FROM SIMPLE TO COMPLEX COMPOUNDS

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Summary

Transition metal ions interact with ligating molecules, giving rise to an ordered array, whose geometrical features are determined by the electronic configuration of the metal center. Metals can act as templates preorienting a set of molecules according a definite spatial arrangement and addressing their reactivity towards the formation of otherwise hardly achievable species, like rings, cages and chains. At the end of the job, the metal can be chemically removed, to leave an intact purely organic structure. On the other hand, metal can behave like no removable building blocks in the synthesis of large and sophisticated architectures, which include double- and triple-stranded helices, squares and a variety of polyhedra. This Chapter is aimed to describe, through some selected examples, the development of inorganic chemistry from classical coordination chemistry to metallo-supramolecular chemistry. The first steps of the younger sister discipline – anion coordination chemistry – are also briefly discussed.

1. Introduction

Molecular chemistry originated in 1828, when Friederich Wöhler reported the synthesis of urea [Wöhler F., 1828], upsetting the ‘vitalistic’ belief that organic substances could be produced only by living organisms, and not inside beakers and glass bottles in a chemical Laboratory. Since then, synthetic organic chemistry developed, making available a continuously increasing number of novel molecules, of varying complexity and sophistication. Organic chemistry is the chemistry of the covalent bond: the formation of a new covalent bond may require drastic conditions, but whenever the bond has been formed, it is extremely difficult to be broken: with a few exceptions, the covalent bond is irreversible. Following a metaphor often mentioned by Jean-Marie Lehn, the atoms are the letters and the molecules are the words. Making a new word may have taken thousands of years, or more, but when a word has been formed, it remains unchanged almost indefinitely. At the end of the the XIX century, thanks to Alfred Werner (Werner A., 1893), a new type of interaction was discovered and systematically studied, between metal ions and non-metal atoms, which is now defined metal-ligand interaction. Transition metal ions, as a consequence of their electronic configuration with a partially filled d level, tend to interact with the donor atoms of up to six molecules (or ligands) and more, which are positioned at the corners of a variety of polyhedra, providing an ordered complexity, not observed in organic chemistry. This discipline is defined coordination chemistry or chemistry of metal complexes. The metal-ligand interaction can be irreversible, as observed with inert metal ions like CoIII and CrIII (and this feature helped Werner in his pioneering studies), but is in many case reversible, as observed with substitutionally labile metal ions. Thus, it may happen that one or more metal ions organize around them many molecules (ligands), giving rise to complex structures, whose geometry is dictated by the electronic features of the metal. Reversibility of the metal-ligand interaction is essential, because it allows repetitive checking and corrections of the ‘wrong’ intermediates that form, along the route to the most thermodynamically stable product. Other non-covalent and reversible interactions, e.g. hydrogen bonding, allow the formation of very complicated and sophisticated molecular structures, still following the trial-and-error protocol. The chemistry of reversible, non-covalent interactions (which includes also π–π donor-acceptor interactions) is now defined supramolecular chemistry, the chemistry of the intermolecular interactions (Lehn J.-M. 1995). Reconsidering the metaphor of the language, the reversible aggregation of molecules (words) gives rise to supramolecular systems (sentences), which can be rearranged at will, easily and at low energy cost, to give many combinations of different sense and significance. No doubts that metal ions play an important role in supramolecular chemistry and in general in the programmed design of complex aggregates.

In this Chapter, we will try to outline, with some illustrative examples, the stepwise progress from classical coordination chemistry of mononuclear complexes to the so-called metallo-supramolecular chemistry (the inorganic side of supramolecular chemistry), through the elucidation of key concepts as the chelate and macrocyclic effects, the template effect, metal directed self-assembling.

