9 Molecular Structures II: Compounds of Transition Metals

9.1 Ligand Field Theory

The mutual interaction between bonding electron pairs is the same for transition metal compounds as for compounds of main group elements. All statements concerning molecular structure apply equally. However, nonbonding valence electrons behave differently. For transition metal atoms these generally are $d$ electrons that can be accommodated in five $d$ orbitals. In what manner the electrons are distributed among these orbitals and in what way they become active stereochemically can be judged with the aid of ligand field theory. The concept of ligand field theory is equivalent to that of the valence shell electron-pair repulsion theory: it considers how the $d$ electrons have to be distributed so that they attain a minimum repulsion with each other and with the bonding electron pairs. In its original version by H. Bethe it was formulated as crystal field theory; it considered the electrostatic repulsion between the $d$ electrons and the ligands, which were treated as point-like ions. After the success of the valence shell electron-pair repulsion theory it appears more appropriate to consider the interactions between nonbonding $d$ electrons and bonding electron pairs; thus the same notions apply for both theories. This way, one obtains qualitatively correct structural statements with relatively simple models. The more exact molecular orbital theory draws the same conclusions.

The relative orientations of the regions with high charge density of $d$ electrons and of bonding electrons about an atom can be described with the aid of a coordinate system that has its origin in the center of the atom. Two sets of $d$ orbitals are to be distinguished (Fig. 9.1): the first set consists of two orbitals oriented along the coordinate axes, and the second set consists of three orbitals oriented toward the centers of the edges of a circumscribed cube.

Octahedral Coordination

If an atom has six ligands, then the mutual repulsion of the six bonding electron pairs results in an octahedral coordination. The positions of the ligands correspond to points on the axes of the coordinate system. If nonbonding electrons are present, these will prefer the orbitals $d_{xy}$, $d_{xz}$, and $d_{yz}$ because the regions of high charge density of the other two $d$ orbitals are especially close to the bonding electron pairs (Fig. 9.1). The three orbitals favored energetically are termed $t_{2g}$ orbitals (this is a symbol for the orbital symmetry; the $t$ designates a triply degenerate state); the other two are $e_g$ orbitals ($e$ = doubly degenerate; from German entartet = degenerate). Cf. the diagram in the margin on the next page.

*The terms crystal field theory and ligand field theory are not used in a uniform way. As only interactions between adjacent atoms are being considered, without referring to crystal influences, the term crystal field theory does not seem adequate. Some authors consider certain electronic interactions (like $\pi$ bonds) as part of ligand field theory, although they originate from MO theory.
Fig. 9.1
Orientation of the regions of high electron density for 3d orbitals.

True-to-scale drawings of areas with constant value for the wave functions. The dots on the circumscribed cubes mark the directions of preferential orientation of the 'partial clouds'.

The energy difference between the occupation of a $t_{2g}$ and an $e_g$ orbital is termed $\Delta_o$. The value of $\Delta_o$ depends on the repulsion exercised by the bonding electron pairs on the $d$ electrons. Compared to a transition metal atom the bonded ligand atoms are usually much more electronegative. The centers of charge of the bonding electron pairs are much closer to them, especially when they are strongly electronegative. Therefore, one can expect a decreasing influence on the $d$ electrons and thus a decrease of $\Delta_o$ with increasing ligand electronegativity. Decreasing $\Delta_o$ values also result with increasing sizes of the ligand atoms; in this case the electron pairs are distributed over a larger space so that the difference of their repulsive action on a $t_{2g}$ and an $e_g$ orbital is less marked. In the presence of multiple bonds between the metal atom and the ligands, for example in metal carbonyls, the electron density of the bonds is especially high and their action is correspondingly large. $\Delta_o$ is a value that can be measured directly with spectroscopic methods: by photoexcitation of an electron from the $t_{2g}$ to the $e_g$ level we have $\Delta_o = h\nu$. The spectrochemical series is obtained by ordering different ligands according to decreasing $\Delta_o$:

$$\text{CO} > \text{CN}^- > \text{PR}_3 > \text{NO}_2^- > \text{NH}_3 > \text{NCS}^- > \text{H}_2\text{O} > \text{RCO}_2^- \approx \text{OH}^-$$

$$> \text{F}^- > \text{NO}_3^- > \text{Cl}^- \approx \text{SCN}^- > \text{S}^{2-} > \text{Br}^- > \text{I}^-$$

