lasers, semiconductors, fungicides, pesticides, vulcanization accelerators, high-temperature

wear-inhibiting additives in lubricants, polymerization and oxidation catalysts and even fingerprint developers in forensic investigations.

Complexes in which dithiolenes are the only ligands present can be classified according to six structural types as shown schematically in Fig. 15.16. For bis(dithiolato) complexes the planar structure (a) with  $D_{2h}$  local symmetry about the metal is the commonest mode but occasionally 5-coordinate dimers (b) are observed. The very rare metal-metal bonded 5-coordinate dimeric bis(dithiolato) structure (c) has been found for the palladium and platinum complexes  $[\{\text{M}(\text{S}_2\text{C}_2\text{H}_2)_2\}_2]$  with Pd-Pd 279 pm and Pt-Pt 275 pm. For tris(dithiolato) complexes two limiting geometries are possible: trigonal prismatic (Fig. 15.16d) and octahedral (Fig. 15.16f). The two geometries are related by a  $30^\circ$  twist of one triangular  $\text{S}_3$  face with respect to the other, and intermediate twists are also known (Fig. 15.16e). As a rough generalization, the less-common trigonal prismatic geometry (local  $D_{3h}$  symmetry) is adopted by "ligand-controlled" complexes which are often neutral or highly oxidized [e.g.  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3$ , where M = V, Cr, Mo, W, Re], whereas the more usual octahedral ( $D_3$ ) geometry tends to be formed when the central metal dominates the stereochemistry as in the reduced anionic complexes. Thus reduction of the trigonal prismatic  $[\text{V}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]$  to the dianion  $[\text{V}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$  results in distortion to an intermediate geometry, whereas the iron analogue  $[\text{Fe}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$  has the chelated octahedral  $D_3$  structure. Intermediate geometries (Fig. 15.16e) have also been found for  $[\text{Mo}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]^{2-}$  and its W analogue.

There has been much discussion about the detailed bonding in 1,2-dithiolene complexes because of the alternative ways that the ring system can be described, e.g.:



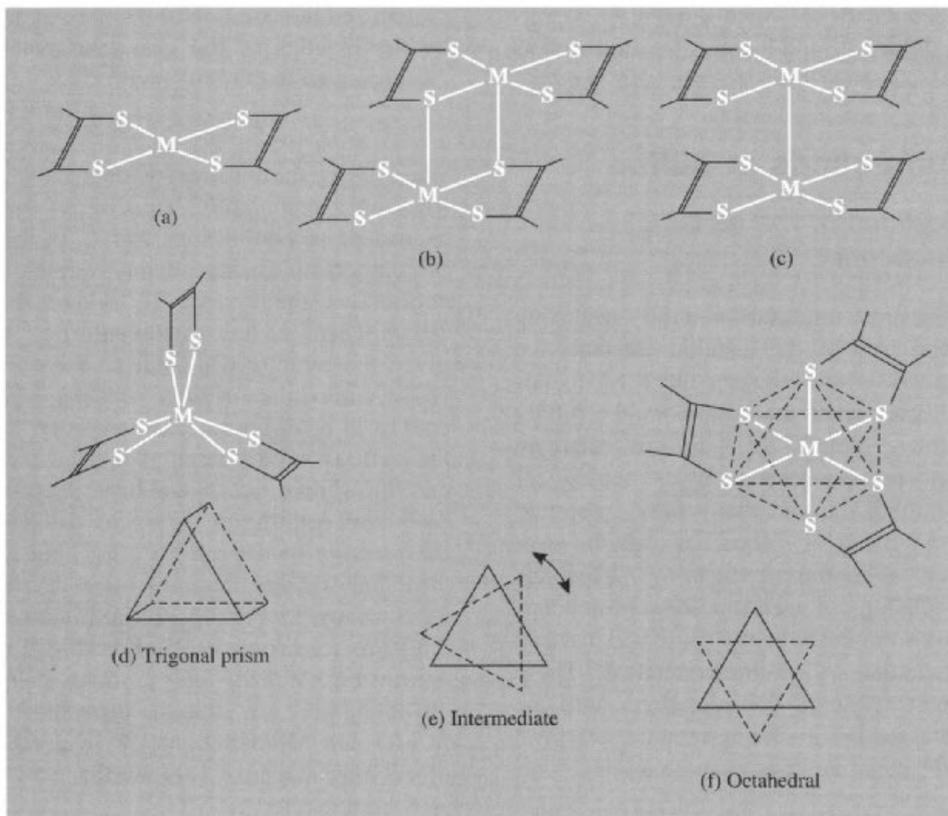
The formal oxidation state of the metal differs by 2 in these two limiting formulations (or