2. Metal Amine Complexes: Bonding and Geometry

Metal ions have a natural tendency to interact with several molecules or anions (ligands, up to six and more) and to arrange them in the space, according to a defined geometrical order. Such a feature was discovered and systematically investigated by Alfred Werner, at the University of Zurich, during the last decade of the 19th century. Werner focused his attention on cobalt(III) and chromium(III) ions, which, because of their inertness to substitution, a rather unusual property among 3d metals, could give rise to a variety of isolated complexes, with subtle, still detectable differences in stoichiometry, geometry and properties. In a very general sense, a complex can be defined as a molecular system, constituted by more particles held together by non-covalent interactions, exhibiting a defined stoichiometry and possessing a rigid geometry. Whereas such a definition was first utilized to describe metal complexes (or coordination complexes), it is today used to classify a variety of systems whose components interact through hydrogen bonding, σ and π donor–acceptor interactions etc. Among Werner's complexes, it is tradition to mention the series of isolated complex salts of formula: $Co(NH_3)_xCl_3$, with x = 6–3. All the complexes exhibit an octahedral geometry. In these complexes, the Cl– ion can behave as a ligand (thus involved in a direct binding to the metal), as a counterion (excluded from the coordination), or both. Peculiarly, the complex [CoIII(NH3)4Cl2]+ can be isolated in two different geometrical isomers, *trans*-dichloro and *cis*-dichloro, whereas the [CoIII(NH3)3Cl3] complex can potentially give rise to the two geometrical isomers *mer*- (meridional) and *fac*- (facial), as illustrated in Figure 1.

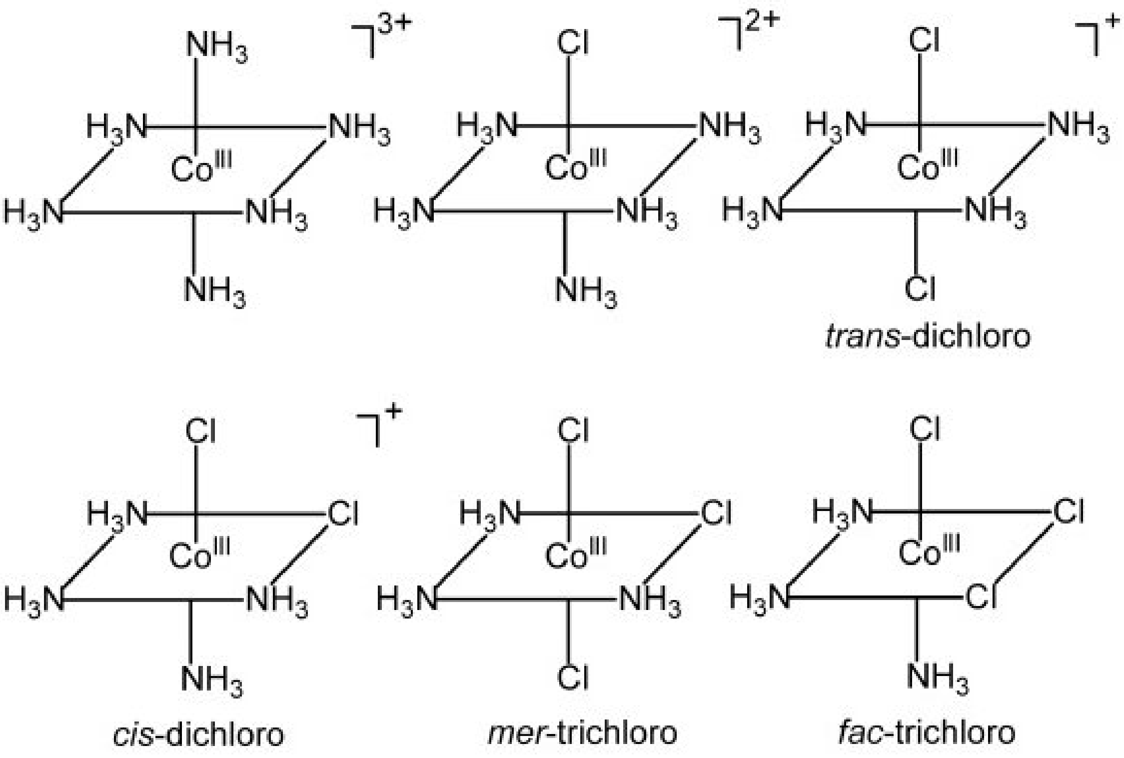

Figure 1: The molecular structure of complex salts of formula: Co(NH3)xCl3, with x = 6-3.