When two or three nonbonding electrons are present, they will occupy two or three of the $t_{2g}$ orbitals (HUND’s rule). This is more favorable than pairing electrons in one orbital because the pairing requires that the electrostatic repulsion between the two electrons be overcome. The energy necessary to include a second electron in an already occupied orbital is called the electron pairing energy $P$. When four nonbonding electrons are present, there are two alternatives for the placement of the fourth electron. If $P > \Delta_o$, then it will be an $e_g$ orbital and all four electrons will have parallel spin: we call this a high-spin complex. If $P < \Delta_o$, then it is more favorable to form a low-spin complex leaving the $e_g$ orbitals unoccupied and having two paired electrons:
9.1 Ligand Field Theory

In a high-spin $d^4$ complex only one of the two $e_g$ orbitals is occupied. If it is the $d_{z^2}$ orbital then it exerts a strong repulsion on the bonding electrons of the two ligands on the $z$ axis. These ligands are forced outwards; the coordination octahedron suffers an elongation along the $z$ axis. This effect is known as the Jahn–Teller effect. Instead of the $d_{z^2}$ orbital the $dx^2-y^2$ orbital could have been occupied, which would have produced elongations along the $x$ and $y$ axes. However, a higher force is needed to stretch four bonds; stretching only two bonds is energetically more favorable, and consequently only examples with octahedra elongated in one direction are known.

The JAHN–TELLER effect is always to be expected when degenerate orbitals are unevenly occupied with electrons. In fact, it is observed for the following electronic configurations:

<table>
<thead>
<tr>
<th>Examples</th>
<th>$d^4$ high-spin</th>
<th>$d^9$</th>
<th>$d^7$ low-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr(II), Mn(III)</td>
<td>Cu(II)</td>
<td>Ni(III)</td>
</tr>
</tbody>
</table>

A JAHN–TELLER distortion should also occur for configuration $d^1$. However, in this case the occupied orbital is a $t_{2g}$ orbital, for example $d_{xy}$; this exerts a repulsion on the ligands on the axes $x$ and $y$ which is only slightly larger than the force exerted along the $z$ axis. The distorting force is usually not sufficient to produce a perceptible effect. Ions like TiF$_6^{3-}$ or MoCl$_6^{-}$ show no detectable deviation from octahedral symmetry.

Not even the slightest JAHN–TELLER distortion and therefore no deviation from the ideal octahedral symmetry are to be expected when the $t_{2g}$ and $e_g$ orbitals are occupied evenly. This applies to the following electronic configurations:

<table>
<thead>
<tr>
<th></th>
<th>$d^0$, $d^3$, $d^5$ high-spin, $d^6$ low-spin, $d^8$ and $d^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CuCl}_4(\text{OH}_2)_2]^{2-}$ ion two of the Cl atoms take the positions in the vertices of the elongated axis of the coordination polyhedron.</td>
<td></td>
</tr>
</tbody>
</table>

Tetrahedral Coordination

We can imagine the four ligands of a tetrahedrally coordinated atom to be placed in four of the eight vertices of a cube. The orbitals $d_{x^2-y^2}$ and $d_{yz}$ ($t_2$ orbitals), which are oriented toward the cube edges, are closer to the bonding electron pairs than the orbitals $d_{z^2-x^2}$ and
The arrows indicate the directions of displacement of the ligands due to repulsion by the nonbonding $d$ electrons. The spheres on the cube edges mark the centers of gravity of the charges of the $t_2$ orbitals; a gray sphere means occupation by one electron more than a white sphere.

