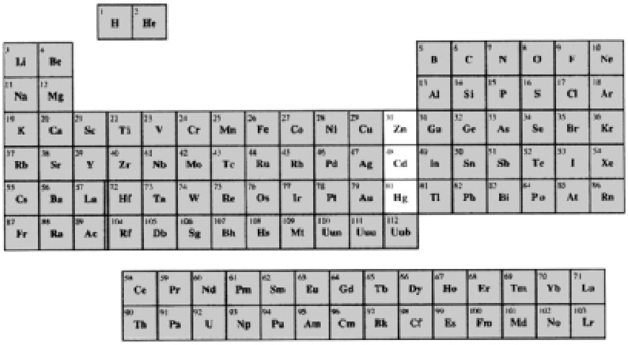

29

Zinc, Cadmium and Mercury

29.1 Introduction

The reduction of ZnO by charcoal requires a temperature of 1000°C or more and, because the metal is a vapour at that temperature and is liable to reoxidation, its collection requires some form of condenser and the exclusion of air. This was apparently first achieved in India in the thirteenth century. The art then passed to China where zinc coins were used in the Ming Dynasty (1368–1644). The preparation of alloyed zinc by smelting mixed ores does not require the isolation of zinc itself and is much more easily achieved. The small amounts of zinc present in samples of early Egyptian copper no doubt simply reflect the composition of local ores, but Palestinian brass dated 1400–1000 BC and containing about 23% Zn must have been produced by the deliberate mixing of copper and zinc ores. Brass was similarly produced by the Romans in Cyprus and later in the Cologne region of Germany.

Zinc was not intentionally made in medieval Europe, though small amounts were obtained by accidental condensation in the production of lead, silver and brass; it was imported from China by the East India Company after about 1605. The English zinc industry started in the Bristol area in the early eighteenth century and production quickly followed in Silesia and Belgium. The origin of the name is obscure but may plausibly be thought to be derived from *Zinke* (German for spike, or tooth) because of the appearance of the metal.

Mercury is more easily isolated from its ore, cinnabar, and was used in the Mediterranean world for extracting metals by amalgamation as early as 500 BC, possibly even earlier. Cinnabar, HgS, was widely used in the ancient world as a pigment (vermilion). For over a thousand years, up to AD 1500, alchemists regarded the metal as a key to the transmutation of base metals to gold and employed amalgams both for gilding and for producing imitation gold and silver. Because of its mobility, mercury is named after the messenger of the gods in Roman mythology, and the symbol, Hg, is derived from *hydrargyrum* (Latin, liquid silver).

Cadmium made its appearance much later. In 1817 F. Stromeyer of Göttingen noticed that a sample of "cadmia" (now known as "calamine"), used in a nearby smelting works, was yellow instead of white. The colour was not due to iron, which was shown to be absent, but arose instead from a new element which was named after the (zinc) ore in which it had been found (Greek καδμεία, cadmean earth, the ancient name of calamine).

29.2 The Elements

29.2.1 Terrestrial abundance and distribution

Zinc (76 ppm of the earth's crust) is about as abundant as rubidium (78 ppm) and slightly more abundant than copper (68 ppm). Cadmium (0.16 ppm) is similar to antimony (0.2 ppm); it is twice as abundant as mercury (0.08 ppm), which is itself as abundant as silver (0.08 ppm) and close to selenium (0.05 ppm). These elements are "chalcophiles" (p. 648) and so, in the reducing atmosphere prevailing when the earth's crust solidified, they separated out in the sulfide phase, and their most important ores are therefore sulfides. Subsequently, as rocks were weathered, zinc was leached out to be precipitated as carbonate, silicate or phosphate.

The major ores of zinc are ZnS (which is known as zinc blende in Europe and as sphalerite in the USA) and $ZnCO_3$ (calamine in Europe, smithsonite in the USA[†]). Large deposits are situated in Canada, the USA and Australia. Less important ores are hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$ and franklinite, $(Zn,Fe)O.Fe_2O_3$. Cadmium is found as greenockite, CdS, but its only commercially important source is the 0.2–0.4% found in most zinc ores. Cinnabar, HgS, is the only important ore and source of mercury and is found along lines of previous volcanic activity. The most famous and extensive deposits are at Almaden in Spain; these contain up to 6–7% Hg and have been worked since Roman times. Other deposits, usually containing <1% Hg, are situated in the former Soviet Union, Algeria, Mexico, Yugoslavia and Italy.

29.2.2 Preparation and uses of the elements[1]

The isolation of zinc, over 90% of which is from sulfide ores, depends on conventional physical concentration of the ore by sedimentation or flotation techniques. This is followed by roasting to produce the oxides; the SO_2 which is generated is used to produce sulfuric acid. The ZnO is then either treated electrolytically or smelted with coke. In the former case the zinc is leached from the crude ZnO with dil H_2SO_4, at which point cadmium is precipitated by the addition of zinc dust. The $ZnSO_4$ solution is then electrolysed and the metal deposited — in a state of 99.95% purity — on to aluminium cathodes.

A variety of smelting processes have been employed to effect the reduction of ZnO by coke:

$$\mathrm{ZnO} + \mathrm{C} \longrightarrow \mathrm{Zn} + \mathrm{CO}$$

These formerly involved the use of banks of externally heated, horizontal retorts, operated on a batch basis. They were replaced by continuously operated vertical retorts, in some cases electrically heated. Unfortunately none of these processes has the thermal efficiency of a blast furnace process (p. 1072) in which the combustion of the fuel for heating takes place in the same chamber as the reduction of the oxide. The inescapable problem posed by zinc is that the reduction of ZnO by carbon is not spontaneous below the boiling point of Zn (a problem not encountered in the smelting of Fe, Cu or Pb, for instance), and the subsequent cooling to condense the vapour is liable, in the presence of the combustion products, to result in the reoxidation of the metal:

$$\mathrm{Zn} + \mathrm{CO_2} \rightleftharpoons \mathrm{ZnO} + \mathrm{CO}$$

The problem can be overcome by spraying the zinc vapour with lead as it leaves the top of the furnace. This chills and dissolves the zinc

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[†] After James Smithson, founder of the Smithsonian Institution, Washington. The name calamine is applied in the USA to a basic carbonate.

[1] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Interscience, New York. For Zn, see Vol. 25, 1998, pp. 789-853. For Cd, see Vol. 4, 1992, pp. 748-60. For Hg, see Vol. 16, 1995. pp. 212-28.

so rapidly that reoxidation is minimal. The zinc then separates as a liquid of nearly 99% purity and is further refined by vacuum distillation to give a purity of 99.99%. Any cadmium present is recovered in the course of this distillation. The use of a blast furnace has the further advantage that the composition of the charge is not critical, and mixed Zn/Pb ores can be used (ZnS and PbS are commonly found together) to achieve the simultaneous production of both metals, the lead being tapped from the bottom of the furnace.

World production of zinc (1995) is about 7 million tonnes pa: of this, about 1 million tonnes pa is produced by each of Canada and Australia and 800 000 tonnes pa by China. Cadmium is produced in much smaller quantities (~20 000 tonnes pa) and these are dependent on the supply of zinc.

Zinc finds a wide range of uses. The most important, accounting for 40% of output, is as an anti-corrosion coating. The application of the coating takes various forms: immersion in molten zinc (hot-dip galvanizing), electrolytic deposition, spraying with liquid metal, heating with powdered zinc ("Sherardizing"), and applying paint containing zinc powder. In addition to brasses (Cu plus 20–50% Zn), a rapidly increasing number of special alloys, predominantly of zinc, are used for diecasting and, indeed, the vast majority of *pressure* diecastings are now made in these alloys. Zinc sheeting is used in roof cladding and the manufacture of dry batteries (see Panel, p. 1204) is a further use, though this has declined considerably in recent years.

The major uses of cadmium are in batteries (67%) and coatings (7%). In the form of its compounds it is used in pigments (CdS –15%) and stabilizers, in PVC for instance, to prevent degradation by heat or ultraviolet radiation (10%).

The isolation of mercury is comparatively straightforward. The most primitive method consisted simply of heating cinnabar in a fire of brushwood. The latter acted as fuel and condenser, and metallic mercury collected in the ashes. Modern techniques are of course less crude than this but the basic principle is much the same. After being crushed and concentrated by flotation, the ore is roasted in a current of air and the vapour condensed:

$$\mathrm{HgS + O_2 \xrightarrow{600^\circ C} Hg + SO_2}$$

Alternatively, in the case of especially rich ores, roasting with scrap iron or quicklime is used:

$$\mathrm{HgS + Fe \longrightarrow Hg + FeS}$$

$$\mathrm{4HgS + CaO \longrightarrow 4Hg + 3CaS + CaSO_4}$$

Blowing air through the hot, crude, liquid metal oxidizes traces of metals such as Fe, Cu, Zn and Pb which form an easily removable scum. Further purification is by distillation under reduced pressure. About 4000 tonnes[†] of mercury are used annually but only half is from primary, mine production the other half being secondary production and sales from stockpiles. The main primary producer is now Spain, but several other countries, including the former Soviet Union, China and Algeria, have capacity for production.

The use of mercury for extracting precious metals by amalgamation has a long history and was extensively used by Spain in the sixteenth century when her fleet carried mercury from Almaden to Mexico and returned with silver. However, environmental concerns have resulted in falling demand and excess production capacity. It is still used in the extraction of gold and in the Castner–Kellner process for manufacturing chlorine and NaOH (p. 72), and a further major use is in the manufacture of batteries. It is also used in street lamps and AC rectifiers, while its small-scale use in thermometers, barometers and gauges of different kinds, are familiar in many laboratories.

29.2.3 Properties of the elements

A selection of some important properties of the elements is given in Table 29.1. Because the elements each have several naturally occurring isotopes their atomic weights cannot be quoted with great precision.

[†] Mercury is sold in iron *flasks* holding 76 lb of mercury and this is the unit in which output is normally measured.

Dry Batteries

A portable source of electricity, if not a necessity, is certainly a great convenience in modern life and is dependent on compact, sealed, dry batteries. The main types are listed below and they incorporate the metals Zn, Ni, Hg and Cd as well as MnO_2

(a) Carbon–zinc cell

The first dry battery was that patented in 1866 by the young French engineer, G. Leclanché. The positive pole consisted of carbon surrounded by MnO_2 (p. 1048) contained in a porous pot, and the negative pole was simply a rod of zinc. These were situated inside a glass jar containing the electrolyte, ammonium chloride solution thickened with sand or sawdust. This is still the basis of the most common type of modern dry cell in which a carbon rod is the positive pole, surrounded by a paste of MnO_2, carbon black, and NH_4Cl, inside a zinc can which is both container and negative pole. The reactions are:

negative pole: $Zn \longrightarrow Zn^{2+} + 2e^-$
electrolyte: $Zn^{2+} + 2NH_4Cl + 2OH^- \longrightarrow [ZnCl_2(NH_3)_2] + 2H_2O$
positive pole: $2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^-$
net reaction: $Zn + 2NH_4Cl + 2MnO_2 \longrightarrow [ZnCl_2(NH_3)_2] + 2MnO(OH)$

(b) Mercury cell

The negative pole of pressed amalgamated zinc powder and the positive pole of mercury(II) oxide and graphite are separated by an absorbent impregnated with the electrolyte, conc KOH:

negative pole: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$
positive pole: $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$
net reaction: $Zn + HgO \longrightarrow Hg + ZnO$

(c) Alkaline manganese cell

This is similar in principle to (a) but is constructed in a manner akin to (b). The negative pole of powdered zinc, formed into a paste with the electrolyte KOH, and the positive pole of compressed graphite and MnO_2 are separated by an absorbent impregnated with the electrolyte:

negative pole: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$
positive pole: $2MnO_2 + H_2O + 2e^- \longrightarrow Mn_2O_3 + 2OH^-$
net reaction: $Zn + 2MnO_2 \longrightarrow ZnO + Mn_2O_3$

(d) Nickel–cadmium cell

Unlike the cells above, which are all primary cells, this is a secondary (i.e. rechargeable) cell, and the two poles are composed in the uncharged condition of nickel and cadmium hydroxides respectively. These are each supported on microporous nickel, made by a sintering process, and separated by an absorbent impregnated with electrolyte. The charging reactions are:

negative pole: $Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$
positive pole: $Ni(OH)_2 + 2OH^- \longrightarrow NiO(OH) + 2H_2O + 2e^-$
net reaction: $Ni(OH)_2 + Cd(OH)_2 \longrightarrow NiO(OH) + Cd + 2H_2O$

During discharge these reactions are reversed. A crucial feature of the construction of this cell is that oxygen produced at the positive pole during charging by the side-reaction:

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

can migrate readily to the negative pole to be recombined in the reaction:

$$O_2 + 2H_2O + 2Cd \longrightarrow 2Cd(OH)_2$$

But for this rapid migration and recombination, the cell could not be sealed.

