

Chapter 18 The d-block metals

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Chapter 18 The d-block metals

39 d-block elements.

One of the most important trends is the variation in **stability of the oxidation states**.

The trends in their properties and **the correlation with their electronic structures**.

D-block metal vs transition metal

	3	4	5	6	7	8	9	10	11	12	
Mg											Al
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg		

Chapter 18 Opener

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The elements

18.1 Occurrence and recovery

Soft metals occur as sulfide minerals;
hard metals occur as oxides.

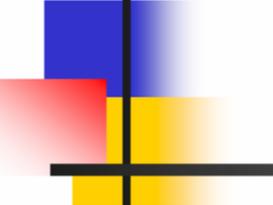
Table 18.1 Mineral sources and methods of recovery of some commercially important metals

Metal	Principal minerals	Method of recovery	Note
Titanium	Ilmenite, FeTiO_3 Rutile, TiO_2	$\text{TiO}_2 + 2 \text{C} + 2 \text{Cl}_2 \rightarrow \text{TiCl}_4 + 2 \text{CO}$ followed by reduction of TiCl_4 with Na or Mg	
Chromium	Chromite, FeCr_2O_4	$\text{FeCr}_2\text{O}_4 + 4 \text{C} \rightarrow \text{Fe} + 2 \text{Cr} + 4 \text{CO}$	(a)
Molybdenum	Molybdenite, MoS_2	$2 \text{MoS}_2 + 7 \text{O}_2 \rightarrow 2 \text{MoO}_3 + 4 \text{SO}_2$ followed by either $\text{MoO}_3 + 2 \text{Fe} \rightarrow \text{Mo} + \text{Fe}_2\text{O}_3$ or $\text{MoO}_3 + 3 \text{H}_2 \rightarrow \text{Mo} + 3 \text{H}_2\text{O}$	
Tungsten	Scheelite, CaWO_4 Wolframite, $\text{FeMn}(\text{WO}_4)_2$	$\text{CaWO}_4 + 2 \text{HCl} \rightarrow \text{WO}_3 + \text{CaCl}_2 + \text{H}_2\text{O}$ followed by $\text{WO}_3 + 3 \text{H}_2 \rightarrow \text{W} + 3 \text{H}_2\text{O}$	
Manganese	Pyrolusite, MnO_2	$\text{MnO}_2 + 2 \text{C} \rightarrow \text{Mn} + 2 \text{CO}$	(b)
Iron	Haematite, Fe_2O_3 Magnetite, Fe_3O_4 Limonite, $\text{FeO}(\text{OH})$	$\text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2$	
Cobalt	CoAsS Smaltite, CoAs_2 Linnaeite, Co_3S_4	By-product of copper and nickel production	
Nickel	Pentlandite, $(\text{Fe,Ni})_9\text{S}_8$	$\text{NiS} + \text{O}_2 \rightarrow \text{Ni} + \text{SO}_2$	(c)
Copper	Chalcopyrite, CuFeS_2 Chalocite, Cu_2S	$2 \text{CuFeS}_2 + 2 \text{SiO}_2 + 5 \text{O}_2 \rightarrow 2 \text{Cu} + 2 \text{FeSiO}_3 + 4 \text{SO}_2$	

(a) The iron–chromium alloy is used directly for stainless steel.

(b) The reaction is carried out in a blast furnace with Fe_2O_3 to produce alloys.

(c) NiS is formed by melting the mineral and separated by physical processes. NiO is used in a blast furnace with iron oxides to produce steel. Nickel is purified by electrolysis or the Mond process via $\text{Ni}(\text{CO})_4$.



HSAB concepts

The gist of this theory is that **soft acids react faster and form stronger bonds with soft bases**, whereas *hard* acids react faster and form stronger bonds with *hard* bases, all other factors being equal.

The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

Hard acids and **hard bases** tend to have:

small size

high oxidation state

low polarizability

high electronegativity

energy low-lying HOMO (bases) or energy high-lying LUMO (acids).

The elements

18.2 Physical properties

The properties of the *d* metals are largely derived from their electronic structure.

The nature of the metallic bonding that binds the atoms together.

Generally speaking, the same band structure is present for all the *d*-block metals and arise from the overlap of the $(n+1)s$ orbitals to give an *s* band and the *nd* orbitals to give a *d* band.

The principal differences between the metals is the number of electrons available to occupy these bands.

Melting point, atomic radii

Trends in chemical properties

18.3 Oxidation states across a series

The ranges of oxidation states → electronic properties of many solid compounds, catalytic properties, role in biochemical processes.

High oxidation states

Group oxidation number – its group number (in the 1-18 notation)

For example- scandium, yttrium in group 3, with configuration $nd^1(n+1)s^2$, are found in aqueous solution only in oxidation state +3.