If the $t_2$ orbitals are occupied unevenly, Jahn–Teller distortions occur. For configuration $d^4$, one of the $t_2$ orbitals is unoccupied; for $d^9$, one has single occupation and the rest double. As a consequence, the ligands experience differing repulsions, and a flattened tetrahedron results (Fig. 9.2). Typical bond angles are, for example in the CuCl$_2$ ion, $116^\circ$ and $106^\circ$.

For the configurations $d^3$ and $d^8$ one $t_2$ orbital has one electron more than the others; in this case an elongated tetrahedron is to be expected; however, the deformation turns out to be smaller than for $d^4$ and $d^9$, because the deforming repulsion force is exerted by only one electron (instead of two; Fig. 9.2). Since the deformation force is small and the requirements of the packing in the crystal sometimes cause opposite deformations, observations do not always conform to expectations. For example, NiCl$_4^{2-}$ ($d^8$) has been observed to have undistorted, slightly elongated or slightly flattened tetrahedra depending on the cation. For uneven occupation of the $e$ orbitals distortions could also be expected, but the effect is even smaller and usually it is not detectable; VCl$_4$ ($d^1$) for example has undistorted tetrahedra.

**Square Coordination**

When the two ligands on the $z$ axis of an octahedral complex are removed, the remaining ligands form a square. The repulsion between bonding electrons on the $z$ axis ceases for the $d_{z^2}$, the $d_{xz}$, and the $d_{yz}$ electrons. Only one orbital, namely $d_{xz}$, still experiences a strong repulsion from the remaining bond electrons and is energetically unfavorable (Fig. 9.3). Square coordination is the preferential coordination for $d^8$ configuration, as for Ni(II) and especially for Pd(II), Pt(II), and Au(III), in particular with ligands that cause a strong
9.2 Ligand Field Stabilization Energy

When ligands approach a central atom or ion, the following energetic contributions become effective:

- Energy gain (freeness energy) by the formation of covalent bonds.
- Energy expenditure due to the mutual repulsion of the bonding electron pairs and due to the repulsion between ligands that approach each other too closely.
- Energy expenditure due to the repulsion exerted by bonding electron pairs on non-bonding electrons of the central atom.

Ligand field theory mainly considers the last contribution. For this contribution the geometric distribution of the ligands is irrelevant as long as the electrons of the central atom have a spherical distribution; the repulsion energy is always the same in this case. All half and fully occupied electron shells of an atom are spherical, namely $d^5$ high-spin and $d^{10}$ (and naturally $d^0$). This is not so for other $d$ electron configurations.

In order to compare the structural options for transition metal compounds and to estimate which of them are most favorable energetically, the ligand field stabilization energy (LFSE) is a useful parameter. This is defined as the difference between the repulsion energy of the bonding electrons toward the $d$ electrons as compared to a notional repulsion energy that would exist if the $d$ electron distribution were spherical.

In an octahedral complex a $d_{z^2}$ electron is oriented toward the ligands (the same applies for $d_{x^2-y^2}$); it exercises more repulsion than if it were distributed spherically. Compared to this imaginary distribution it has a higher energy state. On the other hand, a $d_{xy}$ electron is lowered energetically: it is being repelled less than an electron with spherical distribution. The principle of the weighted mean holds: the sum of the energies of the raised and the lowered states must be equal to the energy of the spherical state. Since there are two raised and three lowered states for an octahedron, the following scheme results:
The energy level diagrams in Fig. 9.3 have been drawn according to the principle of the weighted mean energy. They show how the energy levels are placed relative to the level of the notional state of a spherical $d$ electron distribution. They do not represent absolute energy values, as the absolute level of the notional state also depends on the other energy contributions mentioned above. Even when the central atoms and the ligands are the same, the level of the notional state differs on an absolute scale for different ligand arrangements, i.e. the different term schemes are shifted mutually.