Table 29.1 Some properties of the elements zinc, cadmium and mercury

Property		Zn	Cd	Hg
Atomic number		30	48	80
Number of naturally occurring isotopes		5	8[(a)]	7
Atomic weight		65.39(2)	112.411(8)	200.59(2)
Electronic configuration		$[Ar]3d^{10}4s^2$	$[Kr]4d^{10}5s^2$	$[Xe]4f^{14}5d^{10}6s^2$
Electronegativity		1.6	1.7	1.9
Metal radius (12 coordinate)/pm		134	151	151
Effective ionic radius/pm	II	74	95	102
	I	—	—	119
Ionization energies/kJ mol^{-1}	1st	906.1	876.5	1007
	2nd	1733	1631	1809
	3rd	3831	3644	3300
$E^\circ(M^{2+}/M)/V$		−0.7619	−0.4030	+0.8545
MP/°C		419.5	320.8	−38.9
BP/°C		907	765	357
ΔH_{fus}/kJ mol^{-1}		7.28(±0.01)	6.4(±0.2)	2.30(±0.02)
ΔH_{vap}/kJ mol^{-1}		114.2(±1.7)	100.0(±2.1)	59.1(±0.4)
$\Delta H_{(monatomic\ gas)}$/kJ mol^{-1}		129.3(±2.9)	111.9(±2.1)	61.3
Density (25°C)/g cm^{-3}		7.14	8.65	13.534(1)
Electrical resistivity (20°C)/μohm cm		5.8	7.5	95.8

(a) The half-life of $9.3 \pm 1.9 \times 10^{15}$ y for ^{113}Cd is the longest known for any β-emitter; note that this is 2 million times the age of the earth (4.6×10^9 y).

Their most noticeable features compared with other metals are their low melting and boiling points, mercury being unique as a metal which is a liquid at room temperature. Zinc and cadmium are silvery solids with a bluish lustre when freshly formed. Mercury is also unusual in being the only element, apart from the noble gases, whose vapour is almost entirely monatomic, while its appreciable vapour pressure (1.9×10^{-3} mmHg, i.e. 0.25 Pa, at 25°C), coupled with its toxicity, makes it necessary to handle it with care. The electrical resistivity of liquid mercury is exceptionally high for a metal, and this facilitates its use as an electrical standard (the international ohm is defined as the resistance of 14.4521 g of Hg in a column 106.300 cm long and 1 mm^2 cross-sectional area at 0°C and a pressure of 760 mmHg.

The structures of the solids, although based on the typically metallic hexagonal close-packing, are significantly distorted. In the case of Zn and Cd the distortion is such that, instead of having 12 equidistant neighbours, each atom has 6 nearest neighbours in the close-packed plane with the 3 neighbours in each of the adjacent planes being about 10% more distant. In the case of (rhombohedral) Hg the distortion, again uniquely, is the reverse, with the coplanar atoms being the more widely separated (by some 16%). The consequence is that these elements are much less dense and have a lower tensile strength than their predecessors in Group 11. These facts have been ascribed to the stability of the d electrons which are now tightly bound to the nucleus: the metallic bonding therefore involves only the outer s electrons, and is correspondingly weakened.

29.2.4 Chemical reactivity and trends

Zinc and cadmium tarnish quickly in moist air and combine with oxygen, sulfur, phosphorus and the halogens on being heated. Mercury also reacts with these elements, except phosphorus and its reaction with oxygen was of considerable practical importance in the early work of J. Priestley and A. L. Lavoisier on oxygen (p. 601). The reaction only becomes appreciable at temperatures of about 350°C, but above about 400°C HgO decomposes back into the elements.

None of the three metals reacts with hydrogen, carbon or nitrogen.

Non-oxidizing acids dissolve both Zn and Cd with the evolution of hydrogen. With oxidizing acids the reactions are more complicated, nitric acid for instance producing a variety of oxides of nitrogen dependent on the concentration and temperature. Mercury is unreactive to non-oxidizing acids but dissolves in conc HNO_3 and in hot conc H_2SO_4 forming the Hg^{II} salts along with oxides of nitrogen and sulfur. Dilute HNO_3 slowly produces $Hg_2(NO_3)_2$. Zinc is the only element in the group which dissolves in aqueous alkali to form ions such as aquated $[Zn(OH)_4]^{2-}$ (zincates).

All three elements form alloys with a variety of other metals. Those of zinc include the brasses (p. 1178) and, as mentioned above, are of considerable commercial importance. Those of mercury are known as amalgams and some, such as sodium and zinc amalgams, are valuable reducing agents: in a number of cases, high heats of formation and stoichiometric compositions suggest chemical combination. Na_5Hg_8 and Na_3Hg for instance have been isolated and structurally characterized. They consist of "widespread" close-packed mercury ($Hg-Hg > 500\,pm$) with respectively, all vacancies filled and all octahedral vacancies plus 5/6 tetrahedral vacancies filled with sodium atoms.(2) From caesium amalgams CsHg has been obtained and shown(3) to contain isolated square planar Hg_4 clusters ($Hg-Hg \sim 300\,pm$ whereas intercluster separation $= 419\,pm$). Amalgams are most readily formed by heavy metals, whereas the lighter metals of the first transition series (with the exception of manganese and copper) are insoluble in mercury. Hence iron flasks can be used for its storage.

Chemically, it is clear that Zn and Cd are rather similar and that Hg is somewhat distinct. The lighter pair are more electropositive, as indicated both by their electronegativity coefficients and electrode potentials (Table 29.1), while Hg has a positive electrode potential and is comparatively inert. With the exception of the metallic radii, all the evidence indicates that the effects of the lanthanide contraction have died out by the time this group is reached. Compounds are characterized by the d^{10} configuration and, with the exception of derivatives of the Hg_2^{2+} ion, which formally involve Hg^I, they almost exclusively involve M^{II} (but see page 1213). The ease with which the s^2 electrons are removed compared with the more firmly held d electrons is shown by the ionization energies. The sum of the first and second is in each case smaller than for the preceding element in Group 11, whereas the third is appreciably higher. Even so the first two ionization energies are high for mercury (as they are for gold) — perhaps reflecting the poor nuclear shielding afforded by the filled 4f shell — and this, coupled with the small hydration energy associated with the large Hg^{II} cation, accounts for the positive value of its electrode potential.

In view of the stability of the filled d shell, these elements show few of the characteristic properties of transition metals (p. 905) despite their position in the d block of the periodic table. Thus zinc shows similarities with the main-group metal magnesium, many of their compounds being isomorphous, and it displays the class-a characteristic of complexing readily with *O*-donor ligands. On the other hand, zinc has a much greater tendency than magnesium to form covalent compounds, and it resembles the transition elements in forming stable complexes not only with *O*-donor ligands but with *N*- and *S*-donor ligands and with halides and CN^- (see p. 1216) as well. As mentioned above, cadmium is rather similar to zinc and may be regarded as on the class-a/b borderline. However, mercury is undoubtedly class b: it has a much greater tendency to covalency and a preference for *N*-, *P*- and *S*-donor ligands, with which Hg^{II} forms complexes whose stability is rarely exceeded by those of any other divalent cation. Compounds of the M^{II} ions of this group are characteristically diamagnetic and those of Zn^{II}, like those of Mg^{II}, are colourless. By contrast, many compounds of

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[2] H. J. DEISEROTH and D. TOELSTEDE, *Z. anorg. allg. Chem.* **615**, 43-8 (1992).

[3] H. J. DEISEROTH, A. STRUNK and W. BAUHOFER, *Z. anorg. allg. Chem.* **575**, 31-8 (1989).

Table 29.2 Stereochemistries of compounds of Zn^{II}, Cd^{II} and Hg^{II}

Coordination number	Stereochemistry	Zn	Cd	Hg
2	Linear	$ZnEt_2$	$CdEt_2$	$[Hg(NH_3)_2]^{2+}$
3	Planar	$[ZnMe(NPh_3)]_2$		$[HgI_3]^-$
	T-shaped			$[Hg(SC_6H_2Bu^t_3)_2(py)]$
4	Tetrahedral	$[Zn(H_2O)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$	$[CdCl_4]^{2-}$	$[Hg(SCN)_4]^{2-}$
	Planar	$[Zn(glycinyl)_2]$		
5	Trigonal bipyramidal	$[Zn(terpy)Cl_2]$	$[CdCl_5]^{3-}$	$[Hg(terpy)Cl_2]$
	Square pyramidal	$[Zn(S_2CNEt_2)_2]_2$	$[Cd(S_2CNEt_2)_2]_2$	$[Hg\{N(C_2H_4NMe_2)_3\}I]^+$
6	Octahedral	$[Zn(en)_3]^{2+}$	$[Cd(NH_3)_6]^{2+}$	$[Hg(C_5H_5NO)_6]^{2+}$
7	Pentagonal bipyramidal	$[Zn(H_2dapp)(H_2O)_2]^{2+(a)}$	$[Cd(quin)_2(NO_3)_2H_2O]^{(b)}$	
8	Distorted dodecahedral	$[Zn(NO_3)_4]^{2-(c)}$		
	Distorted square antiprismatic			$[Hg(NO_2)_4]^{2-}$

(a) H_2dapp = 2,6-diacetylpyridinebis(2′-pyridylhydrazone).

(b) The 2 nitrate ions are not equivalent (both are bidentate but one is coordinated symmetrically, the other asymmetrically) and the structure of the complex is by no means regular (p. 1217).

(c) The distortion arises because the bidentate nitrate ions are coordinated asymmetrically to such an extent that the stereochemistry may alternatively be regarded as approaching tetrahedral (p. 1217).

Hg^{II}, and to a lesser extent those of Cd^{II}, are highly coloured due to the greater ease of charge transfer from ligands to the more polarizing cations. The increasing polarizing power and covalency of their compounds in the sequence, $Mg^{II} < Zn^{II} < Cd^{II} < Hg^{II}$, is a reflection of the decreasing nuclear shielding and consequent increasing power of distortion in the sequence: filled p shell < filled d shell < filled f shell.

A further manifestation of these trends is the increasing stability of σ-bonded alkyls and aryls in passing down the group (p. 1221). Those of Zn and Cd are rather reactive and unstable to both air and water, whereas those of Hg are stable to both. (The Hg–C bond is not in fact strong but the competing Hg–O bond is weaker.) However, the M^{II} ions do not form π complexes with CO, NO or olefins (alkenes), no doubt because of the stability of their d^{10} configurations and their consequent inability to provide electrons for "back bonding". Likewise their cyanides presumably owe their stability primarily to σ rather than π bonding. The filled d shell also prevents π acceptance and complexes with cyclopentadienide ions (which are good π donors) are σ- rather than π-bonded.

The range of stereochemistries found in compounds of the M^{II} ions is illustrated in Table 29.2. Since the d^{10} configuration affords no crystal field stabilization, the stereochemistry of a particular compound depends on the size and polarizing power of the M^{II} cation and the steric requirements of the ligands. Thus both Zn^{II} and Cd^{II} favour 4-coordinate tetrahedral complexes though Cd^{II}, being the larger, forms 6-coordinate octahedral complexes more readily than does Zn^{II}. However, the still larger Hg^{II} also commonly adopts a tetrahedral stereochemistry, and octahedral 6-coordination is less prevalent than for either of its congeners.[†] When it does occur it is usually highly distorted with 2 short and 4 long bonds, a distortion which in its extreme form produces the 2-coordinate, linear stereochemistry which is characteristic of

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[†] An example of trigonal prismatic coordination has been reported for Hg in the green, zero-valent mixed-metal cluster $[Hg\{Pt(2,6\text{-}Me_2C_6H_3NC)\}_6]$; Y. YAMAMOTO, H. YAMAZAKI, and T. SAKURAI, *J. Am. Chem. Soc.* **104**, 2329–30 (1982). In $[Hg(mac)_2](HgBr_4)$, (mac = 1-thia-4,7-diazacyclononane) the coordination in the cation is intermediate between octahedral and trigonal prismatic; U. HEINZEL and R. MATTES, *Polyhedron* **11**, 597–600 (1992).

Hg^{II}. This is also found in organozinc and organocadmium compounds but only with Hg^{II} is it one of the predominant stereochemistries. Explanations of this fact have been given in terms of the promotional energies involved in various hybridization schemes, but it may be regarded pictorially as a consequence of the greater deformability of the d^{10} configuration of the large Hg^{II} ion. Thus, if 2 ligands are considered to approach the cation from opposite ends of the z-axis, the resulting deformation increases the electron density in the xy-plane and so discourages the close approach of other ligands. Coordination numbers greater than 6 are rare and generally involve bidentate, O-donor ligands with a small "bite", such as NO_3^- and NO_2^-.

29.3 Compounds of Zinc, Cadmium and Mercury(4-6)

Zinc hydride can be isolated from the reaction of LiH with $ZnBr_2$ or NaH with ZnI_2:

$$2MH + ZnX_2 \xrightarrow{\text{thf}} ZnH_2 + 2MX$$

The alkali metal halide remains in solution and ZnH_2 is precipitated as a white solid of moderate stability at or below room temperature.(7) CdH_2 and HgH_2 are much less stable and decompose rapidly even below 0°. The complex metal hydrides $LiZnH_3$, Li_2ZnH_4 and Li_3ZnH_5 have each been prepared as off-white powders by the reaction of $LiAlH_4$ with the appropriate organometallic complex Li_nZnR_{n+2}.