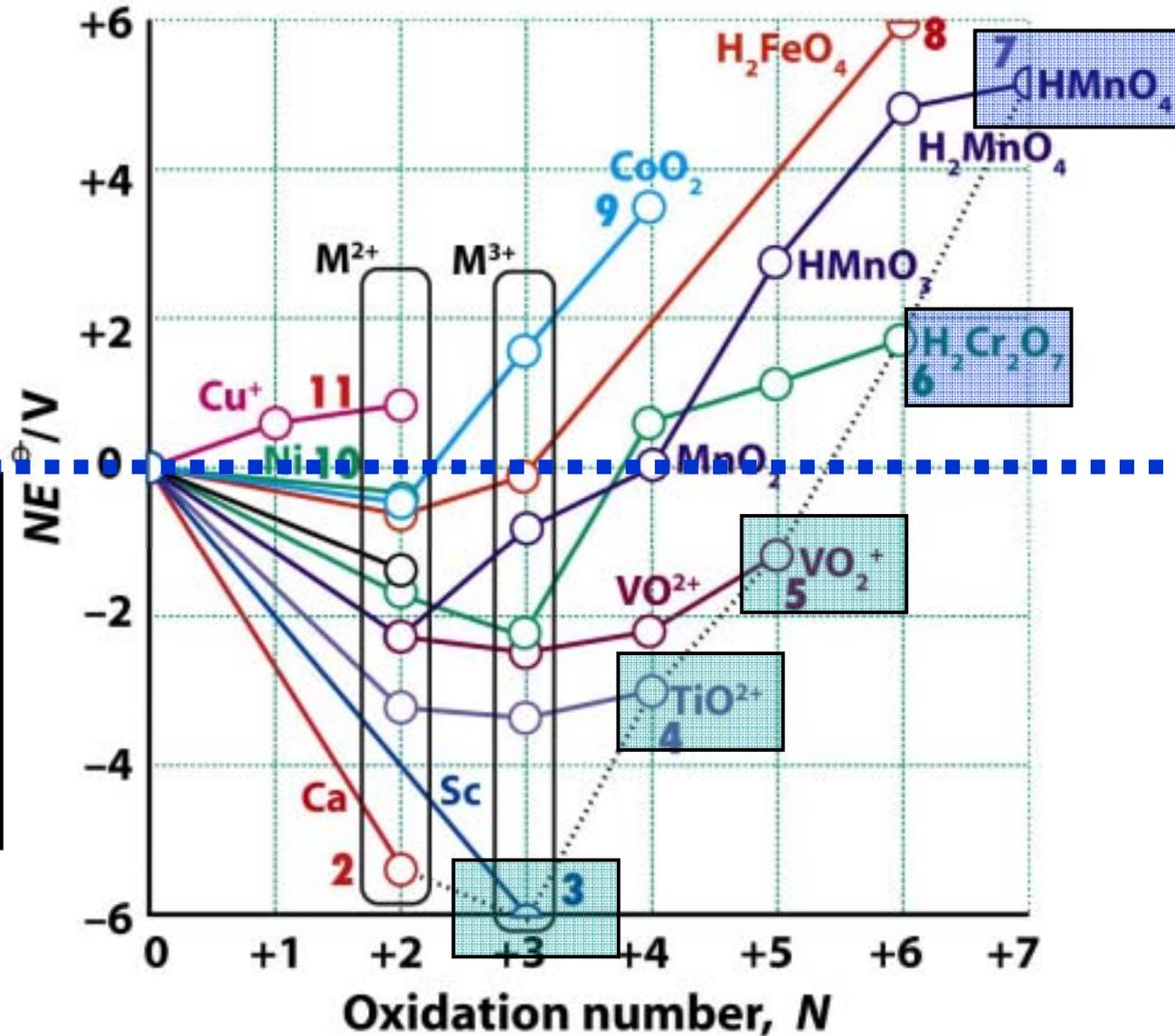
The group oxidation state is never achieved after group 8.

Trends in chemical properties

18.3 Oxidation states across a series

Sc, Ti, V
Cr, Mn
Fe, Co, Ni, Cu, Zn

The trend in thermodynamic stability of the group oxidation states—the Frost diagram



Trends in chemical properties

18.3 Oxidation states across a series

Binary compounds of the 3d-series



$\text{VF}_5, \text{CrF}_6$ - More strongly oxidizing halogen fluorine

Beyond Group 6 in the 3d series, even fluorine cannot produce the group oxidation state.

Oxygen vs halogen – decreasing steric crowding.



Stronger oxidizing agents and become stronger from CrO_4^{2-} to FeO_4^{2-} - the decreasing stability.

Mg													Al
	3	4	5	6	7	8	9	10	11	12			
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			Ga
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd			In
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg			Tl
Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg				

Trends in chemical properties

18.3 Oxidation states across a series

Intermediate oxidation states in the 3d series

Oxidation state **+3** is common to the left of the 3d series and **+2** is common for metals from the middle to the right of the block.

The **+3** oxidation state is the only oxidation state normally encountered for scandium.

Titanium, vanadium, and chromium all form a wide range of compounds in oxidation state **+3**.