Table 9.1 lists the values for the ligand field stabilization energies for octahedral and tetrahedral complexes. The values are given as multiples of $\Delta_o$ and $\Delta_t$. In Fig. 9.4 the values have been plotted; the curves also show the influence of the other energy contributions for $3d$ elements. In the series from $\text{Ca}^{2+}$ to $\text{Zn}^{2+}$ the ionic radii decrease and the bond energies increase; correspondingly the curves run downwards from left to right. The dashed lines apply for the notional ions with spherical electron distributions. The actual energy values for the truly spherical electron distributions $d^0$, $d^3$ high-spin and $d^{10}$ are situated on these lines. Due to the decreasing ionic radii octahedral complexes become less stable than tetrahedral complexes toward the end of the series (because of increasing repulsive forces between the bonding electron pairs and due to the more crowded ligand atoms); for this reason the dashed line for octahedra bends upwards at the end. The ligand field stabilization energy is the reason for the occurrence of two minima in the curves for high-spin complexes. The minima correspond to the configurations $d^3$ and $d^8$ for octahedral and

Table 9.1: Ligand field stabilization energies (LFSE) for octahedral and tetrahedral ligand distributions

| octahedra, high-spin | octahedra, low-spin | tetrahedra, high-spin | number of $d$ electrons | $0$ | $1$ | $2$ | $3$ | $4$ | $5$ | $6$ | $7$ | $8$ | $9$ | $10$
|----------------------|---------------------|----------------------|--------------------------|----------------|---|---|---|---|---|---|---|---|---|---|---|---|
| $\frac{3}{2}A_o \uparrow$ | $\frac{3}{2}A_o \uparrow$ | $\frac{3}{2}A_t \uparrow$ | $e_g$ | $0$ | $0$ | $0$ | $0$ | $1\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $3\times \frac{3}{5}$ | $4\times \frac{3}{5}$ | $e_g$
| $\frac{1}{2}A_o \uparrow$ | $\frac{1}{2}A_o \uparrow$ | $\frac{1}{2}A_t \uparrow$ | $t_{2g}$ | $0$ | $-1\times \frac{1}{5}$ | $-2\times \frac{1}{5}$ | $-3\times \frac{1}{5}$ | $-3\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $-5\times \frac{1}{5}$ | $-6\times \frac{1}{5}$ | $-6\times \frac{1}{5}$ | $-6\times \frac{1}{5}$ | $-6\times \frac{1}{5}$ | $e_t$
| $\frac{1}{2}A_t \downarrow$ | $\frac{1}{2}A_t \downarrow$ | $\frac{1}{2}A_t \downarrow$ | $e$ | $0$ | $-1\times \frac{1}{5}$ | $-2\times \frac{1}{5}$ | $-3\times \frac{1}{5}$ | $-3\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $-4\times \frac{1}{5}$ | $e_t$
| sum = $\text{LFSE/}A_o$ | sum = $\text{LFSE/}A_t$ | sum = $\text{LFSE/}A_t$ | $0$ | $0$ | $0$ | $0$ | $0$ | $1\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $2\times \frac{3}{5}$ | $3\times \frac{3}{5}$ | $4\times \frac{3}{5}$ | $0$
9.2 Ligand Field Stabilization Energy

Fig. 9.4
Relative ligand field stabilization energies for 3d ions.
Thick lines: octahedral field; thin lines: tetrahedral field; dashed lines: energies for (notional) spherical d electron distributions.

To $d^2$ and $d^7$ for tetrahedral complexes. The stabilization energies are less for tetrahedral ligand fields, since generally $\Delta_o > \Delta_t$ (in Fig. 9.4 $\Delta_t = \frac{9}{5} \Delta_o$ was assumed). For octahedral low-spin complexes there is only one minimum at $d^6$.