The carbides of these metals (which are actually acetylides, MC_2, p. 297) and also the nitrides are unstable materials, those of mercury explosively so.

29.3.1 Oxides and chalcogenides

The principal compounds in this category are the monochalacogenides, which are formed by all three metals. It is a notable indication of the stability of tetrahedral coordination for the elements of Group 12 that, of the 12 compounds of this type, only CdO, HgO and HgS adopt a structure other than wurtzite or zinc blende (both of which involve tetrahedral coordination of the cation — see below). CdO adopts the 6-coordinate rock-salt structure; HgO features zigzag chains of almost linear O–Hg–O units; and HgS exists in both a zinc-blende form and in a rock-salt form.

The normal oxide, formed by each of the elements of this group, is MO, and peroxides MO_2 are known for Zn and Cd. Reported lower oxides, M_2O, are apparently mixtures of the metal and MO.

ZnO is by far the most important manufactured compound of zinc(8) and, being an inevitable byproduct of primitive production of brass, has been known longer than the metal itself. It is manufactured by burning in air the zinc vapour obtained on smelting the ore or, for a purer and whiter product, the vapour obtained from previously refined zinc. It is normally a white, finely divided material with the wurtzite structure. On heating, the colour changes to yellow due to the evaporation of oxygen from the lattice to give a nonstoichiometric phase $Zn_{1+x}O$ ($x \leq 70\,\text{ppm}$); the supernumerary Zn atoms produce lattice defects which trap electrons which can subsequently be excited by absorption of visible light.(9) Indeed, by "doping" ZnO with an excess of 0.02–0.03% Zn metal, a whole range of colours — yellow, green, brown, red — can be obtained. The reddish hues of the naturally

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[4] M. FARNSWORTH, *Cadmium Chemicals*, International Lead Zinc Research Org. Inc., New York, 1980, 158 pp.

[5] C. A. MCAULIFFE (ed.), *The Chemistry of Mercury*, Macmillan, London, 1977, 288 pp.

[6] B. J. AYLETT, Group IIB, Chap. 30, pp. 187–328, in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1973.

[7] J. J. WATKINS and E. C. ASHBY, *Inorg. Chem.* **13**, 2350–4 (1974).

[8] See pp. 530–2 of W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH, Weinheim 1989.

[9] N. N. GREENWOOD, *Ionic Crystals, Lattice Defects and Nonstoichiometry*, Chaps. 6 and 7, pp. 111–81, Butterworths, London, 1968.

occurring form, zincite, arise, however, from the presence of Mn or Fe.

The major industrial use of ZnO is in the production of rubber where it shortens the time of vulcanization. As a pigment in the production of paints it has the advantage over the traditional "white lead" (basic lead carbonate) that it is non-toxic and is not discoloured by sulfur compounds, but it has the disadvantage compared to TiO_2 of a lower refractive index and so a reduced "hiding power" (p. 959). It improves the chemical durability of glass and so is used in the production of special glasses, enamels and glazes. Another important use is in antacid cosmetic pastes and pharmaceuticals. In the chemical industry it is the usual starting material for other zinc chemicals of which the soaps (i.e. salts of fatty acids, such as Zn stearate, palmitate, etc.) are the most important, being used as paint driers, stabilizers in plastics, and as fungicides. An important small scale use is in the production of "zinc ferrites". These are spinels of the type $Zn^{II}_xM^{II}_{1-x}Fe^{III}_2O_4$ involving a second divalent cation (usually Mn^{II} or Ni^{II}). When $x = 0$ the structure is that of an inverse spinel (i.e. half the Fe^{III} ions occupy octahedral sites — see p. 1081). Where $x = 1$, the structure is that of a normal spinel (i.e. all the Fe^{III} ions occupy octahedral sites), since Zn^{II} displaces Fe^{III} from the tetrahedral sites. Reducing the proportion of Fe^{III} ions in tetrahedral sites lowers the Curie temperature. The magnetic properties of the ferrite can therefore be controlled by adjustment of the zinc content.

ZnO is amphoteric (p. 640), dissolving in acids to form salts and in alkalis to form zincates, such as $[Zn(OH)_3]^-$ and $[Zn(OH)_4]^{2-}$. The gelatinous, white precipitate obtained by adding alkali to aqueous solutions of Zn^{II} salts is $Zn(OH)_2$ which, like ZnO, is amphoteric.

CdO is produced from the elements and, depending on its thermal history, may be greenish-yellow, brown, red or nearly black. This is partly due to particle size but more importantly, as with ZnO, is a result of lattice defects — this time in an NaCl lattice. It is more basic than ZnO, dissolving readily in acids but hardly at all in alkalis. White $Cd(OH)_2$ is precipitated from aqueous solutions of Cd^{II} salts by the addition of alkali and treatment with very concentrated alkali yields hydroxocadmiates such as $Na_2[Cd(OH)_4]$. Cadmium oxide and hydroxide find important applications in decorative glasses and enamels and in Ni–Cd storage cells. CdO also catalyses a number of hydrogenation and dehydrogenation reactions.

Treatment of the hydroxides of Zn and Cd with aqueous H_2O_2 produces hydrated peroxides of rather variable composition. That of Zn has antiseptic properties and is widely used in cosmetics.

HgO exists in a red and a yellow variety. The former is obtained by pyrolysis of $Hg(NO_3)_2$ or by heating the metal in O_2 at about 350°C; the latter by cold methods such as precipitation from aqueous solutions of Hg^{II} by addition of alkali ($Hg(OH)_2$ is not known). The difference in colour is entirely due to particle size, both forms having the same structure which consists of zigzag chains of virtually linear O–Hg–O units with Hg–O 205 pm and angle Hg–O–Hg 107°. The shortest $Hg \cdots O$ distance between chains is 282 pm.

Zinc blende, ZnS, is the most widespread ore of zinc and the main source of the metal, but ZnS is also known in a second naturally occurring though much rarer form, wurtzite, which is the more stable at high temperatures. The names of these minerals are now also used as the names of their crystal structures which are important structure types found in many other AB compounds. In both structures each Zn is tetrahedrally coordinated by 4 S and each S is tetrahedrally coordinated by 4 Zn; the structures differ significantly only in the type of close-packing involved, being cubic in zinc-blende and hexagonal in wurtzite (Fig. 29.1). Pure ZnS is white and, like ZnO, finds use as a pigment for which purpose it is often obtained (as "lithopone") along with $BaSO_4$ from aqueous solution of $ZnSO_4$ and BaS:

$$ZnSO_4 + BaS \longrightarrow ZnS\downarrow + BaSO_4\downarrow$$

Freshly precipitated ZnS dissolves readily in mineral acids with evolution of H_2S, but roasting renders it far less reactive and it is then an acceptable pigment in paints for children's toys since it is harmless if ingested. ZnS also has

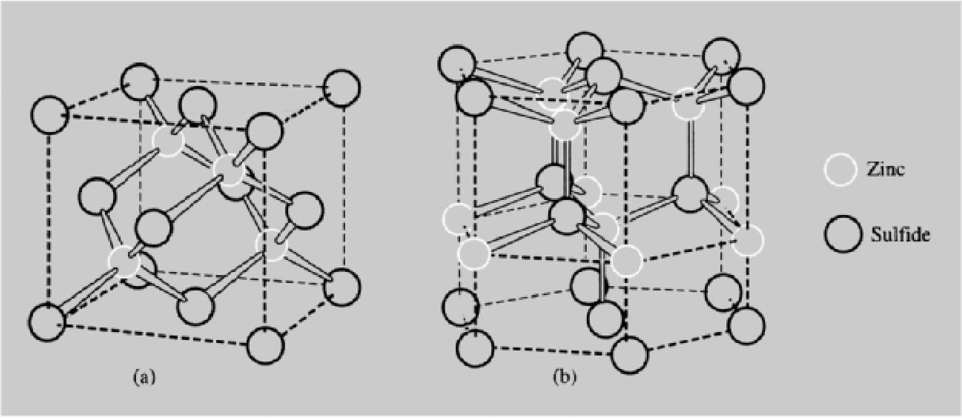

Figure 29.1 Crystal structures of ZnS. (a) Zinc blende, consisting of two, interpenetrating, ccp lattices of Zn and S atoms displaced with respect to each other so that the atoms of each achieve 4-coordination (Zn–S = 235 pm) by occupying tetrahedral sites of the other lattice. The face-centred cube, characteristic of the ccp lattice, can be seen — in this case composed of S atoms, but an extended diagram would reveal the same arrangement of Zn atoms. Note that if all the atoms of this structure were C, the structure would be that of diamond (p. 275). (b) Wurtzite. As with zinc blende, tetrahedral coordination of both Zn and S is achieved (Zn–S = 236 pm) but this time the interpenetrating lattices are hexagonal, rather than cubic, close-packed.

interesting optical properties. It turns grey on exposure to ultraviolet light, probably due to dissociation to the elements, but the process can be inhibited by trace additives such as cobalt salts. Cathode rays, X-rays and radioactivity also produce fluorescence or luminescence in a variety of colours which can be extended by the addition of traces of various metals or the replacement of Zn by Cd and S by Se. It is widely used in the manufacture of cathode-ray tubes and radar screens.

Yellow ZnSe and brown ZnTe are structurally akin to the sulfide and the former especially is used mainly in conjunction with ZnS as a phosphor.

Chalcogenides of Cd are similar to those of Zn and display the same duality in their structures. The sulfide and selenide are more stable in the hexagonal form whereas the telluride is more stable in the cubic form. CdS is the most important compound of cadmium and, by addition of CdSe, ZnS, HgS, etc., it yields thermally stable pigments of brilliant colours from pale yellow to deep red, while colloidal dispersions are used to colour transparent glasses. CdS and CdSe are also useful phosphors. CdTe is a semiconductor used as a detector for X-rays and γ-rays,(10) and mercury cadmium telluride(11) has found widespread (particularly military) use as an ir detector for thermal imaging.

HgS is polymorphic. The red α-form is the mineral cinnabar, or vermilion, which has a distorted rock-salt structure and can be prepared from the elements. β-HgS is the rare, black, mineral metacinnabar which has the zinc-blende structure and is converted by heat to the stable α-form. In the laboratory the most familiar form is the highly insoluble† black precipitate obtained by the action of H_2S on aqueous solutions of Hg^{II}. HgS is an unreactive substance, being attacked only by conc HBr, HI or aqua regia. HgSe and

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[10] M. Hage-Ali and P. Siffert, pp. 219–334 of *Semiconductors and Semimetals*, Vol. 43, Academic Press, San Diego, 1995.

[11] *ibid.* Vol. 18, 1981, 388 pp. devoted to mercury cadmium telluride.

† The solubility product, $[Hg^{2+}][S^{2-}] = 10^{-52}\ mol^2\ dm^{-6}$ but the actual solubility is greater than that calculated from this extremely low figure, since the mercury in solution is present not only as Hg^{2+} but also as complex species. In acid solution $[Hg(SH)_2]$ is probably formed and in alkaline

Table 29.3 Halides of zinc, cadmium and mecury (mp, bp, in parentheses)

Fluorides	Chlorides	Bromides	Iodides
ZnF_2 white (872°, 1500°)	$ZnCl_2$ white (275°, 756°)	$ZnBr_2$ white (394°, 702°)	ZnI_2 white (446°, d > 700°)
CdF_2 white (1049°, 1748°)	$CdCl_2$ white (568°, 980°)	$CdBr_2$ pale yellow (566°, 863°)	CdI_2 white (388°, 787°)
HgF_2 white (d > 645°)	$HgCl_2$ white (280°, 303°)	$HgBr_2$ white (238°, 318°)	HgI_2 α red, β yellow (257°, 351°)
Hg_2F_2 yellow (d > 570°)	Hg_2Cl_2 white (subl 383°)	Hg_2Br_2 White (subl 345°)	Hg_2I_2 yellow (subl 140°)

HgTe are easily obtained from the elements and have the zinc-blende structure.

29.3.2 Halides

The known halides are listed in Table 29.3. All 12 dihalides are known and in addition there are 4 halides of ${Hg_2}^{2+}$ which are conveniently considered separately. It is immediately obvious that the difluorides are distinct from the other dihalides, their mps and bps being much higher, suggesting a predominantly ionic character, as also indicated by their typically ionic three-dimensional structures (ZnF_2, 6:3 rutile; CdF_2 and HgF_2, 8:4 fluorite). ZnF_2 and CdF_2, like the alkaline earth fluorides, have high lattice energies and are only sparingly soluble in water, while HgF_2 is hydrolysed to HgO and HF. The anhydrous difluorides can be prepared by the action of HF (in the case of Zn) or F_2 (Cd and Hg) on the metal.