All these different complexes cannot be isolated with labile metal ions, e.g. NiII, which, like CoIII, prefers six-coordination and octahedral geometry. In solution, NiII exchanges ligands at a very fast rate: in particular, in the aquaion [NiII(H2O)6]2+, the residence time of each water molecule on the metal center is 3 μs. Therefore, each NiII complex instantaneously rearranges to the thermodynamically most stable species, which, in the presence of ammonia and chloride, is [NiII(NH3)6]2+: thus, only the [NiII(NH3)6]Cl2 salt will be isolated on crystallization. This is not the case of the inert CoIII complexes, whose lifetimes exceed that of the crystallization and can be potentially isolated in all the forms illustrated in Figure 1.

Coordination numbers and coordination geometries of metal complexes vary depending upon the electronic configuration of the metal, in a given oxidation state, and upon the donating features of the ligand(s), which include steric effects.

C.N.	**geometry**	**dz2**	**dx2-y2**	**dxy**	**dxz**	**dyz**
4	tetrahedral	–2.67	–2.67	1.78	1.78	1.78
4	square	–4.28	12.28	2.28	–5.14	–5.14
5	trigonal bipyramidal	7.07	–0.82	–0.82	–2.72	–2.72
5	square pyramidal	0.86	9.14	–0.86	–4.57	–4.57
6	octahedral	6.00	6.00	–4.00	–4.00	–4.00
6	trigonal prismatic	0.96	–5.84	–5.84	5.36	5.36

Table 1: Energy of d levels (in Dq) in complexes of different coordination numbers (C.N.) and geometries

Table 1 reports the most common coordination numbers (C.N.) and geometries observed with metal complexes. Moreover, the energies of d orbitals in the different geometrical arrangements are given in Dq units. These energy values have been determined on the basis of Crystal Field Theory (Figgis B. N, 2000), and allow one to calculate the overall energy gained by a transition metal of electronic configuration dn, when forming a complex of a given geometry (such an energy term is currently indicated as Crystal Field Stabilization Energy, CFSE). Each ligand has its own Dq, a value reflecting its capability to perturb the *d* orbitals of the metal ion, and, ultimately, to interact with the metal. Ligands arranged in order of increasing Dq give rise to the spectrochemical series (1).

I–, Br–, **S**CN–, Cl–, N3–, F–, OH–, H2O, **O**NO–, **N**CS–, py ~ NH3, en, bpy, **N**O2–, phen, CN–, CO (1)

Some of the ligands shown in the series are ambidentate, i.e. they can choose to bind the metal through two different donor atoms, thus exerting a different Dq. For such ambidentate ligands, the position in sequence (1) refers to the donor atom in bold red character. For instance, the **O**NO– ligand, which offers to the metal an oxygen atom (nitrito) exerts a less pronounced perturbing effect on d orbitals (and establishes weaker interactions) than the **N**O2– ligand (nitro), ligating through the nitrogen atom.

Table 1 shows that for a given coordination number *n*, two distinct geometrical arrangements may correspond. For instance, when *n* = 4, a metal complex can be either tetrahedral or square. Indeed, simple steric arguments would suggest that when four atoms or groups have to put themselves around a given center, they will choose a tetrahedral arrangement. Such a geometry, in fact, affords a minimized sterical repulsion the four atoms or groups. This is a rather obvious observation in the chemistry of covalent compounds and nobody would argue upon the tetrahedral nature of CCl4 or SiF4. However, in metal complexes there exists a further energy term in addition to the inter-ligand repulsion and refers to CFSE effects. As an example, let us consider the case of the nickel(II) complexes, for which [NiIICl4]2– is tetrahedral and [NiII(CN)4]2– is square.

