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Note

Dedicated to Academician Cristian Silvestru on the occasion of his 70th anniversary

MOLECULAR TOPOLOGIES OF COORDINATION COMPLEXES. DIVERSITY AND SYSTEMATIZATION

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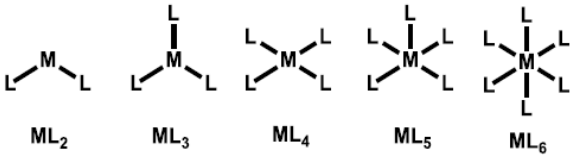
The coordination complexes display a remarkable diversity. Classical complexes are metal-centered, with coordination numbers from two to six, sometimes even higher. This category also includes chelate rings with both organic chelating ligands and inorganic (carbon-free) chelating ligands. A second important is the emerging category of inverse coordination complexes. This includes complexes with non-metallic single atom as coordination centers, complexes with homopolyatomic molecules as coordination centers and complexes with linear and cyclic heteroatom molecules as coordination centers.

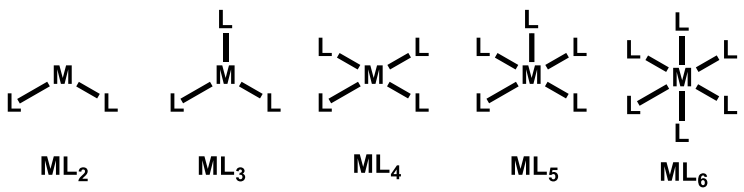


INTRODUCTION

The IUPAC Nomenclature Recommendations for Inorganic Chemistry[1] define a coordination compound as *any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom,* usually that of a metal, *to which is attached a surrounding array of other atoms or groups of atoms*. It seems that the words "usually that of a metal" have in view non-metal centered complexes such as $[BF_4]^-$, $[SiF_6]^{2-}$ and $[PF_6]^-$.

CLASSICAL COMPLEXES

There is a general view that coordination compounds are *metal-atom centered complexes.* This definition covers the classical (Werner) coordination complexes $[ML_n]$ and includes the great majority of coordination compounds.



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As metal-centered coordination complexes one can also recognize several typess of compounds, namely:

– Chelate complexes with five- and six-membered rings (Fig. 1); examples being ethylenediamine $M(H_2NCH_2CH_2NH_2)$ and acetylacetonato $M(OCO)_2C$ compounds.

– Spiro-bis(chelate) complexes with the same organic difunctional donors (Fig. 2).

– Double chelate chelating complexes (Fig. 3).

A particular typey involves inorganic (carbon-free) monochelate complexes (Fig. 4), and inorganic (carbon-free) bis(chelating) rings (Fig. 5).