The other halides of Zn^{II} and Cd^{II} are in general hygroscopic and very soluble in water (~400 g per 100 cm^3 for ZnX_2 and ~100 g per 100 cm^3 for CdX_2). This is at least partly because of the formation of complex ions in solution, and the anhydous forms are best prepared by the dry methods of treating the heated metals with HCl, Br_2 or I_2 as appropriate. Aqueous preparative methods yield hydrates of which several are known. Significant covalent character is revealed by their comparatively low mps, their solubilities in ethanol, acetone and other organic solvents, and by their layer-lattice (2D) crystal structures. In all cases these may be regarded as close-packed lattices of halides ions in which the Zn^{II} ions occupy tetrahedral, and the Cd^{II} ions octahedral, sites. The structures of $CdCl_2$ ($CdBr_2$ is similar) and CdI_2 are of importance (Fig. 29.2) since they are typical of MX_2 compounds in which marked polarization effects are expected (see chap. 3, pp. 37–61 of ref. 9). Electron diffraction studies show that ZnX_2 (X = Cl, Br, I) have linear X–Zn–X structures in the gas phase.(12)

Concentrated, aqueous solutions of $ZnCl_2$ dissolve starch, cellulose (and therefore cannot be filtered through paper!), and silk. Commercially $ZnCl_2$ is one of the important compounds of zinc. It has applications in textile processing and, because when fused it readily dissolves other oxides, it is used in a number of metallurgical fluxes as well as in the manufacture of magnesia cements in dental fillings. Cadmium halides are used in the preparation of electroplating baths and in the production of pigments.

Covalency is still more pronounced in HgX_2 (X = Cl, Br, I) than in the corresponding

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solution, $[HgS_2]^{2-}$: the relevant equilibria are:

$$\begin{array}{rll}
HgS(s) \rightleftharpoons & Hg^{2+}(aq) + S^{2-}(aq); & pK_s\ 51.8 \\
HgS(s) + 2H^+(aq) \rightleftharpoons & Hg^{2+}(aq) + H_2S\ (1\ atm); & pK'\ 30.8 \\
HgS(s) + H_2S(g) \rightleftharpoons & [Hg(SH)_2](aq); & pK\ 6.2 \\
HgS(s) + S^{2-}(aq) \rightleftharpoons & [HgS_2]^{2-}(aq); & pK\ 1.5
\end{array}$$

(12) M. Hargittai, J. Tremmel and I. Hargittai, *Inorg. Chem.* **25**, 3163–6 (1986).

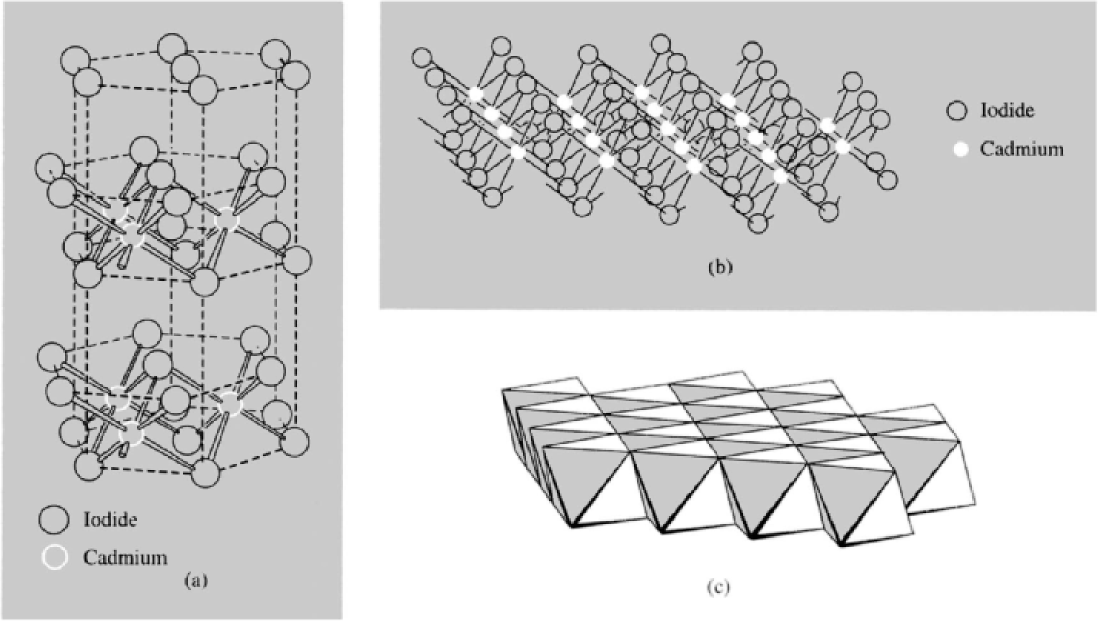

Figure 29.2 The layer structure of crystalline CdI_2: (a) Shows the hexagonal close-packing of I atoms with Cd atoms in alternate layers of octahedral sites sandwiched between layers of I atoms. In $CdCl_2$ the individual composite layers are identical with those in CdI_2, but they are arranged so that the Cl atoms are ccp. (b) Shows a portion of an individual composite layer of CdI_6 (or $CdCl_6$) octahedra. (c) Shows the same portion of a composite layer as in (b) and viewed from the same angle, but with CdI_2 (or $CdCl_2$) units represented by solid, edge-sharing octahedra.

halides of Zn and Cd. These compounds are readily prepared from the elements and are low-melting volatile solids, soluble in many organic solvents. Their solubilities in water, where they exist almost entirely as HgX_2 molecules, decrease with increasing molecular weight, HgI_2 being only slightly soluble, and they may be precipitated anhydrous from aqueous solutions by metathetical reactions. Their crystalline structures reveal an interesting gradation. $HgCl_2$ is composed of linear Cl–Hg–Cl molecules (Hg–Cl = 225 pm and the next shortest Hg $\cdots$ Cl distance is 334 pm); $HgBr_2$ and HgI_2 have layer structures. However, in the bromide although the Hg^{II} may be regarded as 6-coordinated, two Hg–Br distances are much shorter than the other four (248 pm compared to 323 pm). In the red variety of the iodide the Hg^{II} is unambiguously tetrahedrally 4-coordinated (Hg–I = 278 pm). At temperatures above 126°C HgI_2 exists as a less-dense, yellow form similar to $HgBr_2$. In the gaseous phase all 3 of these Hg^{II} halides exist as discrete linear HgX_2 molecules. Comparison of the Hg–X distances in these molecules (Hg–Cl = 228 pm, Hg–Br = 240 pm; Hg–I = 257 pm) with those given above, indicate an increasing departure from molecularity in passing from the solid chloride to the solid iodide.

$HgCl_2$ is the "corrosive sublimate" of antiquity, formerly obtained by sublimation from $HgSO_4$ and NaCl and used as an antiseptic. It is, however, a violent poison and was widely used as such in the Middle Ages.(5)

The halides are the most familiar compounds of mercury(I) and all contain the Hg_2^{2+} ion (see below). Hg_2F_2 is obtained by treating Hg_2CO_3 (itself precipitated by $NaHCO_3$ from aqueous $Hg_2(NO_3)_2$ which in turn is obtained by the action of dil HNO_3 on an excess of metallic mercury) with aqueous HF. It dissolves in water but is at once hydrolysed to the "black oxide" which is actually a mixture of Hg and HgO. On heating, it disproportionates to the metal and HgF_2. The other halides are virtually insoluble in water and so, being free from the possibility of hydrolysis, may be precipitated from aqueous solutions of $Hg_2(NO_3)_2$ by addition of X^-. Alternatively, they may be prepared by treatment of HgX_2 with the metal. Hg_2Cl_2 and Hg_2Br_2 are easily volatilized and their vapour densities correspond to "monomeric HgX". However, the diamagnetism of the vapour (Hg^I in HgX would be paramagnetic) and the ultraviolet absorption at the wavelength (253.7 nm) characteristic of Hg vapour, make it clear that decomposition to $Hg + HgX_2$ is the real reason for the halved vapour density. Hg_2I_2 decomposes similarly but even more readily, and the presence of finely divided metal is thought to be the cause of the greenish tints commonly found in samples of this otherwise yellow solid.

Calomel,[†] Hg_2Cl_2, has been widely used medicinally but possible contamination by the more soluble and poisonous $HgCl_2$ renders this a hazardous nostrum.

29.3.3 Mercury(I)

Raman spectra, indicative of $[M-M]^{2+}$ ions, are produced by the yellow glass obtained from the melt of Zn in $ZnCl_2$ and also by the colourless, very moisture sensitive crystals of $Cd_2Al_2Cl_8$ obtained from melts of Cd in $CdCl_2$ and $AlCl_3$. X-ray studies show that the latter contains "ethane-like" $[Cd_2Cl_6]^{4-}$ groups with Cd–Cd reported as 257.6 pm(13) and 256.1 pm(14) (cf 302 pm in the metal itself). The ^{113}Cd nmr spectrum(15) of $[Cd\{HB(3,5\text{-}Me_2pz)_3\}]_2$ (pz = polycyclic pyrazolyl ligand) yields a $^{111}Cd-^{113}Cd$ coupling constant of 20 646 Hz, indicating a Cd–Cd bond; the first to be observed in a molecular complex of Cd. However, only for mercury is the formal oxidation state I of importance.

Mercury(I) compounds in general may be prepared, like the halides just discussed, by the reduction of the corresponding Hg^{II} salt, often by the metal itself, or by precipitation from aqueous solutions of the nitrate. The nitrate is known as the dihydrate, $Hg_2(NO_3)_2.2H_2O$, and is stable in water if this is acidified, otherwise basic salts such as $Hg(OH)(NO_3)$ and $Hg_2(OH)(NO_3)$ are precipitated. The perchlorate is the only other appreciably soluble salt, the rest being either insoluble or, like the sulfate, chlorate and salts of organic acids, only sparingly soluble. In all cases the dinuclear $Hg_2{}^{2+}$ ion is present rather than mononuclear Hg^+. The evidence for this is overwhelming and includes the following:

1. In crystalline mercury(I) compounds, instead of the sequence of alternate M^+ and X^- expected for MX compounds, Hg–Hg pairs are found in which the separation, though not constant, lies in the range 250–270 pm(5) which is shorter than the Hg–Hg separation of 300 pm found in the metal itself.
2. The Raman spectrum of aqueous mercury(I) nitrate has, in addition to lines characteristic of the $NO_3{}^-$ ion, a strong absorption at 171.7 cm^{-1} which is not found in the spectra of other metal nitrates and is not active in the infrared; it is therefore diagnostic of the Hg–Hg stretching vibration since homonuclear diatomic vibrations are Raman active not infrared active.[†] Similar data have subsequently been produced for a number of other compounds in the solid state and in solution.

[†] Calomel, derived from the Greek words καλό-ς (beautiful) and μέλας (black), seems an odd name for a white solid. It might arise from the colour of the material obtained when Hg_2Cl_2 is treated with ammonia; this is a product of variable composition (see below) which owes its colour to the presence of metallic mercury. Other more fanciful derivations are listed in the *Oxford English Dictionary* **2**, 41 (1970).

[13] R. FAGGIANI, R. J. GILLESPIE and J. E. VEKRIS, *J. Chem. Soc., Chem. Commun.*, 517–8 (1986).

[14] T. STAFFEL and G. MEYER, *Z. anorg. allg. Chem.* **548**, 45–54 (1987).

[15] D. L. REGER, S. S. MASON and A. L. RHEINGOLD, *J. Am. Chem. Soc.* **115**, 10406–7 (1993).

[†] Indeed, this is perhaps the earliest example of a new structural species to be established by Raman spectroscopy. (L. A. WOODWARD, *Phil. Mag.* **18**, 823–7 (1934).)

(3) Mercury(I) compounds are diamagnetic, whereas the monatomic Hg^+ ion would have a $d^{10}s^1$ configuration and so be paramagnetic.

(4) The measured emfs of concentration cells of mercury(I) salts are only explicable on the assumption that a 2-electron transfer is involved. This would not be the case if Hg^+ were involved: [$E = (2.303RT/nF)\log a_1/a_2$ where $n = 2$ for $Hg_2{}^{2+}$ and $n = 1$ for Hg^+].

(5) It is found that "equilibrium constants" are in fact only constant if the concentration $[Hg_2{}^{2+}]$ is employed rather than $[Hg^+]^2$, i.e. the equilibria must be of the type:

$$2Hg + 2Ag^+ \rightleftharpoons Hg_2{}^{2+} + 2Ag$$

(rather than

$$Hg + Ag^+ \rightleftharpoons Hg^+ + Ag)$$

$$\text{or } Hg + Hg^{2+} \rightleftharpoons Hg_2{}^{2+}$$

(rather than

$$Hg + Hg^{2+} \rightleftharpoons 2Hg^+)$$

In order to understand the formation and stability of mercury(I) compounds it is helpful to consider the relevant reduction potentials:

$$Hg_2{}^{2+} + 2e^- \rightleftharpoons 2Hg(1); \quad E^\circ +0.7889\,V$$

$$\text{and} \quad 2Hg^{2+} + 2e^- \rightleftharpoons Hg_2{}^{2+}; \quad E^\circ +0.920\,V$$

From this it follows that

$$Hg^{2+} + 2e^- \rightleftharpoons Hg(l); \quad E^\circ +0.8545\,V$$

$$\text{and} \quad Hg_2{}^{2+} \rightleftharpoons Hg(l) + Hg^{2+}; \quad E^\circ -0.131\,V$$

Now, $E^\circ = (RT/nF)\ln K$,

i.e. $E^\circ = (0.0591/n)\log_{10} K$

Hence, $\log_{10} K = -(0.131/0.0591) = -2.217$,

i.e. $K = [Hg^{2+}]/[Hg_2{}^{2+}] = 0.0061$

Thus, at equilibrium, aqueous solutions of mercury(I) salts will contain around 0.6% of mercury(II) and the rather finely balanced equilibrium is easily displaced. The presence of any reagent which reduces the activity (in effect the concentration) of Hg^{2+} more than that of $Hg_2{}^{2+}$, either by forming a less-soluble salt or a more-stable complex of Hg^{2+} will displace the equilibrium to the right and cause the disproportionation of the $Hg_2{}^{2+}$. There are many such reagents, including S^{2-}, OH^-, CN^-, NH_3 and acetylacetone. This is why the most stable $Hg_2{}^{2+}$ salts are the insoluble ones and why there are few stable complexes. Those which are known all involve either *O*- or *N*-donor ligands,† the linear O–Hg–Hg–O group being a common feature of the former.