<sup>93</sup> R. L. MARTIN, in D. BANERJEA (ed.), *Coordination Chemistry - 20*, (International Conf. Calcutta, 1979) pp. 255-65, Pergamon Press, Oxford, 1980.

<sup>94</sup> R. EISENBERG, *Prog. Inorg. Chem.* **12**, 295-369 (1970).

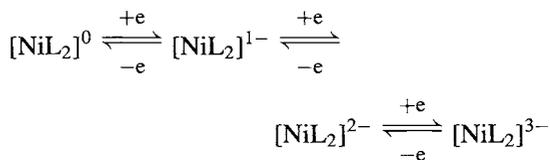
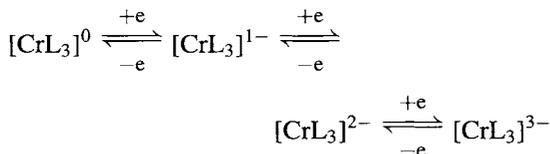
<sup>95</sup> R. P. BURNS and C. A. MCAULIFFE, *Adv. Inorg. Chem. Radiochem.* **22**, 303-48 (1979); R. P. BURNS, F. P. MCCULLOUGH and C. A. MCAULIFFE, *Adv. Inorg. Chem. Radiochem.* **23**, 211-80 (1980).

<sup>96</sup> A. M. BOND and R. L. MARTIN, *Coord. Chem. Revs.* **54**, 23-98 (1984).

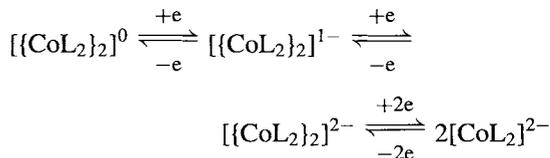


**Figure 15.16** Coordination geometries of bis- and tris-1,2-dithiolene complexes (see text).

by 6 in a tris complex). On this basis it is unclear whether the complex  $[\text{V}\{\text{S}_2\text{C}_2(\text{CN})_2\}_3]$  mentioned in the preceding paragraph should be formulated as  $\text{V}^{\text{VI}}(!)$  or  $\text{V}^0$ : it seems probable that an intermediate value would be more likely, but the example emphasizes the difficulty of assigning meaningful oxidation numbers to metal atoms in a redox series when the electronic configuration of the ligands themselves may also be undergoing change during reduction. Such reversible oxidation–reduction sequences are a characteristic feature of many 1,2-dithiolene complexes, e.g. for  $\text{L} = \{\text{S}_2\text{C}_2(\text{CN})_2\}$ :



and similarly for the Pd, Pt and other analogues.<sup>(97)</sup> Likewise for dimeric species with  $\text{L} = \{\text{S}_2\text{C}_2(\text{CF}_3)_2\}$ :



<sup>97</sup> W. E. GEIGER, T. E. MINES and F. E. SENFTLEBER, *Inorg. Chem.* **14**, 2141–7 (1975); W. E. GEIGER, C. S. ALLEN, T. E. MINES and F. C. SENFTLEBER, *Inorg. Chem.* **16**, 2003–8 (1977).