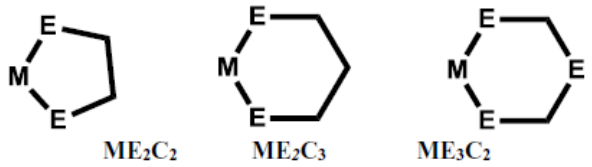


Fig. 1

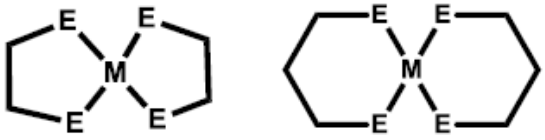


Fig. 2

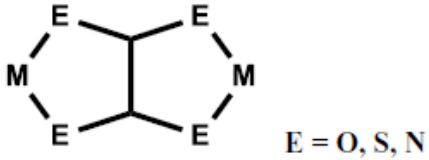


Fig. 3

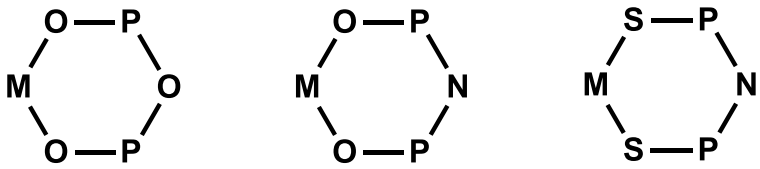


Fig. 4

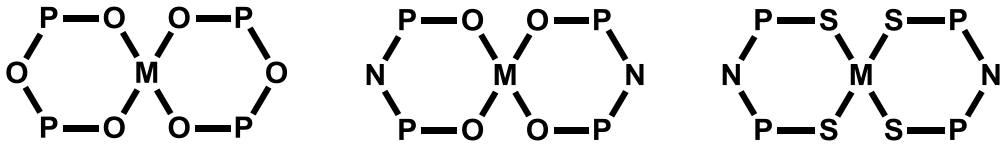


Fig. 5

COORDINATION POLYMERS

Inveerse coordination complexes

In parallel with the Werner complexes another type of compounds emerged, namely the inverse coordination complexes $[EM_x]^2$ ()Fig. 6.

With non-metal molecular coordination centers, numerous homopolyatomic inverse cordination complexes can be cited with dinuclear moieties [3] (Fig. 7) and polynuclear monocyclic moieties as centroligands,[4] (Fig. 8), as well as bicycic centroligands[5] (Fig. 9) and polycyclic centroligands[6] (Fig. 10).

Among inverse coordination complexes those with heterocyclic centroligands are remarquable[7] (Fig. 11)

Oxalates and thiooxalates and nitrogen analogues[8] add to the list (Fig. 12).

A comprehensive family comprises spirobicylic chelates with sulfur,[9] phosphorus[10] and arsenic[11] centroligands (Fig. 13).

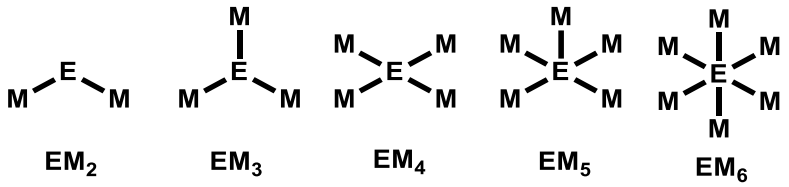
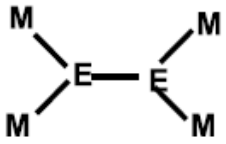
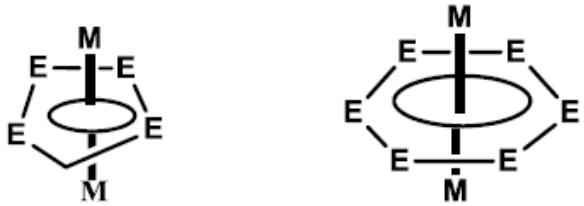