Polycations of mercury

The Hg–Hg bond in $Hg_2{}^{2+}$ may be ascribed to overlap of the 6s orbitals with little involvement of 6p orbitals or of the filled d^{10} shell of each atom. If this is regarded as the coordination of Hg to an Hg^{2+} cation, the coordination of a second Hg ligand is also feasible. Accordingly, $Hg_3(AlCl_4)_2$ can be obtained from a molten mixture of $HgCl_2$, Hg and $AlCl_3$ and contains the discrete, virtually linear cation

$$[Hg \overset{255\,\text{pm}}{\text{———}} Hg \text{———} Hg]^{2+}$$

in which the formal oxidation state of Hg is $+\frac{2}{3}$.

Still more interesting is the oxidation of Hg by AsF_5 in liquid SO_2:(16,17) in this process the AsF_5 serves both as an oxidant (being reduced to AsF_3) and also as a fluoride-ion acceptor to give $AsF_6{}^-$. In a matter of minutes the colour of the solution becomes bright yellow then deepens to red as the Hg simultaneously turns to a shiny golden-yellow solid; the solid then begins to dissolve to give an orange and, finally, a colourless solution. By controlling the quantity of oxidant, AsF_5, and removing the solution at the appropriate stages, it is possible to crystallize a series of extremely moisture-sensitive materials:

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† For this reason, although $Hg_2{}^{2+}$ must be regarded as a class-b cation (e.g. the aqueous solubilities of its halides decrease in the order F^- to I^-), it is evidently less so than Hg^{2+} which has a notable preference for *S* donors.

[16] I. D. Brown, W. R. Datars and R. J. Gillespie, pp. 1–41 in *Extended Linear Chain Compounds*, Plenum Press, New York, Vol. III (1982).

[17] R. J. Gillespie, P. Granger, K. R. Morgan and G. J. Schrobilgen, *Inorg. Chem.* **23**, 887–91 (1984).

(a) deep red-black $Hg_4(AsF_6)_2$, the cation of which is the almost linear

$$[\mathrm{Hg} \xrightarrow{255\,\mathrm{pm}} \mathrm{Hg} \xrightarrow{262\,\mathrm{pm}} \mathrm{Hg} \xrightarrow{259\,\mathrm{pm}} \mathrm{Hg}]^{2+}$$

with Hg in the formal average oxidation state $+\frac{1}{2}$;

(b) orange $Hg_3(AsF_6)_2$, containing the trimeric cation mentioned above; and

(c) colourless $Hg_2(AsF_6)_2$, containing the dimeric Hg^I cation.

By working at lower temperatures (−20°C) to reduce the reaction rate, or by using specially designed apparatus which limits the access of AsF_5 to the Hg, it has been possible to isolate large single crystals of the intermediate golden-yellow solid having dimensions up to $35 \times 35 \times 2\,\mathrm{mm}^3$. X-ray analysis, supported by neutron diffraction, shows that it consists of a tetragonal lattice ($a = b \neq c$) of octahedral AsF_6^- anions with two non-intersecting and mutually perpendicular chains of Hg atoms running through it in the a and b directions. Chemical analysis suggests the composition $Hg_3(AsF_6)$ and a formal oxidation state of Hg $= +\frac{1}{3}$. However, the measured Hg–Hg separation of 264 pm along the chains is not commensurate with the parallel dimensions of the lattice unit cell, $a = b = 754\,\mathrm{pm}$ (cf. $3 \times 264\,\mathrm{pm} = 792\,\mathrm{pm}$) and implies instead the nonstoichiometric composition $Hg_{2.82}(AsF_6)$ or more generally $Hg_{3-\delta}(AsF_6)$ since the composition apparently varies with temperature. Partially filled conduction bands formed by overlap of Hg orbitals produce a conductivity in the a–b plane which approaches that of liquid mercury and the material becomes superconducting at 4 K.

Use of SbF_5 instead of AsF_5 produces a series of entirely analogous compounds including $Hg_{3-\delta}(SbF_6)$ but because the unit cell of the $(SbF_6)^-$ lattice is somewhat larger than that of $(AsF_6)^-$, it is formulated as $Hg_{2.90}(SbF_6)$. Oxidations of Hg by $Hg(MF_6)_2$ (M = Nb, Ta) in SO_2 also yield $Hg_{3-\delta}(MF_6)$ but, unlike the As and Sb compounds, these convert in a few hours into silver platelets of Hg_3MF_6 which consist of two sheets of F atoms separated by hexagonal sheets (rather than linear chains) of Hg atoms.[18]

29.3.4 Zinc(II) and cadmium(II)[19]

The almost invariable oxidation state of these elements is +2 and, in addition to the oxides, chalcogenides and halides already discussed, salts of most anions are known. Oxo-salts are often isomorphous with those of Mg^{II} but with lower thermal stabilities. The carbonates, nitrates, and sulfates all decompose to the oxides on heating. Several, such as the nitrates, perchlorates and sulfates, are very soluble in water and form more than one hydrate. $[Zn(H_2O)_6]^{2+}$ is probably the predominant aquo species in solutions of Zn^{II} salts. Aqueous solutions are appreciably hydrolysed to species such as $[M(OH)(H_2O)_x]^+$ and $[M_2(OH)(H_2O)_x]^{3+}$ and a number of basic (i.e. hydroxo) salts such as $ZnCO_3.2Zn(OH)_2.H_2O$ and $CdCl_2.4Cd(OH)_2$ can be precipitated. Distillation of zinc acetate under reduced pressure yields a crystalline basic acetate, $[Zn_4O(OCOMe)_6]$. The molecular structure of this consists of an oxygen atom surrounded by a tetrahedron of Zn atoms bridged across each edge by acetates. It is isomorphous with the basic acetate of beryllium (p. 122) but, in contrast, the Zn^{II} compound hydrolyses rapidly in water, no doubt because of the ability of Zn^{II} to increase its coordination number above 4.

The coordination chemistry of Zn^{II} and Cd^{II}, although much less extensive than for preceding transition metals, is still appreciable. Neither element forms stable fluoro complexes but, with the other halides, they form the complex anions $[MX_3]^-$ and $[MX_4]^{2-}$, those of Cd^{II} being moderately stable in aqueous solution.[4] By using the large cation $[Co(NH_3)_6]^{3+}$ it is also possible to isolate the trigonal bipyramidal $[CdCl_5]^{2-}$

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[18] I. D. Brown, R. J. Gillespie, K. R. Morgan, Z. Tun and P. K. Ummat, *Inorg. Chem.* **23**, 4506–8 (1984).

[19] R. H. Prince, Zinc and Cadmium Chap. 56.1, pp. 925–1045, in *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.

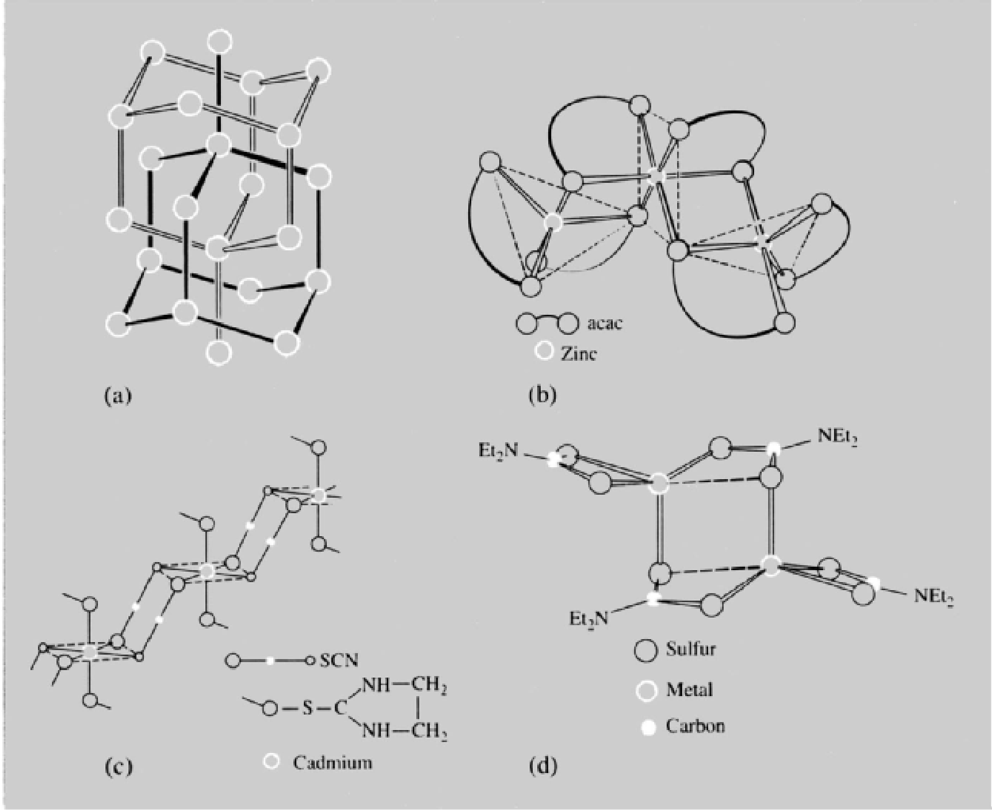

Figure 29.3 Some polymeric complexes: (a) Interpenetrating "adamantine" frameworks in $M(CN)_2$, M = Zn, Cd. (Only M shown; straight lines are CN forming linear MCNM "rods".) (b) $[Zn(acac)_2]_3$, (c) $[Cd\{S{=}C(NHCH_2)_2\}_2(SCN)_2]$, and (d) $[M(S_2CNEt_2)_2]_2$, M = Zn, Cd, Hg. (Note that M is 5-coordinate but with one M–S distance appreciably greater than the other four.)

$[MX_3]^-$ and $[MX_4]^{2-}$ are formed in CH_3CN solutions also.(20) Tetrahedral complexes are the most common type and are formed with a variety of *O*-donor ligands (more readily with Zn^{II} than Cd^{II}), more stable ones with *N*-donor ligands such as NH_3 and amines. Some of the apparently 3-coordinate complexes have a higher coordination number because of aquation or association but, no doubt because the ligand is bulky, 2-coordinated Zn occurs in $[Zn\{N(CMe_3)(SiMe_3)\}_2]$, the first homoleptic zinc amide to be structurally characterized.(21)

The ability of CN^- to co-ordinate through either C or N has interesting stereochemical consequences. Crystalline $M(CN)_2$ consist of linear M–C–N–M "rods" and tetrahedrally co-ordinated M^{II}, arranged so as to form interpenetrating "adamantine" frameworks (Fig. 29.3a). Each "rod" projects through a cyclohexane-like "window" of the other framework with the M atoms at each end occupying cavities of the other framework.(22) When aqueous solutions of $CdCl_2 + K[Cd(CN)_4]$ are left in contact with liquids such as CCl_4, $CMeCl_3$ ...... CMe_4, crystals of the clathrates $Cd(CN)_2.G$ form at the interface

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(20) D. P. GRADDON and C. S. KHOO, *Polyhedron* **7**, 2129–33 (1988).

(21) W. S. REES Jr., D. M. GREEN and W. HESSE, *Polyhedron*, **11**, 1697–9 (1992).