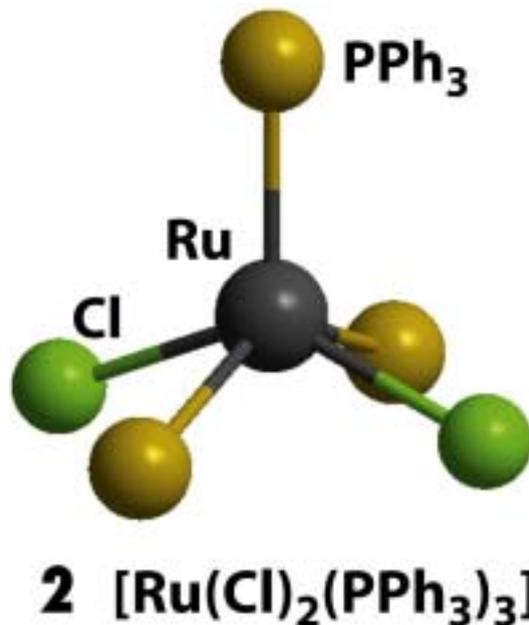
In line with increasing ionization energy, the stability of **M(III)** decreases across the period.

Trends in chemical properties

18.3 Oxidation states across a series

Intermediate oxidation states in the 4d and 5d series

Complexes of M(II) of the 4d- and 5d-series metals generally contain π -acceptor ligands.



Trends in chemical properties

18.4 Oxidation states down a group

In Groups 4-10, the highest oxidation state of an element becomes more stable on descending a group.

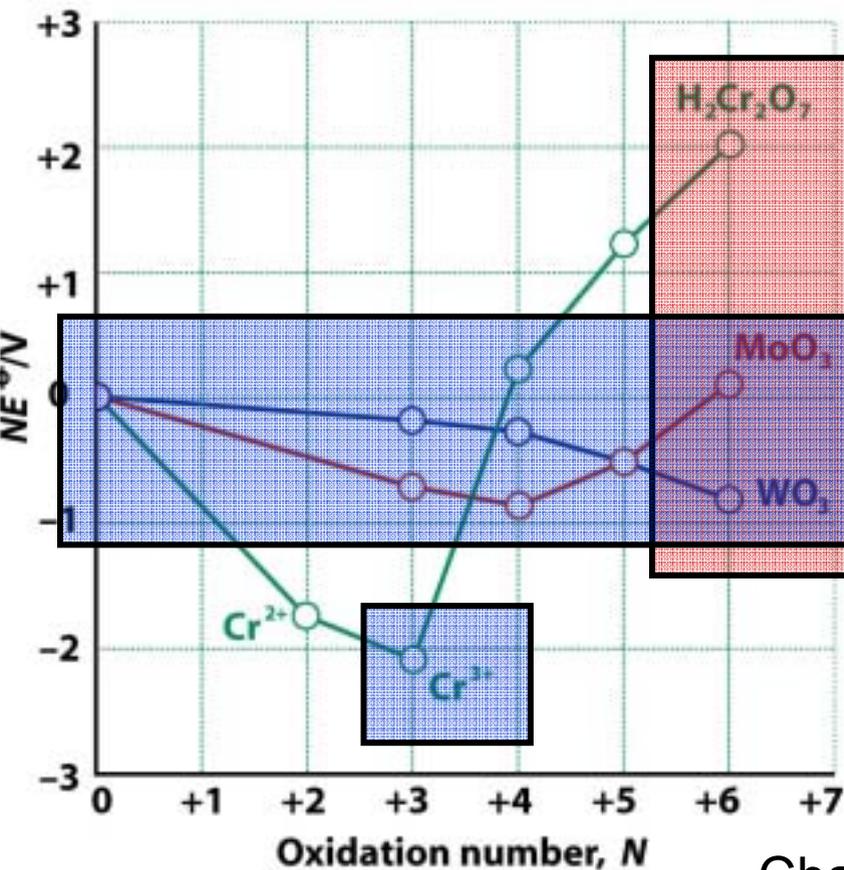


Table 18.3 Highest oxidation states of the *d*-block binary halides*

Group	4	5	6	7	8	9	10	11
TiX ₄		VF ₅	CrF ₅ ¹	MnF ₄	FeBr ₃	CoF ₃	NiF ₄	CuBr ₂
ZrX ₄		NbI ₅	MoF ₆	TcCl ₆	RuF ₆	RhF ₆	PdF ₄	AgF ₃
HfX ₄		TaI ₅	WF ₆	ReF ₇	OsF ₆	IrF ₆	PtF ₆	AuCl ₆

* The formulas show the least electronegative halide that brings out the highest oxidation state of the *d* metal.

¹CrF₅ exists for several days at room temperature in a passivated Monel chamber.

Table 18-3
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Characteristic of chromium

Trends in chemical properties

18.4 Oxidation states down a group

WF_6 is not a significant oxidizing agent. However, the oxidizing character of the hexafluorides increases to the right, and PtF_6 is so potent that it can oxidize O_2 to O_2^+ .