For high-spin compounds only rather small stabilization differences result between octahedral and tetrahedral coordination for the configurations $d^7$ and $d^8$ (Fig. 9.4). $\text{Co}^{2+}$ shows a tendency to tetrahedral coordination, whereas this tendency is overcompensated for Ni$^{2+}$ by the larger ligand field stabilization for octahedra, so that Ni$^{2+}$ prefers octahedral coordination. Here the different locations of the maxima of the ligand field stabilization energies takes effect (Table 9.1): it is largest for tetrahedra at configuration $d^7$ ($\text{Co}^{2+}$) and for octahedra at $d^8$ (Ni$^{2+}$). With increasing ligand sizes the tendency toward tetrahedral coordination becomes more marked; in other words, the octahedral arrangement becomes relatively less stable; in Fig. 9.4 this would be expressed by an earlier upwards bending of the thick dashed line. Fe$^{2+}$ and Mn$^{2+}$ also form tetrahedral complexes with larger ligands like Cl$^-$ or Br$^-$.

In Fig. 9.4 the additional stabilization by the JAHN–TELLER effect has not been taken into account. Its inclusion brings the point for the (distorted) octahedral coordination for Cu$^{2+}$ further down, thus rendering this arrangement more favorable.

The ligand field stabilization is expressed in the lattice energies of the halides MX$_2$. The values obtained by the BORN–HABER cycle from experimental data are plotted vs. the $d$ electron configuration in Fig. 9.5. The ligand field stabilization energy contribution is no more than 200 kJ mol$^{-1}$, which is less than 8% of the total lattice energy. The ionic radii also show a similar dependence (Fig. 9.6; Table 6.4, p. 50).
9.3 Coordination Polyhedra for Transition Metals

According to the preceding statements certain coordination polyhedra occur preferentially for compounds of transition metals, depending on the central atom, the oxidation state, and the kind of ligand. The general tendencies can be summarized as follows:

The series of 3\(d\) elements from scandium to iron as well as nickel preferably form octahedral complexes in the oxidation states I, II, III, and IV. Octahedra and tetrahedra are known for cobalt, and tetrahedra for zinc and copper(I). Copper(II) (\(d^9\)) forms JAHN-TELLER distorted octahedra and tetrahedra. With higher oxidation states (= smaller ionic radii) and larger ligands the tendency to form tetrahedra increases. For vanadium(V), chromium(VI) and manganese(VII) almost only tetrahedral coordination is known (VF\(_5\) is an exception). Nickel(II) low-spin complexes (\(d^8\)) can be either octahedral or square.

Among the heavier 4\(d\) and 5\(d\) elements, tetrahedral coordination only occurs for silver, cadmium, and mercury and when the oxidation states are very high as in MoO\(_2^2\)-, ReO\(_4^-\) or OsO\(_4\). Octahedra are very common, and higher coordination numbers, especially 7, 8, and 9, are not unusual, as for example in ZrO\(_2\) (c.n. 7), Mo(CN)\(_8^\) or LaCl\(_3\) (c.n. 9). A special situation arises for the electronic configuration \(d^8\), namely for Pd(II), Pt(II), Ag(III), and Au(III), which almost always have square coordination. Pd(0), Pt(0), Ag(I), Au(I), and Hg(II) (\(d^{10}\)) frequently show linear coordination (c.n. 2). In Table 9.2 the most important coordination polyhedra are summarized with corresponding examples.
**Table 9.2** Most common coordination polyhedra for coordination numbers 2 to 6 for transition metal compounds