(22) B. F. HOSKINS and R. ROBSON, *J. Am. Chem. Soc.* **112**, 1546–54 (1990).

of the immiscible liquids.(23) In these, the guest molecules G, occupy the cavities of a single adamantine framework. $(NMe_4)[Cu^IZn(CN)_4]$ consists of a similar framework but this time half the cavities are occupied by NMe_4^+ cations. Another type of framework is found in $Cd(CN)_2.\frac{2}{3}H_2O.Bu^tOH$ *which crystallizes from* 50% aqueous Bu^tOH solutions of $Cd(CN)_2$. It contains CdCNCd "rods" but this time they are bent, $\frac{2}{3}$ of the Cd atoms are tetrahedrally co-ordinated by $4CN^-$, the other $\frac{1}{3}$ being octahedrally co-ordinated by $4CN^-$ and $2H_2O$. The result is a honeycomb framework with linear channels of hexagonal cross-section containing disordered Bu^tOH molecules.(24) Linear channels are also found in $Cd(CN)_2.G$ ($G = $ dmf, dmso)(25) but the large cation in $(PPh_4)_3[(CN)_3CdCNCd(CN)_3]$ apparently prevents the formation of a 3D framework and instead stabilizes the discrete anion.(26)

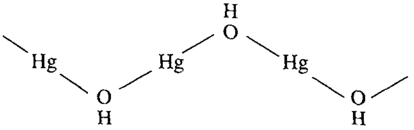
Complexes of higher coordination number are often in equilibrium with the tetrahedral form and may be isolated by increasing the ligand concentration or by adding large counter ions, e.g. $[M(NH_3)_6]^{2+}$, $[M(en)_3]^{2+}$ or $[M(bipy)_3]^{2+}$. With acetylacetone, zinc achieves both 5- and 6-coordination by trimerizing to $[Zn(acac)_2]_3$ (Fig. 29.3b). Five-coordination is also found in adducts such as the distorted trigonal bipyramidal $[Zn(acac)_2(H_2O)]$ and $[Zn(glycinate)_2(H_2O)]$ while the hydrazinium sulfate $(N_2H_5)_2Zn(SO_4)_2$ contains 6-coordinated zinc. This is isomorphous with the Cr^{II} compound (p. 1031) and in the crystalline form consists of chains of Zn^{II} bridged by SO_4^{2-} ions, with each Zn^{II} additionally coordinated to two *trans*-$N_2H_5^+$ ions. The zinc porphyrin complex, [Zn(porph)(thf)], (porph = *meso*-tetraphenyltetrabenzoporphyrin) is approximately square pyramidal with thf at its apex. Being somewhat flexible the porphyrin is distorted into a saddle shape, 2 N being displaced above its mean plane and 2 N below it.(27)

Complexes with SCN^- throw light on the relative affinities of the two metals for *N*- and *S*-donors. In $[Zn(NCS)_4]^{2-}$ the ligand is *N*-bonded whereas in $[Cd(SCN)_4]^{2-}$ it is *S*-bonded. SCN^- can also act as a bridging group, as in $[Cd\{S{=}C(NHCH_2)_2\}_2(SCN)_2]$ when linear chains of octahedrally coordinated Cd^{II} are formed (Fig. 29.3c). A number of zinc–sulfur compounds are used as accelerators in the vulcanization of rubber. Among these are the dithiocarbamates, of which $[Zn(S_2CNEt_2)_2]_2$, and the isostructural Cd^{II} and Hg^{II} compounds achieve 5-coordination by dimerizing (Fig. 29.3d).

Coordination numbers higher than 6 are rare and in some cases are known to involve chelating NO_3^- *ions which not only have a small "bite"* but, may also be coordinated asymmetrically so that the coordination number is not well defined.

29.3.5 Mercury(II)(28)

The oxide (p. 1209), chalcogenides (p. 1210) and halides (p. 1211) have already been described. Of them, the only ionic compound is HgF_2 but other compounds in which there is appreciable charge separation are the hydrated salts of strong oxoacids, e.g. the nitrate, perchlorate, and sulfate. In aqueous solution such salts are extensively hydrolysed (HgO is only very weakly basic) and they require acidification to prevent the formation of polynuclear hydroxo-bridged species or the precipitation of basic salts such as $Hg(OH)(NO_3)$ which contains infinite zigzag chains:



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[23] T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 413–5 (1992); T. Kitazawa, T. Kikoyama, M. Takeda and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, 3715–20 (1995).

[24] B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 60–1 (1990).

[25] J. Kim, D. Whang, Y.-S. Koh and K. Kim, *J. Chem. Soc., Chem. Commun.*, 637–8 (1994).

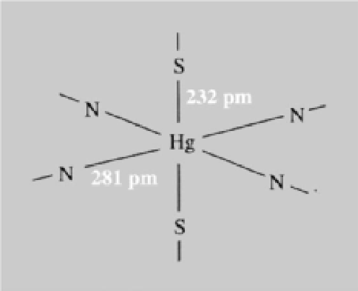
[26] T. Kitazawa and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 309–10 (1993).

[27] R.-J. Cheng, Y.-R. Chen, S. L. Wang and C. Y. Cheng, *Polyhedron*, **12**, 1353–60 (1993).

[28] K. Brodersen and H.-U. Hummel, Mercury, Chap. 56.2, pp. 1047–1130, in *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.

Their ionic character is symptomatic of the marked reluctance of Hg^{II} to form covalent bonds to oxygen. In the presence of excess NO_3^- ions the aqueous nitrate forms the complex anion $[Hg(NO_3)_4]^{2-}$ in which 8 oxygen atoms from the bidentate nitrate groups are equidistant from the mercury at 240 pm, which is almost precisely the sum of the ionic radii (140 + 102 pm). Also, the unusual regular octahedral coordination is found in complexes with *O*-donor ligands: $[Hg(C_5H_5NO)_6]^{2+}$ ($Hg-O = 235$ pm), $[Hg(H_2O)_6]^{2+}$ ($Hg-O = 234$ pm), and $[Hg(Me_2SO)_6]^{2+}$ ($Hg-O = 234$ pm). In contrast, the more covalently bonding β-diketonates do not form complexes.

The most usual type of coordination in compounds of Hg^{II} with other donor atoms is a distorted octahedron with 2 bonds much shorter than the other 4. In the extreme, this results in linear 2-coordination in which case the bonds are largely covalent. $Hg(CN)_2$ is actually composed of discrete linear molecules (*C*-bonded CN^-), whereas crystalline[†] $Hg(SCN)_2$ is built up of distorted octahedral units, all SCN groups being bridging:



With both these pseudo halides, an excess produces complex anions $[HgX_3]^-$ and the tetrahedral $[HgX_4]^{2-}$.

Similar halogeno complexes are produced in solution, and several salts of $[HgX_3]^-$ have been isolated and characterized; they display a variety of stereochemistries. In $[HgCl_3]^-$ the environment of the Hg^{II} is either distorted octahedral (with small cations such as NH_4^+ or Na^+) or distorted trigonal bipyramidal (with larger cations such as $[NEt_4]^+$, $[SMe_3]^+$ or $[NH_2\{(CH_2)_2NH_3\}_2]^{3+}$(29)), whereas in salts of $[HgBr_3]^-$ and $[HgI_3]^-$ the coordination is more commonly distorted tetrahedral. In $[NBu^n_4][HgI_3]$ the anion is planar but, with one I–Hg–I angle 115°, its symmetry is C_{2v} rather than D_{3h}. In aqueous solution spectroscopic evidence suggests that $[HgCl_3]^-$ is planar with $2H_2O$ completing a trigonal bipyramidal coordination sphere; $[HgI_3]^-$ is pyramidal with H_2O completing a tetrahedral coordination sphere, while $[HgBr_3]^-$ shows features of both structures.(30)

In the presence of excess halide, $[HgX_4]^{2-}$ complex ions are produced and in comparison with those of Zn^{II} and Cd^{II} it can be seen that their stabilities increase with the sizes of the anion and the cation so that $[HgI_3]^{2-}$ is the most stable of all. Thus, the normally very insoluble HgI_2 will dissolve in aqueous solutions of I^- which can then be made strongly alkaline without precipitation occurring. Such solutions are known as Nessler's reagent, which is used as a sensitive test for ammonia since this produces a yellow or brown coloration due to the formation of $Hg_2NI.H_2O$, the iodo salt of Millon's base (see p. 1220). Adducts of the halides HgX_2, with *N*-, *S*-, and *P*-donor ligands are known, those with *N*-donors being especially numerous. Their stereochemistries are largely of the expected tetrahedral, or grossly distorted octahedral, types.

Hg^{II}–N compounds(5,28)

Mercury has a characteristic ability to form not only conventional ammine and amine complexes but also, by the displacement of hydrogen, direct covalent bonds to nitrogen, e.g.:

$$Hg^{2+} + 2NH_3 \rightleftharpoons [Hg-NH_2]^+ + NH_4^+$$

[†] Pellets of the dry powder, when ignited in air, form snake-like tubes of spongy ash of unknown composition — the so-called "Pharaoh's serpents".

[29] The compound $[NH_2\{(CH_2)_2NH_3\}_2]_2HgCl_8$ contains the trigonal bipyramidal anion $[HgCl_5]^{3-}$; see L. P. BATTAGLIA, A. B. CORRADI, L. ANTOLINI, T. MANFREDINI, L. MENABUE, G. C. PELLACANI and G. PONTICELLI, *J. Chem. Soc., Dalton Trans.*, 2529–33 (1986).

[30] T. R. GRIFFITHS and R. A. ANDERSON, *J. Chem. Soc., Faraday*, **86**, 1425–35 (1990).

Thus in the presence of an excess of NH_4^+, which suppresses this forward reaction, and counteranions such as NO_3^- and ClO_4^-, which have little tendency to coordinate, complexes such as $[Hg(NH_3)_4]^{2+}$, $[Hg(L\text{-}L)_2]^{2+}$ and even $[Hg(L\text{-}L)_3]^{2+}$ (L-L = en, bipy, phen) can be prepared. But, in the absence of such precautions, amino, or imino-compounds are likely to be formed, often together. Because of this variety of simultaneous reactions and their dependence on the precise conditions, many reactions between Hg^{II} and amines, although first performed by alchemists in the Middle Ages, remained obscure until the application of X-ray crystallography and, still more recently, spectroscopic techniques such as nmr, infrared and Raman.

The action of aqueous ammonia on $HgCl_2$, for instance, may be described by the three reactions:

$$HgCl_2 + 2NH_3 \rightleftharpoons [Hg(NH_3)_2Cl_2] \tag{1}$$

$$[Hg(NH_3)_2Cl_2] \rightleftharpoons [Hg(NH_2)Cl] + NH_4Cl \tag{2}$$

$$2[Hg(NH_2)Cl] + H_2O \rightleftharpoons [Hg_2NCl(H_2O)] + NH_4Cl \tag{3}$$

In general, all these products are obtained in proportions which depend on the concentrations of NH_3 and NH_4^+ and on the temperature, but more or less pure products can be prepared by suitably adjusting the conditions.

The diammine $[Hg(NH_3)_2Cl_2]$, descriptively known as "fusible white precipitate", can be isolated by maintaining a high concentration of NH_4^+, since reactions (2) and (3) are thereby inhibited, or better still by using non-polar solvents. It is made up of a cubic lattice of Cl^- ions with linear $H_3N\text{-}Hg\text{-}NH_3$ groups inserted so as to give the common, distorted octahedral coordination about Hg^{II} (Hg–N = 203 pm, Hg–Cl = 287 pm) (Fig. 29.4a).

By using a low concentration of NH_3 and with no NH_4^+ initially present, the amide $[Hg(NH_2)Cl]$, "infusible white precipitate" is

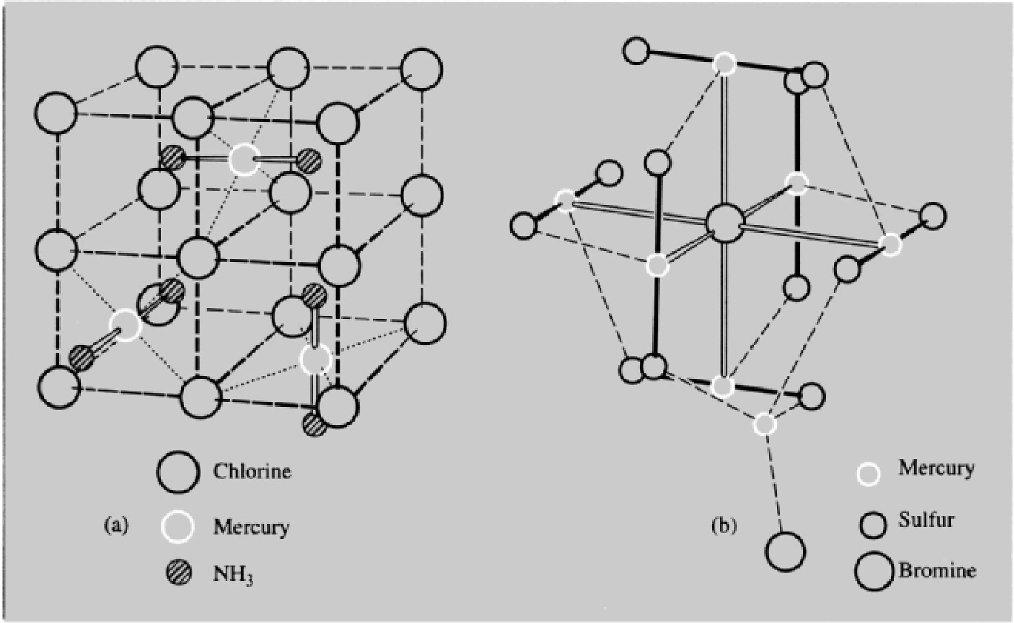
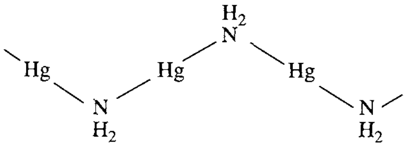


Figure 29.4 (a) Crystal structure of $Hg(NH_3)_2Cl_2$ showing linear $NH_3\text{-}Hg\text{-}NH_3$ groups inside a lattice of chloride ions. (b) Central $Hg_7S_{12}Br_2$ core of $[Hg_7(SC_6H_{11})_{12}Br_2]$ showing, in an idealized manner, the octahedron of Hg atoms around a central Br. The tetrahedral coordination of the seventh Hg is completed with the second Br.



obtained. This consists of parallel chains of $\{Hg(NH_2)\}_\infty$ as above, separated by Cl^- ions.