The ability to achieve the highest oxidation state does not correlate with the ease of oxidation of the bulk metal to an intermediate oxidation state.

Elemental iron is susceptible to oxidation by $\text{H}^+(\text{aq})$, however no chemical oxidizing agent has been found that will take it to its group oxidation state.

Ruthenium and osmium are not oxidized by H^+ , however, they can be oxidized by oxygen to the +8 state.

Trends in chemical properties

18.5 Structural trends

The 4d- and 5d-series elements often exhibit higher coordination numbers than their 3d-series congeners.

Low oxidation state compounds often exist as ionic solids, whereas high oxidation state compounds tend to take on covalent character.

Table 18.4 Coordination numbers of some early *d*-block fluoro and cyano complexes*

	Group		
	3	4	5
3d	(NH ₄) ₃ [ScF ₆] (6)	Na ₂ [TiF ₆] (6)	K[VF ₆] (6); K ₂ [V(CN) ₇] · 2H ₂ O (7)
4d	Na ₆ [YF ₉] (9)	Na ₃ [ZrF ₇] (7)	K ₂ [NbF ₇] (7); K ₂ [Nb(CN) ₈] (8)
5d	Na ₆ [LaF ₉] (9)	Na ₃ [HfF ₇] (7)	K ₃ [TaF ₈] (8)

* The number in parentheses is the coordination number of the *d*-metal atom in the complex anion enclosed in square brackets.

Table 18-4

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Trends in chemical properties

18.6 Nobel character

Copper, silver, and gold are not susceptible to oxidation by H^+ . Jewellery and ornaments.

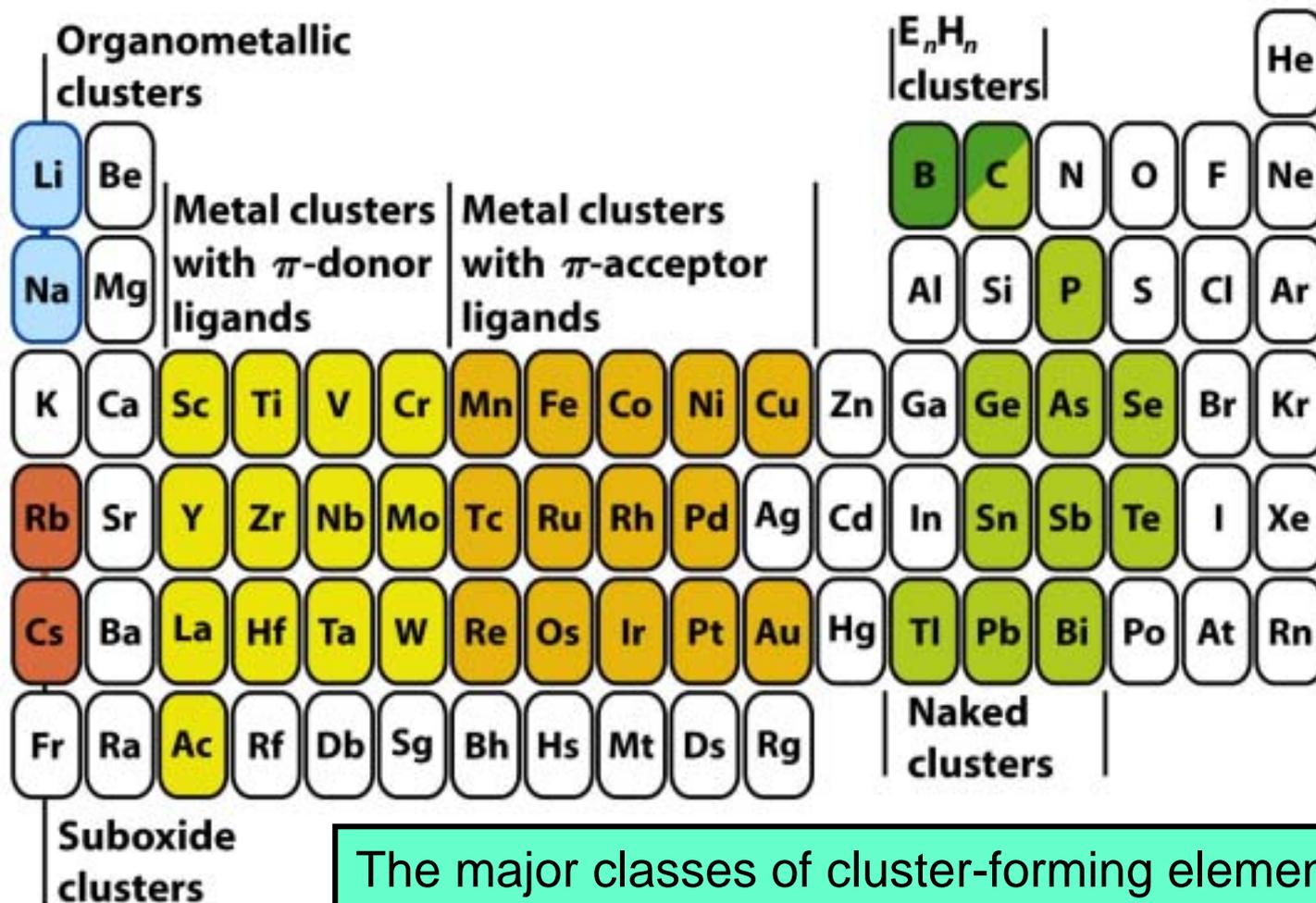
The soft character of Cu^+ , Ag^+ , and Au^+ is illustrated by their affinity order, which is $I^- > Br^- > Cl^-$.