<table>
<thead>
<tr>
<th>polyhedron</th>
<th>c.n.</th>
<th>electron config.</th>
<th>central atom</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear arrangement</td>
<td>2</td>
<td>$d^{10}$</td>
<td>Cu(I), Ag(I), Au(I), Hg(II)</td>
<td>Cu$_2$O, Ag(CN)$_2^-$, AuCN$^-$, AuCl$_2^-$, HgCl$_2$, HgO$^-$</td>
</tr>
<tr>
<td>triangle</td>
<td>3</td>
<td>$d^{10}$</td>
<td>Cu(I), Ag(I), Au(I), Hg(II)</td>
<td>Cu(CN)$_2^-$, Ag$_2$Cl$_5^-$, Au(PPh$_3$)$_2^-$, HgI$_2$</td>
</tr>
<tr>
<td>square</td>
<td>4</td>
<td>$d^8$</td>
<td>Ni(II), Pd(II), Pt(II), Au(III)</td>
<td>Ni(NCN)$_2$$^-$, PdCl$_3$$^-$, PtH$_2$$^-$, Pt(NH$_3$)$_2$Cl$_2$, AuCl$_3$$^-$</td>
</tr>
<tr>
<td>tetrahedron</td>
<td>4</td>
<td>$d^0$</td>
<td>Ti(IV), V(V), Cr(VI), Mo(VI), Mn(VII), Re(VII)</td>
<td>TiCl$_4$, VO$_2^-$, CrO$_2^-$, MoO$_4^2$-, WO$_2^-$, Mn$_2$O$_7$, ReO$_7^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^1$</td>
<td>V(IV), Cr(V), Mn(VI), Ru(VII)</td>
<td>RuO$_4^-$, OsO$_4^-$, VCl$_4$, CrO$_3^2$-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^5$</td>
<td>Mn(II), Fe(III)</td>
<td>MnBr$_2$$^-$, Fe$_2$Cl$_6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^6$</td>
<td>Fe(II)</td>
<td>FeCl$_3$$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^7$</td>
<td>Co(II)</td>
<td>CoCl$_3$$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^8$</td>
<td>Ni(II)</td>
<td>NiCl$_4$$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^9$</td>
<td>Cu(II)</td>
<td>CuCl$_4$$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^{10}$</td>
<td>Ni(0), Cu(I), Zn(II), Hg(II)</td>
<td>Zn(CN)$_4$$^2$-, HgI$_2$$^-$</td>
</tr>
<tr>
<td>square pyramid</td>
<td>5</td>
<td>$d^0$</td>
<td>Ti(IV), V(V), Nb(V), Mo(VI), W(VI), V(IV), Cr(V), Mo(V), W(V), Re(VI)</td>
<td>TiOCl$_2$$^-$, VOF$_2$$^-$, NbSCl$_4$$^-$, MoNCl$_4$$^-$, WNCI$_4$$^-$, VCl$_4$, VO(NCS)$_2$$^-$, CrOCl$_4$$^-$, MoOCl$_5$$^-$, WSCI$_7$$^-$, ReOCl$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^1$</td>
<td>V(IV), Cr(V), Mo(V), W(V), Re(VI)</td>
<td>OsNCI$_4$$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^2$</td>
<td>Os(VI)</td>
<td>OsNCI$_4$$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^3$</td>
<td>Mn(III), Re(III)</td>
<td>MnCl$_2$$^-$, Re$_2$Cl$_8$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^4$</td>
<td>Co(II)</td>
<td>Co(CN)$_5$$^3$-</td>
</tr>
<tr>
<td>trigonal bipyramid</td>
<td>5</td>
<td>$d^2$</td>
<td>V(IV)</td>
<td>VCl$_3$(NMe$_3$)$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d^8$</td>
<td>Fe(0)</td>
<td>Fe(CO)$_5$</td>
</tr>
<tr>
<td>octahedron</td>
<td>6</td>
<td>nearly all; rarely Pd(II), Pt(II), Au(III), Cu(I)</td>
<td>nearly all; rarely Pd(II), Pt(II), Au(III), Cu(I)</td>
<td></td>
</tr>
</tbody>
</table>

* endless chain  † Jahn–Teller distorted

### 9.4 Isomerism

Two compounds are *isomers* when they have the same chemical composition but different molecular structures. Isomers have different physical and chemical properties.