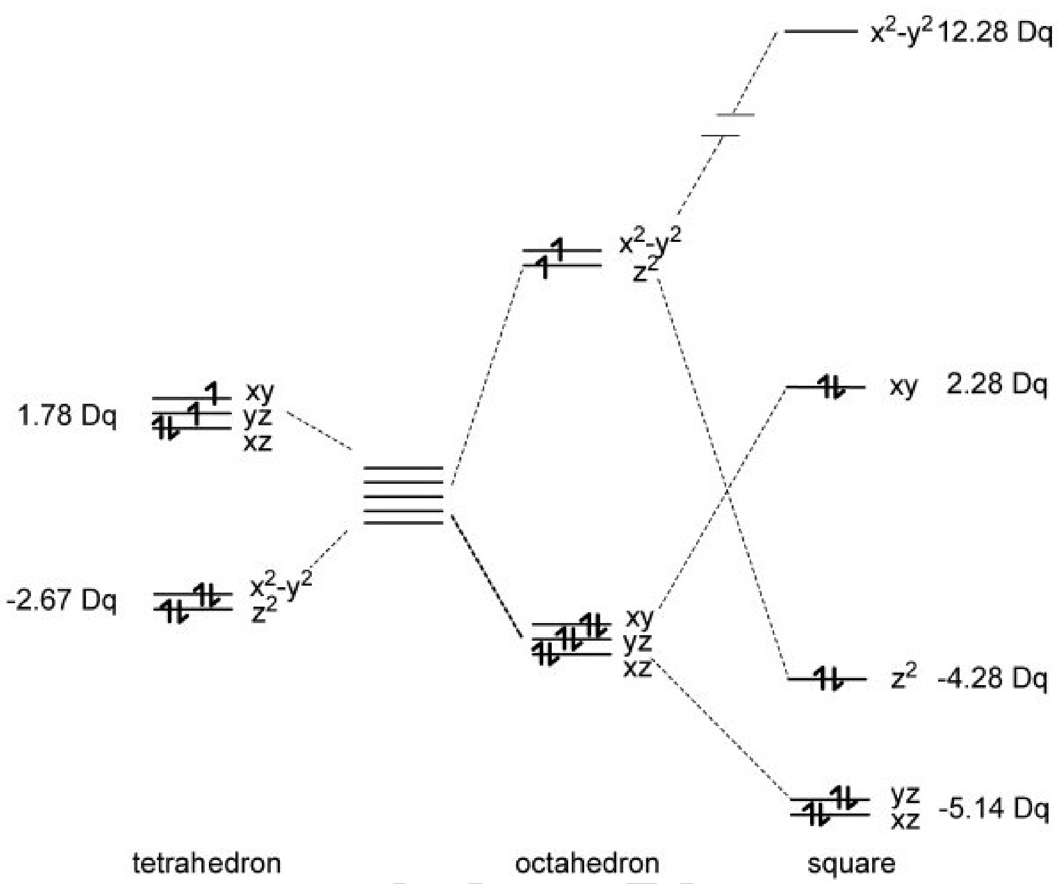

Figure 2: Crystal Field energy levels and electron distribution for a d8 cation (e.g. NiII) in a tetrahedral and in a square coordination geometry. The corresponding CFSE terms are –3.56 Dq for the tetrahedron and –24.56 Dq for the square

Figure 2 shows the energy sequence of *d* orbitals in tetrahedral and square geometries, which have been drawn on the basis of the energy values (in Dq) reported in Table 1. NiII has a 3d8 electronic configuration and, after dropping the eight electrons in the pertinent *d* orbitals, the following CFSE terms result: tetrahedral, –3.56 Dq; square, –24.56 Dq. Thus, there exists a definite advantage of the square coordination in terms of CFSE: the higher the Dq value, the more favored the square geometry. It derives that, for ligands characterized by a moderate Dq, like Cl–, the CFSE term is still too small for overcoming the steric effect associated to the inter-ligand repulsion, and a regular tetrahedral coordination geometry remains favored. However, with ligands high in the spectrochemical series like CN–, characterized by a large Dq value, the difference of the CFSE terms dominates and addresses the complex toward the square geometry.

The same ligand can contain two or more donor atoms, capable to coordinate the same metal center. This is the case of ethylenediamine (**1**, en), which possesses two sp3 nitrogen atoms (the same donor atoms of ammonia), linked by a –(CH2)2– spacer. It is essential that the spacer has the proper length to allow the donor atoms to span two adjacent positions of the coordination polyhedron. The –(CH)2– spacer shows the most favorable length; in presence of the –(CH2)3– spacer, less stable metal complexes are formed; with –(CH2)n– spacers with n ≥ 4, diamine complexes usually do not form.