7	8	9	10	11	12	
Mn	Fe	Co	Ni	Cu	Zn	Al
Tc	Ru	Rh	Pd	Ag	Cd	Ga
Re	Os	Ir	Pt	Au	Hg	In
						Tl

Platinum metals Coinage metals

Representative compounds

A single central metal ion vs clusters (metal-metal bond)



Representative compounds

18.7 Metal halides

Binary metal halides of the d-block elements occur for all the elements with nearly all oxidation states represented.

The more **strongly oxidizing halogens** bring out the higher oxidation states.

The members of **Group 11** have simple monohalides.

More common are the **dihalides** which are typically ionic solids that dissolve in water to give M^{2+} ions.

Higher halides exist for most of the d block, and **covalent character** becomes more prevalent with high oxidation state.

MoF_6 and WF_6 are liquids at RT.

Representative compounds

18.8 Metal oxides and oxo complexes

The ability of oxygen to bring out the highest oxidation state for some elements.

The early d-block monoxides are strong reducing agents.

TiO, MnO

High oxidation state oxides can show covalent structures.

Osmium tetroxide are low melting, highly volatile, toxic, molecular compounds that are used as selective oxidizing agents.

Table 18.5 Structures of *d*-block MO compounds

	Group						
	4	5	6	7	8	9	10
Rock-salt structure (shaded)	Ti Zr	V		Mn	Fe	Co	Ni Pd*

* PtS structure (square-planar, four-coordinate metal atom).

Adapted from A.F. Wells, *Structural inorganic chemistry*. Oxford University Press (1984).

Representative compounds

18.8 Metal oxides and oxo complexes

Mononuclear oxo complexes

Table 18.6 Some common monoxo and dioxo complexes

Group	Element, configuration	Structure	Formula
5	V(IV), d^1	Square pyramidal	$[\text{V}(\text{O})(\text{acac})_2]$, $[\text{V}(\text{O})\text{Cl}_4]^{2-}$
	V(V), d^0	<i>cis</i> -Octahedral	$[\text{V}(\text{O})_2(\text{OH}_2)_4]^+$
6	Mo(VI), d^0 ; W(VI), d^0	Tetrahedral	$[\text{M}(\text{O})_2(\text{Cl})_2]$
7, 8	Re(V), d^2 ; Os(VI), d^2	<i>trans</i> -Octahedral	$[\text{Re}(\text{O})_2(\text{CN})_4]^{3-}$
			$[\text{Os}(\text{O})_2(\text{Cl})_2]$
			$[\text{Os}(\text{O})_2(\text{Cl})_4]^{2-}$

Table 18-6

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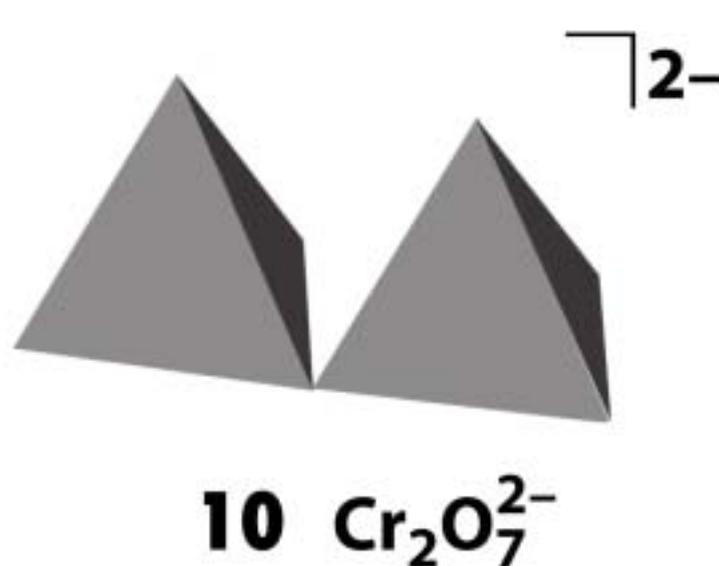
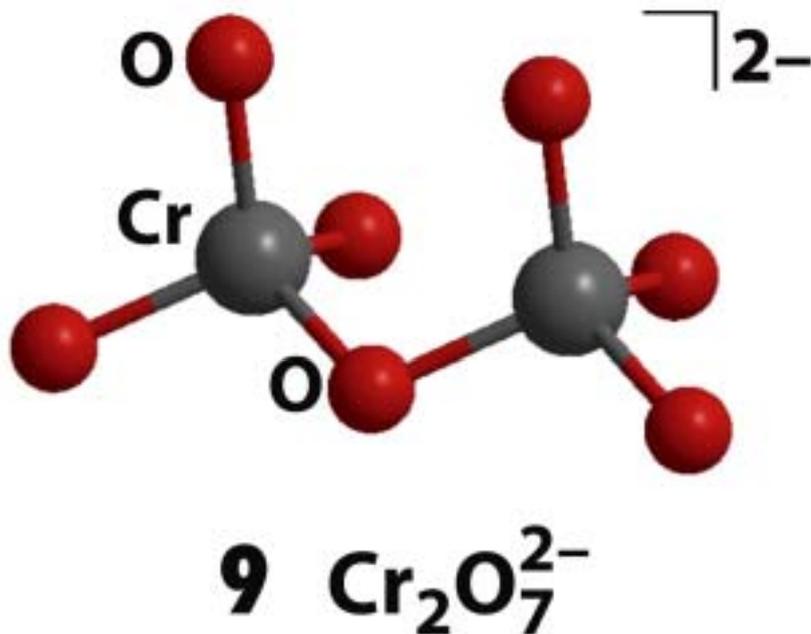
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Representative compounds