**Constitution isomers** have molecules with different *constitutions*, *i.e.* the atoms linked with one another differ. For example:

- **Constitution isomers**
  - S\(\equiv\)S
  - S\(\equiv\)S

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  - S\(\equiv\)S
  - S\(\equiv\)S
Transition metal complexes in particular show several kinds of constitution isomers, namely:

**Bonding isomers**, differing by the kind of ligand atom bonded to the central atom, for example:

\[
\begin{align*}
\text{Ph}_3\text{As} & \quad \text{AsPh}_3 \\
\text{Pt} & \quad \text{Pt} \\
\text{N} & \quad \text{S} \\
\text{S} & \quad \text{C} \\
\text{N} & \quad \text{C} \\
\end{align*}
\]

Further ligands that can be bonded by different atoms include \(\text{OCN}^-\) and \(\text{NO}_2^-\). Cyanide ions always are linked with their \(\text{C}\) atoms in isolated complexes, but in polymeric structures as in Prussian blue they can be coordinated via both atoms (\(\text{Fe} \quad \text{C} \quad \text{N} \quad \text{Fe}\)).

**Coordination isomers** occur when complex cations and complex anions are present and ligands are exchanged between anions and cations, for example:

\[
\begin{align*}
[\text{Cu(NH}_3)_4][\text{PtCl}_4] & \quad [\text{Pt(NH}_3)_4][\text{CuCl}_4] \\
[\text{Pt(NH}_3)_4][\text{PtCl}_6] & \quad [\text{Pt(NH}_3)_4\text{Cl}_2][\text{PtCl}_4]
\end{align*}
\]

Further variations are:

**Hydrate isomers**, e.g. \([\text{Cr(OH}_2)_6]\text{Cl}_3, [\text{Cr(OH}_2)_5\text{Cl}]\text{Cl}_2\text{H}_2\text{O}, [\text{Cr(OH}_2)_4\text{Cl}_2]\text{Cl}\text{H}_2\text{O}\)

**Ionization isomers**, e.g. \([\text{Pt(NH}_3)_4\text{Cl}_2]\text{Br}_2, [\text{Pt(NH}_3)_4\text{Br}_2]\text{Cl}_2\)

**Stereo isomers** have the same constitution, but a different spatial arrangement of their atoms; they differ in their *configuration*. Two cases have to be distinguished: geometric isomers (diastereomers) and enantiomers.

**Geometric isomers** occur as *cis–trans* isomers in compounds with double bonds like in \(\text{N}_2\text{F}_2\) and especially when coordination polyhedra have different kinds of ligands. The most important types are square and octahedral complexes with two or more different ligands (Fig. 9.7). To designate them in more complicated cases, the polyhedron vertices are numbered alphabetically, for example *abf*-triaqua-\(\text{cde}-\text{tribromoplatinum(IV)}* for *mer*-[\text{PtBr}_3(\text{OH}_2)]^3^+*. No geometric isomers exist for tetrahedral complexes. With other

Fig. 9.7
Geometric isomers for square and octahedral coordination with two different ligands. Top right: designation of ligand positions in an octahedral complex.
coordination polyhedra the number of possible isomers increases with the number of different ligands (Table 9.3); however, usually only one or two of them are known.

**Enantiomers** have structures of exactly the same kind and yet are different. Their structures correspond to mirror images. In their physical properties they differ only with respect to phenomena that are polar, *i.e.* that have some kind of a preferred direction. This especially includes polarized light, the polarization plane of which experiences a rotation when it passes through a solution of the substance. For this reason enantiomers have also been called optical isomers. In their chemical properties enantiomers differ only when they react with a compound that is an enantiomer itself.

The requirement for the existence of enantiomers is a *chiral* structure. Chirality is solely a symmetry property: a rigid object is chiral if it is not superposable by pure rotation or translation on its image formed by inversion. Such an object contains no rotoinversion axis (or rotoreflection axis; *cf.* Section 3.1). Since the reflection plane and the inversion center are special cases of rotoinversion axes (e.g. 2 and 1), they are excluded.