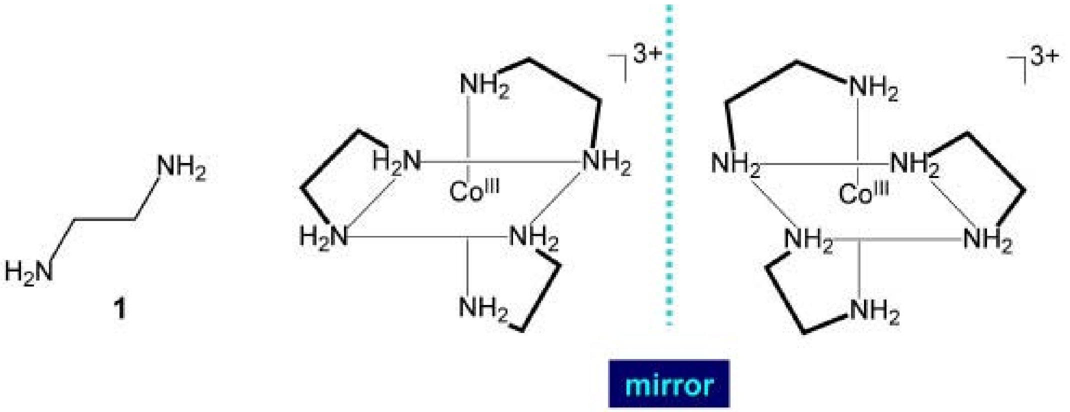

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Figure 3: The two chiral isomers of the [CoIII(en)3]3+ complex (en = 1)

Notice that one en ligand is the equivalent of two ammonia molecules and an octahedral complex will have the formula [M(en)3]n+. As an example, Figure 3 shows the geometrical arrangement of the [CoIII(en)3]3+ complex, which displays similar properties as the parent [CoIII(NH3)6]3+ complex (for instance, the yellow-orange color). Noticeably, [CoIII(en)3]3+ is non-superimposable on its mirror image, is therefore chiral and can be isolated in two enantiomers. Such a feature is obviously restricted to substitutionally inert cations (e.g. having a d8 low-spin electronic configuration, e.g. RuII, RhIII) and cannot be observed with labile metal centers, e.g. [NiII(en)3]2+, in which en molecules continuously rearrange within the coordination polyhedron.

3. Metal Complexes of Multidentate Ligands: Deviations from Regular Geometries

Coordinating systems containing more donor atoms are said multidentate ligands (from the Latin *dens, dentis*: tooth) or chelating agents (in agreement with the metaphor of the crab, which takes an object with two claws – Latin: *chelae* – as an en molecules binds a metal ion with two sp3 nitrogen atoms). Multidentate ligands can possess structural constraints that affect and address the coordination arrangement of the formed complex toward a given geometry. This is the case of the previously mentioned bidentate en ligand and this is also the case of the two quadridentate isomeric ligands *trien* (**2**, linear tetramine) and *tren* (**3**, branched, tripodal tetramine), shown in Figure 4. When reacting with copper(II), the linear trien molecule (**2**) will span the four corners of a square. As CuII has a definite tendency to reach five-coordination, a further ligand, either an anion X– or a solvent molecule, will go to occupy the apical position of a square pyramidal coordination polyhedron (**4**). On the other hand, the tetramine tren (**3**) addresses the CuII ion toward a trigonal bipyramidal coordination geometry: in particular, tren occupies with its amine nitrogen atoms four coordination sites and leaves one of the axial positions available for the coordination of an X– ion or of a solvent molecule (**5**). In the case of 5-coordination, simple inter-ligand repulsive effects would favor the trigonal bipyramidal geometry. However, the structural constraints of the tetramine ligand control the formation of the square-pyramidal [CuII(trien)X]+ complex.

Also the most common of coordination numbers – 6 – can be achieved through two different geometric arrangements: *octahedral* and *trigonal prismatic*. Inter-ligand repulsive effects favor the octahedral geometry and, actually, six-coordinated metal complexes with monodentate ligands typically exhibit an octahedral structure.