18.8 Metal oxides and oxo complexes

Polyoxometallates

A polyoxometallate is an oxoanion containing more than one metal atom.



Polyhedra representation: metal-centre, oxygen-vertic

Representative compounds

18.8 Metal oxides and oxo complexes

Polyoxometallates

4	5	6	7
Ti	V +4, +5	Cr +6	Mn
Zr	Nb +5	Mo +6	Tc
Hf	Ta +5	W +6	Re

Figure 18-11

Elements in the d-block that form polyoxometallates

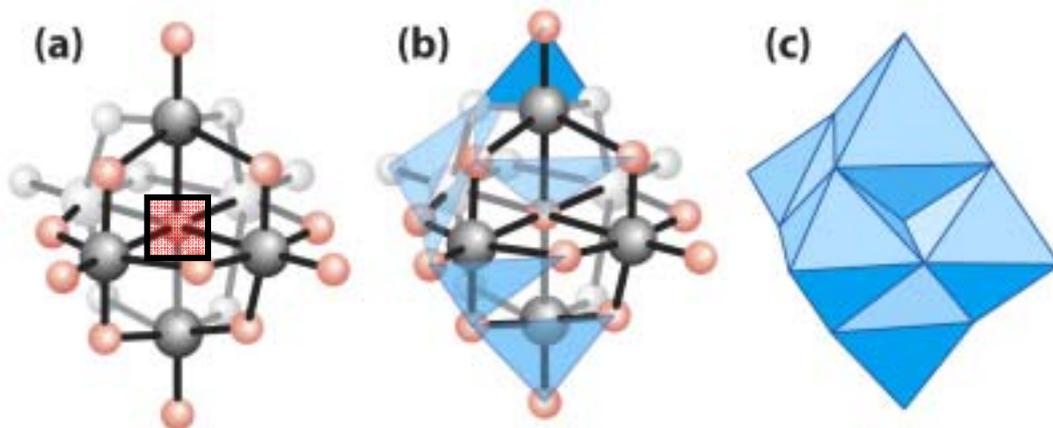


Figure 18-12
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The six edge-shared octahedra found in $[M_6O_{19}]^{2-}$

Representative compounds

18.8 Metal oxides and oxo complexes

Polyoxometallates



Representative compounds

18.9 Metal sulfides and sulfide complexes

Less electronegative than oxygen – a broader range of oxidation, a stronger affinity for the softer metals on the right of the d block.

A broad set of compounds containing S_n^{2-} ions can be prepared.

Monosulfides

As with the d-metal monoxides, the monosulfides are most common in the 3d series.

Monoxides (rock-salt structure, harder) vs monosulfides (nickel-arsenide structure, softer)

Table 18.7 Structures of *d*-block MS compounds*

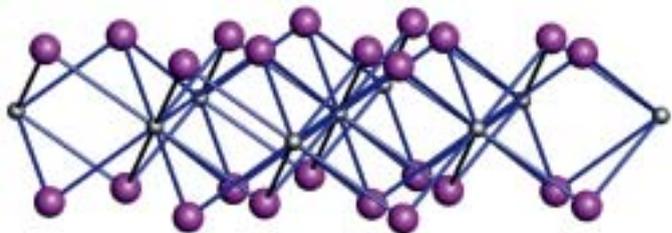
	Group						
	4	5	6	7	8	9	10
Nickel-arsenide structure (shaded)	Ti	V		Mn [†]	Fe	Co	Ni
Rock-salt structure (unshaded)	Zr	Nb					

* Metal monosulfides of Group 6 are not shown; some of the heavier metals have more complex structures.

[†] MnS has two polymorphs; one has a rock-salt structure, the other has a wurtzite structure.