A chiral object and the opposite object formed by inversion form a pair of *enantiomers*. If an enantiomorph is a molecular entity, it is called an enantiomer. An equimolar mixture of enantiomers is a *racemate*.

In crystals, in addition, no glide planes may occur. Rotation axes and screw axes are permitted. As a consequence, only 65 out of the 230 space-group types may occur; these are called *Sohncke space-group types* after L. SOHNCKE who was the first to describe them. Among the 65 SOHNCKE space group types there are 11 enantiomorphic pairs which have only one kind of right- or left-handed screw axis (e.g. $P4_1$ and $P4_3$). Only these 22 space-group types are chiral themselves. The remaining 43 SOHNCKE space-group types do permit chiral crystal structures, but their space groups are not chiral.*

The great majority of known chiral compounds are naturally occurring organic substances, their molecules having one or more *asymmetrically substituted carbon atoms* (stereogenic atoms). Chirality is present when a tetrahedrally coordinated atom has

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*In literature, SOHNCKE space-group types are often termed ‘chiral space groups’, which is not correct. Most chiral molecular compounds do not crystallize in a chiral (enantiomorphic) space group. For details see [86].
Fig. 9.8
Examples of some chiral complexes with octahedral coordination.

Four different ligands. Known inorganic enantiomers are mainly complex compounds, mostly with octahedral coordination. In Table 9.3 ligand combinations are listed for which chiral molecules are possible. Well known chiral complexes are chelate complexes, some examples being shown in Fig. 9.8. The configuration of trichelate complexes like $\text{[Co(H}_2\text{N(CH}_2\text{)}_3\text{NH}_2\text{)]^3}^{+}$ can be designated by $\Delta$ or $\Lambda$: view the structure along the threefold rotation axis, as shown in Fig. 9.8; if the chelate groups are oriented like the turns of a right-handed screw, then the symbol is $\Delta$.

### 9.5 Problems

1. State which of the following octahedral high-spin complexes should be Jahn–Teller distorted.
   - $\text{TiF}_6^{2-}$, $\text{MoF}_6$,
   - $\text{[Cr(OH}_2\text{)]}_6^{3+}$, $\text{[Mn(OH}_2\text{)]}_6^{3+}$, $\text{[Mn(OH}_2\text{)]}_6^{3+}$, $\text{FeCl}_6^{2-}$, $\text{[Ni(NH}_3\text{)]}_6^{2+}$, $\text{[Cu(NH}_3\text{)]}_6^{3+}$.

2. State which of the following tetrahedral complexes should be Jahn–Teller distorted, and what kind of a distortion it should be.
   - $\text{CrCl}_4^{2-}$, $\text{MnBr}_2^{2-}$, $\text{FeCl}_4^{2-}$, $\text{NiBr}_2^{2-}$, $\text{CuBr}_2^{2-}$, $\text{Cu(CN)}_4^{3-}$, $\text{Zn(NH}_3\text{)}_4^{2+}$.

3. Decide whether the following complexes are tetrahedral or square.
   - $\text{Co(CO)}_4$, $\text{Ni(PF}_3\text{)}_4$, $\text{PtCl}_2(\text{NH}_3)_2$, $\text{Pt(NH}_3\text{)}_2^{2+}$, $\text{Cu(OH)}_2^{2-}$, $\text{Au}_2\text{Cl}_6$ (dimeric via chloro bridges).

4. What are the point groups of the complexes shown in Fig. 9.8 and why are they chiral?

5. How many isomers do you expect for the following complexes?
   - (a) $\text{PtCl}_2(\text{NH}_3)_2$; (b) $\text{ZnCl}_2(\text{NH}_3)_2$; (c) $\text{[OsCl}_4\text{F}_2\text{]}^{2-}$; (d) $\text{[CrCl}_3(\text{OH}_2\text{)}_3\text{]}^{3-}$; (e) $\text{Mo(CO)}_3\text{OR}_2$.