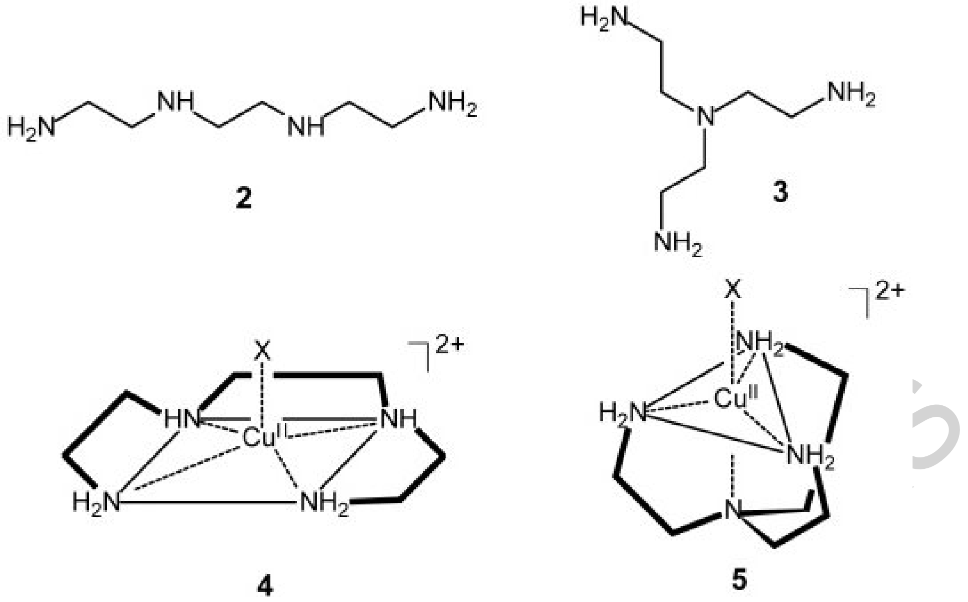

Figure 4: The geometrical arrangement of the CuII complexes with the two isomeric tetramines trien (2) and tren (3): trien favors a square pyramidal geometry (4), tren imposes the trigonal bipyramidal geometry (5). The fifth site of the coordination polyhedron is occupied by the X– anion

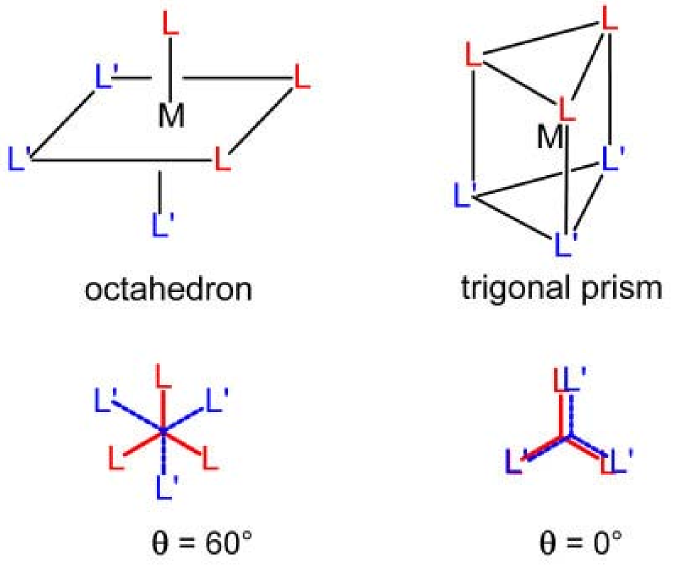

Figure 5: Structural features of six-coordinate metal complexes. The twist angle θ defines the coordination geometry, whether octahedral or trigonal prismatic

Figure 5 illustrates the structural features of the two geometrical arrangements of six-coordination. In particular, the two geometries can be distinguished on the basis of the twist angle θ, which defines whether two opposite triangular faces of the polyhedron are *staggered* (θ = 60°, octahedron) or *eclipsed* (θ = 0°, trigonal prism). The achievement of the sterically less stable trigonal prismatic arrangement can be favored by structurally constrained multidentate ligands. This could be the case of the cage hexamines of type **6**, whose trivial names, 'sepulchrands' and 'sarcophagines', refer to the attitude of the macropolycyclic ligand to irreversibly include and 'bury' metal ions [Creaser I., Harrowfield J. M., 1977].

Formula 1:

Nevertheless, it is observed that metal ions that do not profit from CFSE effects form with **6** complexes, whose geometry is neither trigonal prismatic, nor octahedral, but halfway, as indicated by the corresponding values of θ: MgII d0 (X = NH3+): 27.8°; MnII, d5 (X = NH3+): 27.6°; ZnII, d10 (X = NH3+): 28.6°. Figure 6 shows the crystal and molecular structure of the MgII complex (a), as well as the top view of the two triangles made by the coordinated primary amine nitrogen atoms (b).