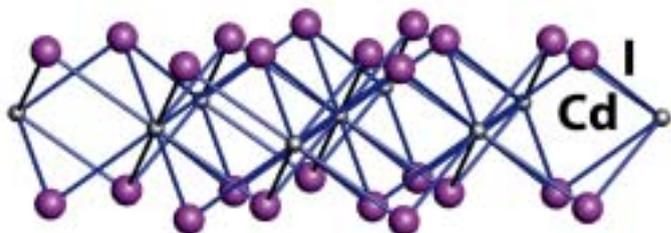
Representative compounds

18.9 Metal sulfides and sulfide complexes

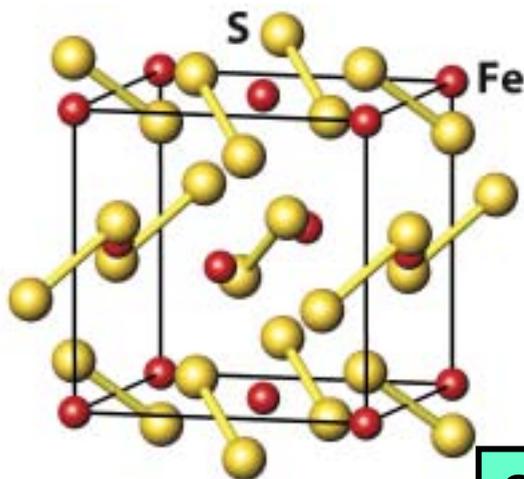


Disulfides

Two broad classes



Layered CdI_2 structure



Structure of pyrite

Table 18.8 Structures of *d*-block MS_2 compounds*

	Group							
	4	5	6	7	8	9	10	11
Layered (shaded)	Ti			Mn	Fe	Co	Ni	Cu
Pyrite or marcasite (unshaded)	Zr	Nb	Mo		Ru	Rh		
	Hf	Ta	W	Re	Os	Ir	Pt	

* Metals not shown do not form disulfides or have disulfides with complex structures. Adapted from A.F. Wells, *Structural inorganic chemistry*. Oxford University Press (1984).

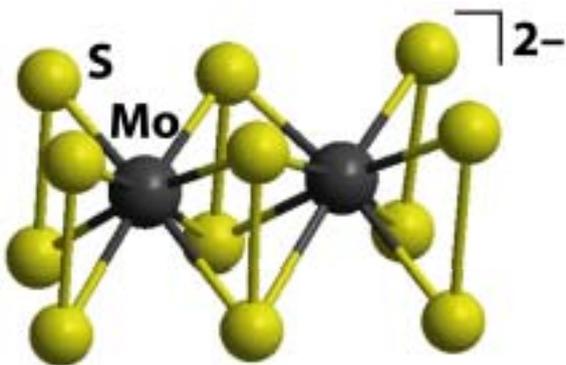
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Representative compounds

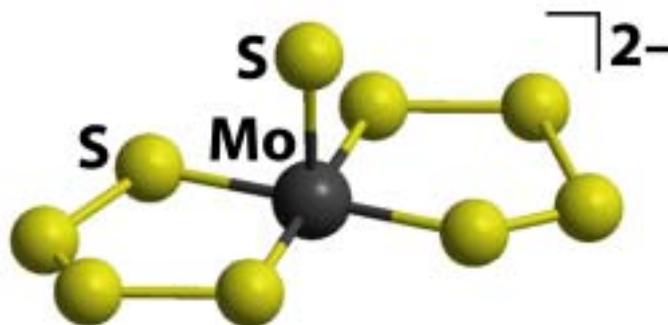
18.9 Metal sulfides and sulfide complexes

Sulfido complexes

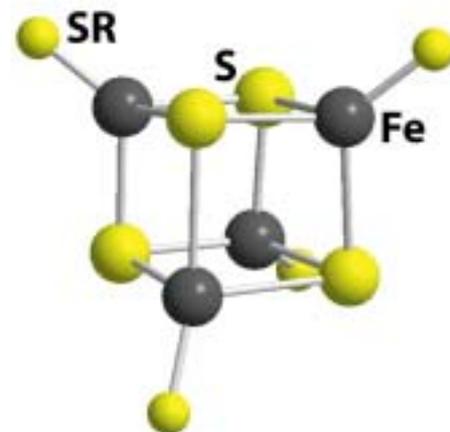
Differences from that of oxygen: the ability of sulfur to catenate (form chains), the availability of low-lying empty 3d orbitals that allow sulfur to act as a π acceptor, and the preference of sulfur for metal centres that are not highly oxidizing.