Fig. 6



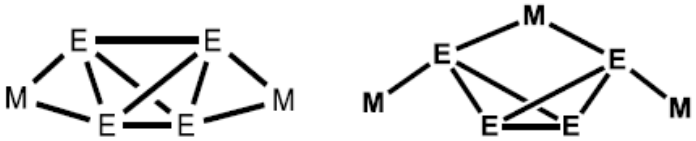
E = O, S, Se, Te, P, As, Sb,

Fig. 7



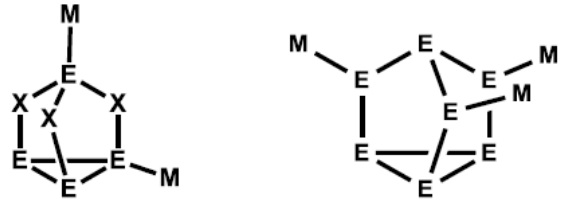
E = P, As, Sb E = P, As, Sb

Fig. 8



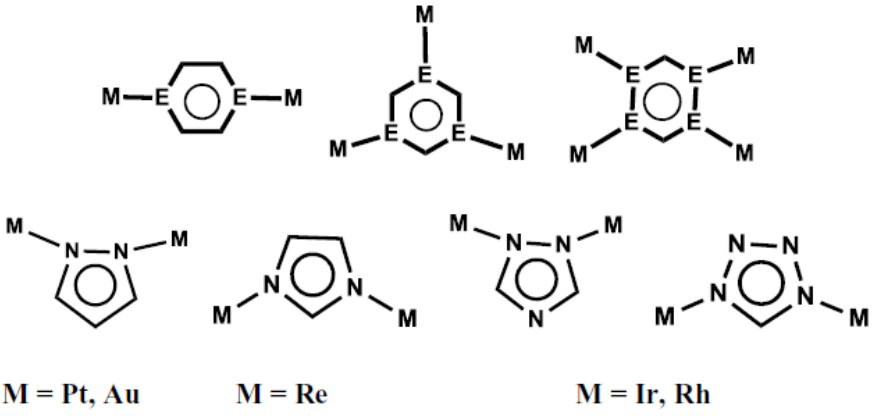
E = P, As E = P, As

Fig. 9



E = P, As; X = S E = P, As

Fig. 10



M = Pt, Au M = Re M = Ir, Rh

Fig. 11

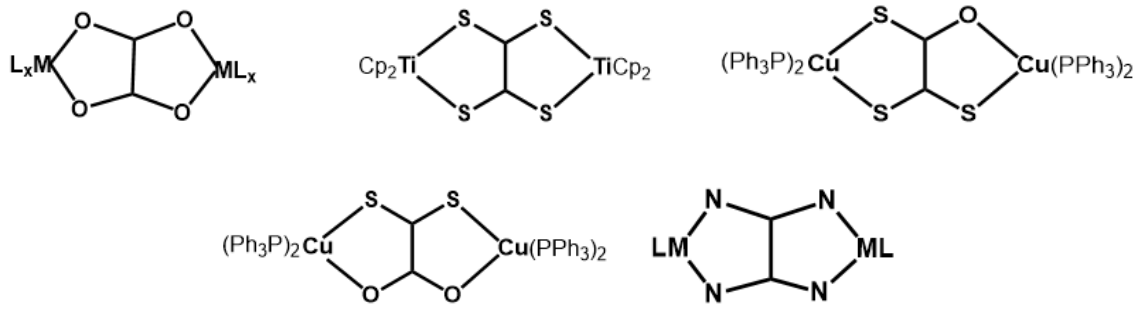


Fig. 12

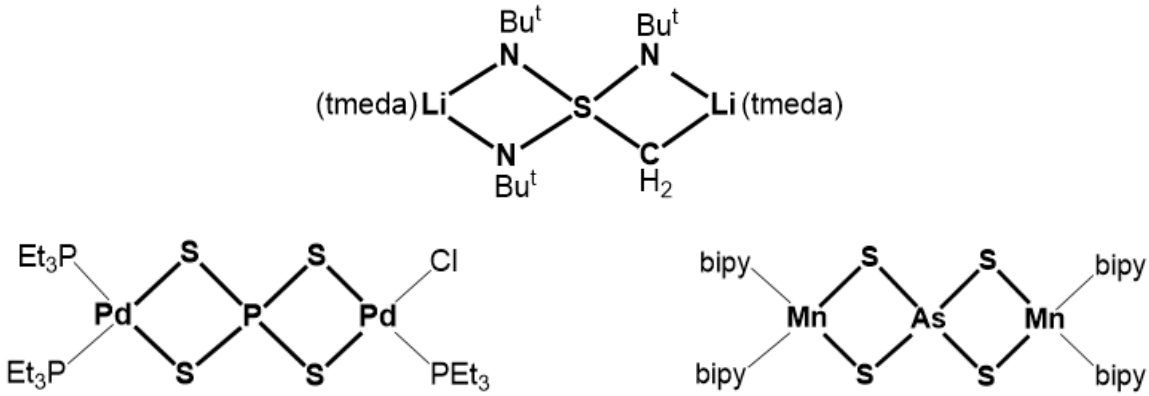


Fig. 13

The examples cited represent only an illustrative selection to demonstrate the possible great diversity of coordination complexes, which should be cited in all coordination chemistry textbooks, to give the students and readers in general, the real image of this branch of inorganic chemistry.

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