$[Hg_2NCl(H_2O)]$ is the chloride of Millon's base, $[Hg_2N(OH).(H_2O)_2]$, and can be obtained either by heating the diammine, or amide with water or, better still, by the action of hydrochloric acid on Millon's base which is best prepared by the method, used in 1845 by its discoverer, of warming yellow HgO with aqueous NH_3. Replacement of the OH^- yields a series of salts, $[Hg_2NX(H_2O)]$, the structures of which (and that of the base itself) consist, with only minor variations, of a network of $\{Hg_2N\}^+$ units linked so that each N is tetrahedrally linked to 4 Hg and each Hg is linearly linked to 2 N (Hg–N = 204–209 pm depending on X).(31) The X^- ions and water molecules are accommodated interstitially and these materials behave as anion exchangers.

When Hg_2Cl_2 is treated with aqueous NH_3 disproportionation occurs ($Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$); the $HgCl_2$ then reacts as outlined above to give a precipitate of variable composition. The liberated mercury, however, renders the precipitate black, as previously mentioned, and so forms the basis of a distinctive qualitative test for Hg_2^{2+}.

Hg^{II}–S compounds(32)

As indicated by the insolubility and inertness of HgS, Hg^{II} has a great affinity for sulfur. HgO reacts vigorously with mercaptans (which is why RSH were given the name mercaptans†), displacing the H as with amines:

$$HgO + 2RSH \longrightarrow Hg(SR)_2 + H_2O$$

These mercaptides are low-melting solids, soluble in $CHCl_3$ and C_6H_6. Though their structures depend on R and some, such as $Hg(SR)_2$, (R = Bu^t, Ph) are polymers containing tetrahedral HgS_4 units, most contain linear (or nearly linear) S–Hg–S. Even in $[Hg(SC_6H_2Bu^t_3)_2(py)]$ where the Hg is 3-coordinate and T-shaped the S–Hg–S is still nearly linear (172°).(33) Most of the thioether (SR_2) complexes which have been prepared are adducts of the Hg^{II} halides and include both monomeric and polymeric (i.e. X-bridged) species as is the case with mixed thiolate–halide complexes. In $[Hg_7(SC_6H_{11})_{12}Br_2]$, which is obtained as colourless crystals when methanolic solutions of $HgBr_2$ and sodium cyclohexanethiolate are mixed, six Hg atoms are 4-coordinate but contain almost linear S–Hg–S (av. angle = 159.3°) and the seventh Hg is tetrahedrally coordinated. The six Hg atoms form a distorted octahedron around a central Br (Fig. 29.4b).(34) The dithiocarbamate $[Hg(S_2CNEt_2)_2]$ exists in two forms, one of which has the same structure as the corresponding Zn^{II} and Cd^{II} compounds (Fig. 29.3d), while the other is polymeric.

Cluster compounds involving mercury(35,36)

Mercury has a marked ability to bond to other metals. In addition to the amalgams already mentioned (p. 1206) it acts as a versatile structural building block by forming Hg–M bonds with cluster fragments of various types: e.g. reduction

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(31) A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984: the structural chemistry of mercury is reviewed on pp. 1156–69.

(32) J. G. Wright, M. J. Natan, F. M. MacDonnell, D. M. Ralston and T. V. O'Halloran, *Prog. Inorg. Chem.* **38**, 323–412 (1990).

† Mercaptans were discovered in 1834 by W. C. Zeise (pp. 930, 1167) who named them from the Latin *mercurium captans*, catching mercury.

(33) M. Bochmann, K. J. Webb and A. K. Powell, *Polyhedron* **11**, 513–6 (1992).

(34) T. Alsina, W. Clegg, K. A. Fraser and J. Sola, *J. Chem. Soc., Chem. Commun.*, 1010–1 (1992).

(35) L. H. Gade, *Angew. Chem. Int. Edn. Engl.* **32**, 23–40 (1993).

(36) R. B. King, *Polyhedron*, **7**, 1813–7 (1988).

Table 29.4 Comparison of some typical organometallic compounds MR_2

R	Zn		Cd		Hg	
	MP/°C	BP/°C	MP/°C	BP/°C	MP/°C	BP/°C
Me	−29.2	46	−4.5	105.5	—	92.5
Et	−28	117	−21	64 (19 mmHg)	—	159
Ph	107	d 280	173	—	121.8 (subl)	204 (10 mmHg)

of $[RhCl(PMe_3)_3]$ with Na amalgams gives $Hg_6[Rh(PMe_3)_3]_4$ which consists of an Hg_6 octahedron, four faces of which are capped by $Rh(PMe_3)_3$ groups. Again, Hg^{II} halides react with carbonylate anions yielding products such as $[Os_3(CO)_{11}Hg]_3$ comprising a most unusual "raft" structure in which three Os_3 triangles surround a central Hg_3 triangle in a planar array. From $[Os_{10}C(CO)_{24}]^{2-}$ it is possible to obtain $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ the central portion of which is an $HgOs_2$ triangle. Whereas the "raft" cluster has no redox chemistry, the $\{Os_{20}Hg\}$ cluster like the Os_{10} cluster (p. 1108) from which it is formed, gives rise to five different redox states.

29.3.6 Organometallic compounds[37]

Although they were not the first organometallic compounds to be prepared (Zeise's salt was discovered in 1827) the discovery of zinc alkyls in 1849 by Sir Edward Frankland may be taken as the beginning of organometallic chemistry. Frankland's studies led to their employment as intermediates in organic synthesis, while the measurements of vapour densities led to his suggestion, crucial to the development of valency theory, that each element has a limited but definite combining capacity. After their discovery in 1900 Grignard reagents largely superseded the zinc alkyls in organic synthesis, but by then many of the reactions for which they are now used had already been worked out on the zinc compounds.

Alkyls of the types RZnX and ZnR_2 are both known and may be prepared by essentially the original method of heating Zn with boiling RX in an inert atmosphere (CO_2 or N_2):

$$Zn + RX \longrightarrow RZnX$$

and then raising the temperature to distil the dialkyl:

$$2RZnX \longrightarrow ZnR_2 + ZnX_2$$

These reactions work best with X = I but the less-expensive RBr can be used in conjunction with a Zn–Cu alloy instead of pure Zn. Diaryls are best obtained from appropriate organoboranes or organomercury compounds:

$$3ZnMe_2 + 2BR_3 \longrightarrow 3ZnR_2 + 2BMe_3$$

or $$Zn + HgR_2 \longrightarrow ZnR_2 + Hg$$

ZnR_2 are covalent, non-polar liquids or low-boiling solids (Table 29.4). They are invariably monomeric in solution with linear C–Zn–C coordination at the Zn atom. They are very susceptible to attack by air and those of low molecular weight are spontaneously flammable, producing a smoke of ZnO. Their reactions with water, alcohols and ammonia, etc., are generally similar to, but less vigorous than, those of Grignard reagents (p. 132) with the important difference that they are unaffected by CO_2; indeed, they are often prepared under an atmosphere of this gas.

Organocadmium compounds are normally prepared from the appropriate Grignard reagents:

$$CdX_2 + 2RMgX \longrightarrow CdR_2 + 2MgX_2$$

and then if desired:

$$CdR_2 + CdX_2 \longrightarrow 2RCdX$$

They are thermally less stable than their Zn counterparts but generally less reactive (not normally

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[37] J. L. WARDELL, *Organometallic Compounds of Zinc, Cadmium and Mercury*, Chapman & Hall, London, 1985, 220 pp.

catching fire in air), and so their most important use (but see also ref. 38) is to prepare ketones from acid chlorides:

$$2R'COCl + CdR_2 \longrightarrow 2R'COR + CdCl_2$$

The use of Grignard reagents is impracticable here since they react further with the ketone.

An enormous number of organomercury compounds are known. They are predominantly of the same stoichiometries as those of Zn and Cd, viz. RHgX and HgR_2, and may be prepared by the action of sodium amalgam on RX:

$$2Hg + 2RX \longrightarrow HgR_2 + HgX_2$$
$$HgCl_2 + 2Na \longrightarrow Hg + 2NaCl$$

More usually they are made by the reaction of Grignard reagents on $HgCl_2$ in thf:

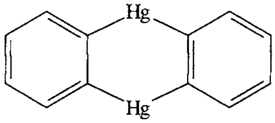
$$RMgX + HgCl_2 \longrightarrow RHgCl + MgXCl$$
$$RMgX + RHgCl \longrightarrow HgR_2 + MgXCl$$

or simply by the action of HgX_2 on a hydrocarbon:

$$HgX_2 + RH \longrightarrow RHgX + HX \text{ (mercuration).}$$

RHgX are crystalline solids, and HgR_2 are extremely toxic liquids or low-melting solids (Table 29.4). They are essentially covalent materials except when $X^- = F^-$, $NO_3{}^-$ or $SO_4{}^{2-}$, in which cases the former are water-soluble and apparently ionic, $[RHg]^+X^-$. There are several reasons for the attention which these compounds have received. The search for pharmacologically valuable drugs has provided a continuing stimulus, and the existence of convenient preparative methods, coupled with their remarkable stability to air and water, has led to their extensive use in mechanistic studies. This stability sets them apart from the organic derivatives of Zn, Cd and Group 2 metals but arises from the extreme weakness of the Hg–O bond rather than an inherently strong Hg–C bond. In fact the latter is weak, being commonly only ~60 kJ mol^{-1} and organomercury compounds are thermally and photochemically unstable, in some cases requiring to be stored at low temperatures in the dark. Indeed, because of the weakness of the bond, Hg can be replaced by many metals which give stronger M–C bonds and the preparation of organo derivatives of other metals (e.g. of Zn and Cd as referred to above) is the most important application of these compounds.

It appears that all RHgX and HgR_2 compounds are made up of linear R–Hg–X or R–Hg–R units, which could arise from sp hybridization of the metal.† In some cases polymerization is necessary to achieve this linearity. Thus, for instance, *o*-phenylene-mercury, which could conceivably be formulated as



is in fact a cyclic trimer (Fig. 29.5a).(39) Organomercury compounds generally have little tendency to coordinate to further ligands. Exceptions include irregularly 3-coordinated $[HgMe(bipy)]NO_3$(40) and [HgR(Hdz)],(41) T-shaped [Hg(2-pyridylphenyl)Cl](42) (Fig. 29.5b, c, d) and the tetrahedral $[HgMe(np_3)]^+$ (np_3 is the "tripod" phosphine $N\{CH_2CH_2PPh_2\}_3$).(43)

Among the versatile and synthetically useful reactions are those typified by the absorption of alkenes (olefins) by methanolic solutions of salts, particularly, the acetate of Hg^{II}. The products are not π complexes, but σ-bonded addition

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(38) P. R. Jones and P. J. Desio, *Chem. Revs.* **78**, 491–516 (1978).

† Other possibilities which have been suggested include ds hybridization and minimization of interaction between metal d and non bonding ligand p orbitals — see pp. 351–2 of ref. 32.

(39) D. S. Brown, A. G. Massey and D. A. Wickens, *Acta. Cryst.* **B34**, 1695–7 (1978).

(40) A. J. Canty and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.*, 2018–20 (1976).

(41) A. T. Hutton and H. M. N. H. Irving, *J. Chem. Soc., Chem. Commun.*, 1113–4 (1979).

(42) E. C. Constable, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 570–1 (1989).

(43) C. A. Ghilardi, P. Innocenti, S. Midollini, A. Orlandini and A. Vacca, *J. Chem. Soc., Chem. Commun.*, 1691–3 (1992).