13 $[\text{Mo}_2(\text{S}_2)_6]^{2-}$



14 $[\text{MoS}(\text{S}_4)_2]^{2-}$



15

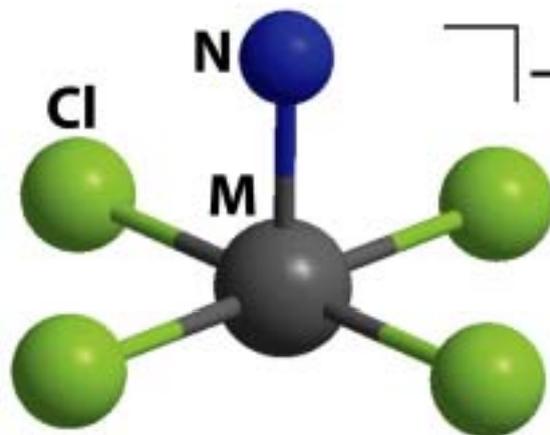
Representative compounds

18.10 Nitrido and alkylidyne complexes

The nitrido ligand (N⁻) and alkylidyne ligand (RC⁻) are present formally as N^{3-} and RC^{3-} .

Complexes containing them are usually of very **high oxidation state**.

Short M-N and M-C bond lengths.



Representative compounds

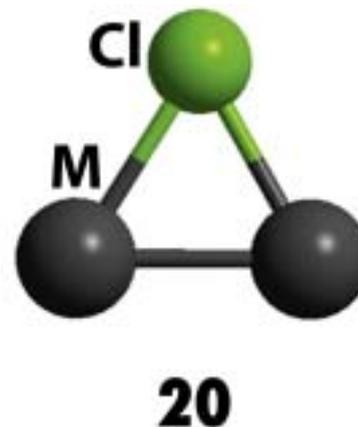
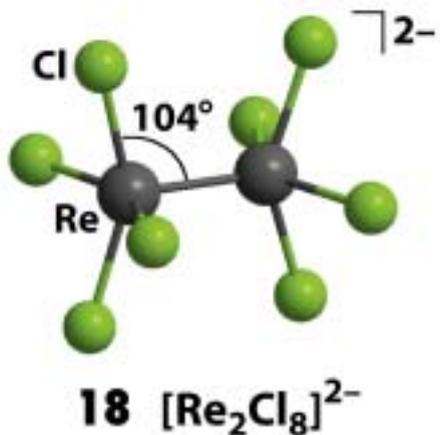
18.11 Metal-metal bonded compounds and clusters

Clusters of the early d-block elements and the lanthanoids generally contain donor ligands such as Br⁻.

These ligands can fill some of the low-lying orbitals of these electron-poor metal atoms by σ - and π -electron donation.

By contrast, electron-rich metal clusters on the right of the d block generally contain π -acceptor ligands such as CO, which remove some of the electron density from the metal.

No bridging ligands vs bridging ligands



Representative compounds

18.11 Metal-metal bonded compounds and clusters

There is an increase in M-M bond strength down a group, perhaps on account of the greater spatial extension of d-orbitals in heavier atoms.

This trend may be the reason why there are so many more metal-metal bonded compounds for the 4d- and 5d-series metals than their 3d-series counterparts.

Multiple chain and layered compounds

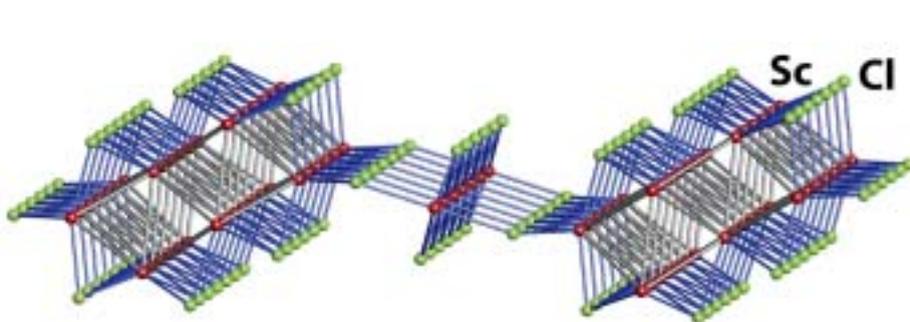


Figure 18-15
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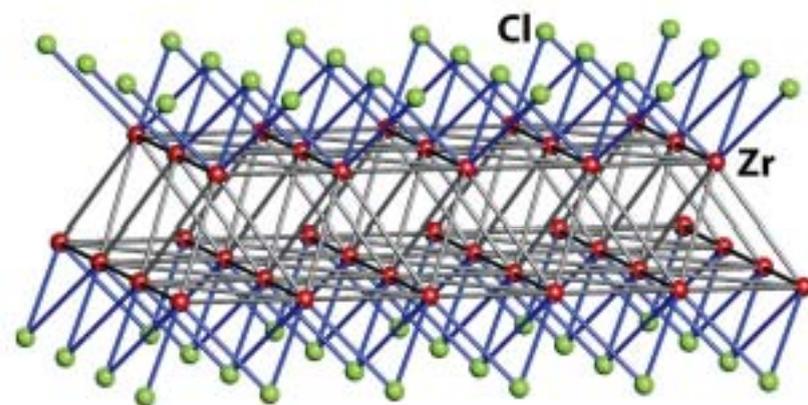


Figure 18-16
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