Synthesis and characterization of inorganic complexes
Content:

Review of coordination compounds
General synthesis methods
Prevalent characterization
Review some experiment

Laboratory
12 section advanced experiment
Interoperation of results
References:

Direct Synthesis Of Coordination and Organmetallic Compounds

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نیم سال اول ۹۲-۹۳
References:

Purification of laboratory Chemical 6th
By:
W. L. F. Armarego
Ch. L. L. Chai

Practical Skills in Chemistry
By:
J. R. Dean & et al
“Probably the greatest conceptual contribution to inorganic chemistry—comparable in both direct and indirect impact to the concept of the tetrahedral carbon atom in organic chemistry—is Alfred Werner’s concept of coordination compounds and his general theory of how they behave.” Albert Cotton
Compounds that contain metal complexes are called coordination compounds.

CoCl$_3$ and NH$_3$.

[Co(NH$_3$)$_6$]Cl$_3$ and [CoCl(NH$_3$)$_5$]Cl$_2$

Differing reactivity with AgNO$_3$.

Alfred Werner 1866-1919
THE METALS

Transition element

Elements with incomplete d shell
Mercury (Hg) is the only transition metal that is not a solid.
Form cations in beautifully coloured
Is Zn a transition metal?
THE TRANSITION METALS

(A) Position

First/second/third row TMs

- Size decreases down a group
- Lanthanide contraction (filling of f orbitals)

Sizes of 2nd row and 3rd row TMs are similar (why)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Cr$^{3+}$</th>
<th>Mo$^{3+}$</th>
<th>Ru$^{3+}$</th>
<th>Ir$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size/Å</td>
<td>0.76</td>
<td>0.83</td>
<td>0.82</td>
<td>0.82</td>
</tr>
<tr>
<td>(CN = 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(B) Early/late Transition element

Early: on the LHS of the periodic table (e.g. Ti)
Late: on the RHS of the periodic table (e.g. Pt)

Usually, for metal complexes

- Early TM : high metal oxidation state, e.g. Ti(IV), V(V) (high valent);
- hard metal ions (binds to hard ligands)

- Late TM : low metal oxidation state, e.g. Pt(II), Au(I) (low valent);
- soft metal ions (binds to soft ligands)
### d-block transition elements

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>La*</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
<tr>
<td>Ac†</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Rg</td>
<td>Uub</td>
</tr>
</tbody>
</table>

### f-block transition elements

<table>
<thead>
<tr>
<th>*Lanthanides</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>†Actinides</td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>No</td>
<td>Lr</td>
</tr>
</tbody>
</table>
Metal Oxidation states

Variable

Up to +8 in Os & Ru

Re has widest range: -3 $\Rightarrow$ +7!
Werner's Coordination Theory

primary valence => ion charge
secondary valence => coordination number
inner sphere => ligands bonded directly to metal ion
outer sphere => next sheath of ions or molecules
Coordination compounds:

* Combination of two or more atoms, ions, or molecules where a bond is formed by sharing a pair of electrons originally associated with only one of the compounds.

• Co-ordination complexes are compounds in which several ligands are co-ordinated to a transition metal cation.
Coordination compounds:

-Ion containing central metal ion bound to one or more ligands

Lewis base (or e⁻ donor) that forms bond w/metal

When complex ion combines w/counter-ions (non-ligands) they yield a neutral compound
Coordination compounds:

Some co-ordination complexes and complex salts contain extra water molecules which were trapped during crystallization. These complexes are also hydrates.
Coordination compounds (metal complexes)

Metal

Ligand

Counter anion

Common geometry

Tetrahedral

Square pyramidal

Square planar

Trigonal bipyramidal

Octahedral
LIGANDS

(A) Charge (formal charge)
Neutral (e.g. :CO, :PR₃, :NH₃)
Anionic (e.g. Cl⁻, O²⁻, CH₃⁻)
Cationic (rare!) (e.g. NO⁺, C₇H₇⁺)

(B) Hard/Soft properties
Hard : period 1 donor (NH₃, OH₂)
Soft : carbon (CO, CH₃⁻, CH₂=CH₂) & period 2 donors (PR₃, SR₂)
No. of donor atom

<table>
<thead>
<tr>
<th>unidentate</th>
<th>bidentate</th>
<th>tridentate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃, ammonia</td>
<td>NH₂CH₂CH₂NH₂, ethylenediamine (en)</td>
<td>NH(CH₂NH₂)₂, diethylenetriamine (dien)</td>
</tr>
<tr>
<td>or ammine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Metals complexes with polydentate (chelating) ligands are more stable than those with unidentate analogues. **Chelate effect**