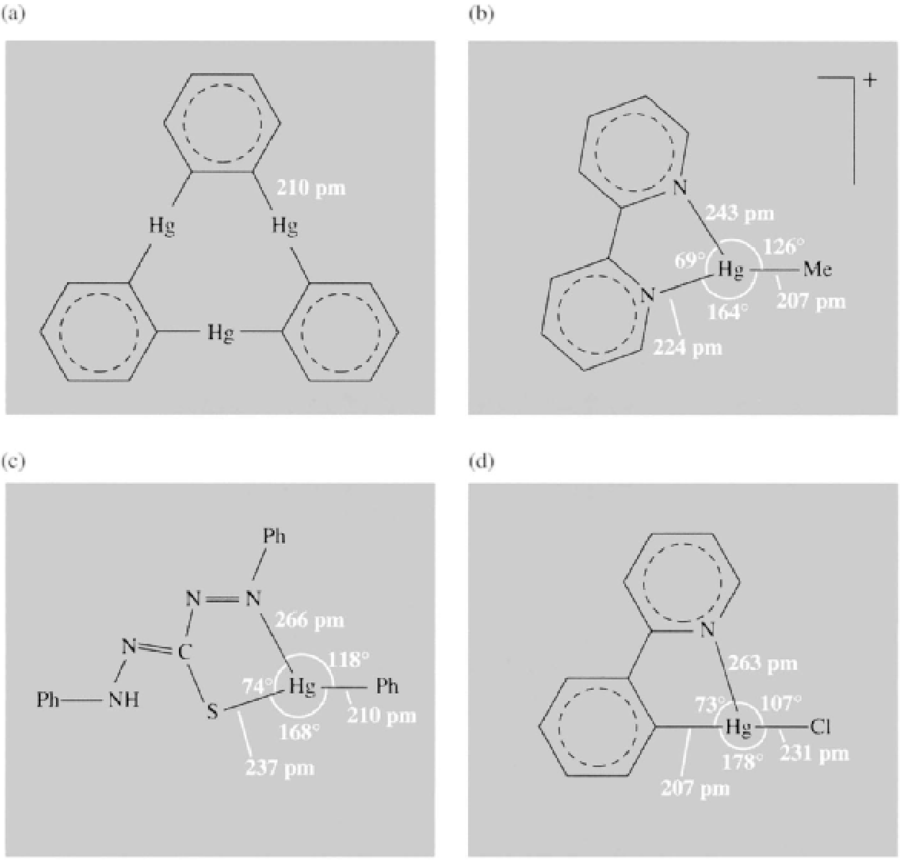
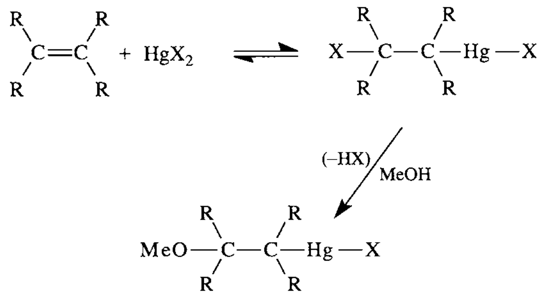


Figure 29.5 (a) *o*-Phenylenemercury trimer, (b) the planar cation in [HgMe(bipy)]NO_3, (c) phenylmercury(II)dithizonate, and (d) the approximately T-shaped [Hg(2-pyridylphenyl)Cl].

compounds, e.g.:



Regeneration of the alkene occurs on acidification, e.g. with HCl:

$$R_2C(OMe)C(HgX)R_2 + HCl \longrightarrow R_2C{=}CR_2 + MeOH + HgXCl$$

Methanolic solutions of Hg^{II} also absorb CO and the products, of the type XHgC(=O)OMe are again σ-bonded.

A similar reluctance to form π bonds is seen in the cyclopentadienyls of mercury such as $[Hg(\eta^1\text{-}C_5H_5)_2]$ and $[Hg(\eta^1\text{-}C_5H_5)X]$. As they are photosensitive and single crystals are very difficult to obtain, structural information has been derived mainly from infrared and nmr data. These show that the rings are monohapto and the compounds fluxional, i.e. the point of attachment of the Hg to the ring changes rapidly on the nmr time scale so that the 5 carbons are indistinguishable — the phenomenon of "ring whizzing". In the case of $[Hg(\eta^1\text{-}C_5H_4PPh_3)I_2]_2$ it has been possible to determine the structure by

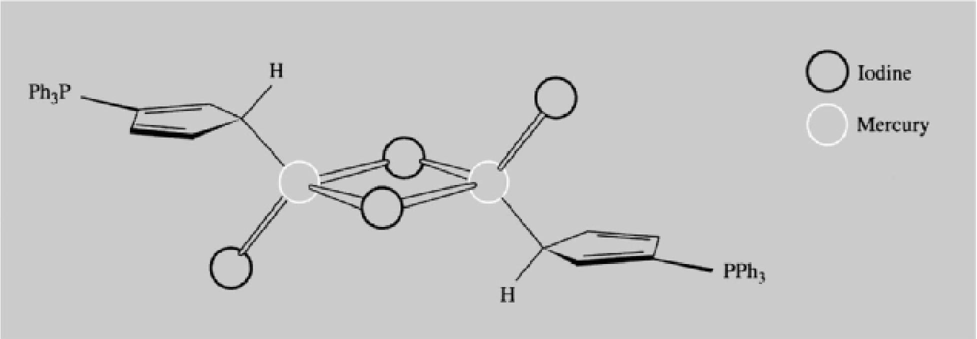


Figure 29.6 The structure of $[Hg(\eta^1\text{-}C_5H_4PPh_3)I_2]_2$ showing the essentially tetrahedral coordination of the mercury atoms and of the carbon atoms attached to them.

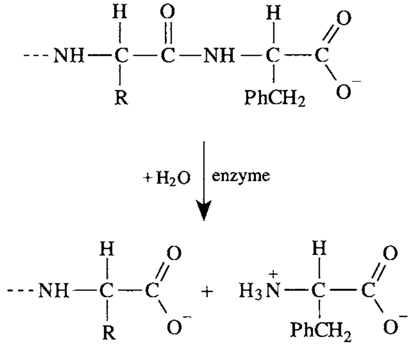
X-ray diffraction(44) which confirms the presence of an Hg–C σ bond (Fig. 29.6).

29.3.7 Biological and environmental importance(45,46,46a)

It is a remarkable contrast that, whereas Zn is biologically one of the most important metals and is apparently necessary to all forms of life,(47) Cd and Hg have no known beneficial biological role and are amongst the most toxic of elements.

The body of an adult human contains about 2 g of Zn but, as Zn enzymes are present in most body cells, its concentration is very low and realization of its importance was therefore delayed. The two Zn enzymes which have received most attention are carboxypeptidase A and carbonic anhydrase.

Carboxypeptidase A catalyses the hydrolysis of the terminal peptide bond in proteins during the process of digestion:



It has a molecular weight of about 34 000 and contains one Zn tetrahedrally coordinated to two histidine N atoms, a carboxyl O of a glutamate residue, and a water molecule. The precise mechanism of its action is not finally settled in spite of the intensive study of model systems,(48) but it is agreed that the first step is coordination of the terminal peptide to the Zn by its $\rangle C{=}O$ group. This is thereby polarized, giving the C a positive charge and making it susceptible to nucleophilic attack. This attack is probably by the –OH of the attached water molecule, followed by proton-rearrangement and breaking of the C–N peptide bond,(49) though alternative possibilities,

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[44] N. L. Holy, N. C. Baenziger, R. M. Flynn, and D. C. Swenson, *J. Am. Chem. Soc.* **98**, 7823–4 (1976).

[45] W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester 1994; pp. 242–66 for Zn and pp. 335–43 for Cd, Hg.

[46] A. S. Prasad, *Biochemistry of Zinc*, Plenum Press, New York, 1993, 303 pp.

[46a] A. Sigel and H. Sigel (eds.) *Metal Ions in Biological Systems*, Vol. 34, *Mercury and its Effects on the Environment and Biology*, Dekker, New York, 1997 604 pp.

[47] D. Bryce-Smith, *Chem. Brit.* **25**, 783–6 (1989) but see also *ibid.* p. 1207.

[48] E. Kimura, *Prog. Inorg. Chem.* **41**, 443–91 (1994); E. Kimura and T. Koike, *Adv. Inorg. Chem.* **44**, 229–61 (1997).

[49] D. W. Christianson and W. N. Lipscomb, *Acc. Chem. Res.* **22**, 62–9 (1989).

such as attack by the carboxyl group of a second glutamate residue in the enzyme have also been considered. In any event it is evident that the conformation of the enzyme provides a hydrophobic pocket, close to the Zn, which accommodates the non-polar side-chain of the protein being hydrolysed, and that this protein is, throughout, held in the correct position by H bonding to appropriate groups in the enzyme.

Carbonic anhydrase was the first Zn metalloenzyme to be discovered (1940) and in its several forms is widely distributed in plants and animals. It catalyses the equilibrium reaction:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

In mammalian erythrocytes (red blood-cells) the forward (hydration) reaction occurs during the uptake of CO_2 by blood in tissue, while the backward (dehydration) reaction takes place when the CO_2 is subsequently released in the lungs. The enzyme increases the rates of these reactions by a factor of about one million.

The molecular weight of the enzyme is about 30 000 and the roughly spherical molecule contains just one zinc atom situated in a deep protein pocket, which also contains a number of water molecules arranged in an ice-like order. This Zn is coordinated tetrahedrally to 3 imidazole nitrogen atoms of histidine residues and to a water molecule. Once again the precise details of the enzyme's action are not settled, but it seems probable that the coordinated H_2O ionizes to give $Zn{-}OH^-$ and the nucleophilic OH^- then interacts with the C of CO_2 (which may be held in the correct position by H bonds to its two oxygen atoms) to yield HCO_3^-. This is equivalent to replacing the slow hydration of CO_2 with H_2O, by the fast reaction:

$$CO_2 + OH^- \longrightarrow HCO_3^-$$

The latter would normally require a high pH and the contribution of the enzyme is therefore presumed to be the provision of a suitable environment, within the protein pocket, which allows the dissociation of the coordinated H_2O to occur in a medium of pH 7 which would otherwise be much too low.

A more recently established function of zinc is in proteins responsible for recognizing base-sequences in DNA and so regulating the transfer of genetic information during the replication of DNA. These so-called "zinc-finger" proteins contain 9 or 10 Zn^{2+} ions each of which, by coordinating to 4 amino acids, stabilizes a protruding fold (finger) in the protein. The protein wraps around the double strand of DNA, each of the fingers binding to the DNA, their spacing matching the base sequence in the DNA and thus ensuring accurate recognition.(50)

Cadmium is extremely toxic and accumulates in humans mainly in the kidneys and liver; prolonged intake, even of very small amounts, leads to dysfunction of the kidneys. It acts by binding to the —SH group of cysteine residues in proteins and so inhibits SH enzymes. It can also inhibit the action of zinc enzymes by displacing the zinc.

The toxic effects of mercury have long been known,(5) and the use of $HgCl_2$ as a poison has already been mentioned. The use of mercury salts in the production of felt[†] for hats and the dust generated in ill-ventilated workshops by the subsequent drying process, led to the nervous disorder known as "hatter's shakes" and possibly also to the expression "mad as a hatter".

The metal itself, having an appreciable vapour pressure, is also toxic, and produces headaches, tremors, inflammation of the bladder and loss of memory. The best documented case is that of Alfred Stock (p. 151) whose constant use of mercury in the vacuum lines employed in his studies of boron and silicon hydrides, caused him to suffer for many years. The cause was eventually recognized and it is largely due to Stock's publication in 1926 of details of his experiences that the need for care and adequate ventilation is now fully appreciated.

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[50] N. P. Pavletich and C. O. Pabo, *Science* **261**, 1701-7 (1993).

[†] It was apparently helpful to add Hg^{II} to the dil HNO_3 used to roughen the surface of the animal hair employed in the making of felt which is a non-woven fabric of randomly oriented hairs.

Still more dangerous than metallic mercury or inorganic mercury compounds are organomercury compounds of which the methyl mercury ion $HgMe^+$ is probably the most ubiquitous.(51) This and other organomercurials are more readily absorbed in the gastrointestinal tract than Hg^{II} salts because of their greater ability to permeate biomembranes. They concentrate in the blood and have a more immediate and permanent effect on the brain and central nervous system, no doubt acting by binding to the –SH groups in proteins. Naturally occurring anaerobic bacteria in the sediments of sea or lake floors are able to methylate inorganic mercury (Co–Me groups in vitamin B_{12} are able to transfer the Me to Hg^{II}) which is then concentrated in plankton and so enters the fish food chain.

The Minamata disaster in Japan, when 52 people died in 1952, occurred because fish, which formed the staple diet of the small fishing community, contained abnormally high concentrations of mercury in the form of MeHgSMe. This was found to originate from a local chemical works where Hg^{II} salts were used (inefficiently) to catalyse the production of acetylene from acetaldehyde, and the effluent then discharged into the shallow sea. Evidence of a similar bacterial production of organomercury is available from Sweden where methylation of Hg^{II} in the effluent from paper mills has been shown to occur. The use of organomercurials as fungicidal seed dressings has also resulted in fatalities in many parts of the world when the seed was subsequently eaten.

It is now apparent that bacteria have developed resistance to heavy metals and the detoxifying process is initiated and controlled by *metalloregulatory* proteins which are able selectively to recognize metal ions. MerR is a small DNA-binding protein which displays a remarkable sensitivity to Hg^{2+}. The metal apparently binds to S atoms of cysteine and this has been a major incentive to recent work on Hg–S chemistry.(32)

Public concern about mercury poisoning has led to more stringent regulations for the use of mercury cells in the chlor-alkali industry (pp. 71–3, 798). The health record of this industry has, in fact, been excellent, but the added costs of conforming to still higher standards have led manufacturers to move from mercury cells to diaphragm cells, and this change has been made a legal requirement in Japan.

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[51] S. Krishnamurthy, *J. Chem. Ed.* **69**, 347–50 (1992).