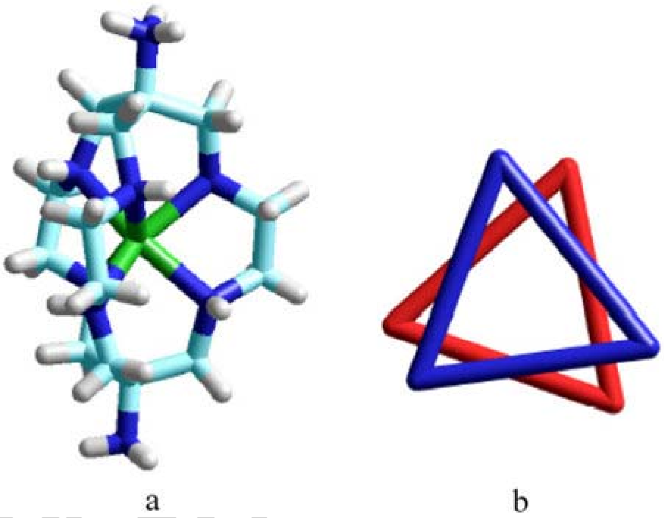

Figure 6: (a) The molecular structure of complex [MgII(diAMsarH2]4+ (diAMsarH22+ = 6, X = NH3+); (b) a top view of the triangles whose corners are occupied by secondary amine nitrogen atoms: the twist angle θ (27.8°) indicates a coordination polyhedron intermediate between trigonal prism (θ = 0°) and octahedron (θ = 60°). Structural data for this and other compounds, whose structures will be illustrated in the next Figures, have been taken from the Cambridge Crystallographic Data Centre

This is the most favorable arrangement from a purely steric point of view and corresponds to the most relaxed conformation of the cage ligand. However, in the CoIII complex (X = H) θ is 58.3°, which corresponds to an almost regular octahedral geometry. This results from the fact that a low-spin d6 metal profits more from the octahedral coordination (CFSE = –24 Dq) than from the trigonal prismatic coordination (CFSE = –21.44 Dq). Such a favorable contribution compensates for the endothermic conformational rearrangement experienced the hexamine ligand when moving from θ ~ 30° toward 60°. Figure 6a shows the crystal and molecular structure of the CoIII sarcophagine complex, whose almost regular octahedral coordination is demonstrated by the top view of the complex shown in Figure 6b.

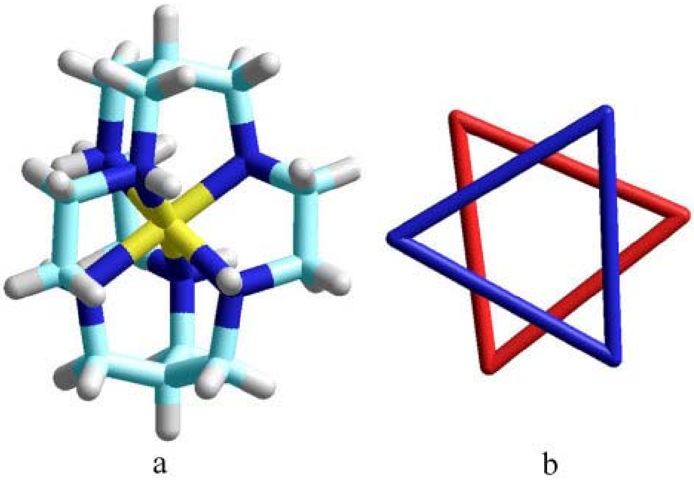

Figure 7: (a) The molecular structure of complex [CoIII(sar]3+ (sar = 6, X = H); (b) a top view of the triangles whose corners are occupied by secondary amine nitrogen atoms: the magnitude of the twist angle θ (58.3°) points towards a regular octahedral coordination geometry (θ = 60°)

The distortion towards the octahedron is less pronounced in the case of the cage complex of NiII (X = NH3+, θ = 47.1°), in view of lower the CFSE experienced by a d8 metal (octahedron: –12 Dq; trigonal prism: –10.72 Dq).

Small distortions from the regular geometry can be induced by the metal itself, when it gives rise to a degenerate electronic state. In particular, the geometry will be modified and symmetry will be reduced in order to remove degeneracy. This effect, which is correctly described as a consequence of a classical theorem of physics, the Jahn-Teller theorem, can be seen as a way offered to the metal to take a further advantage in terms of CFSE.

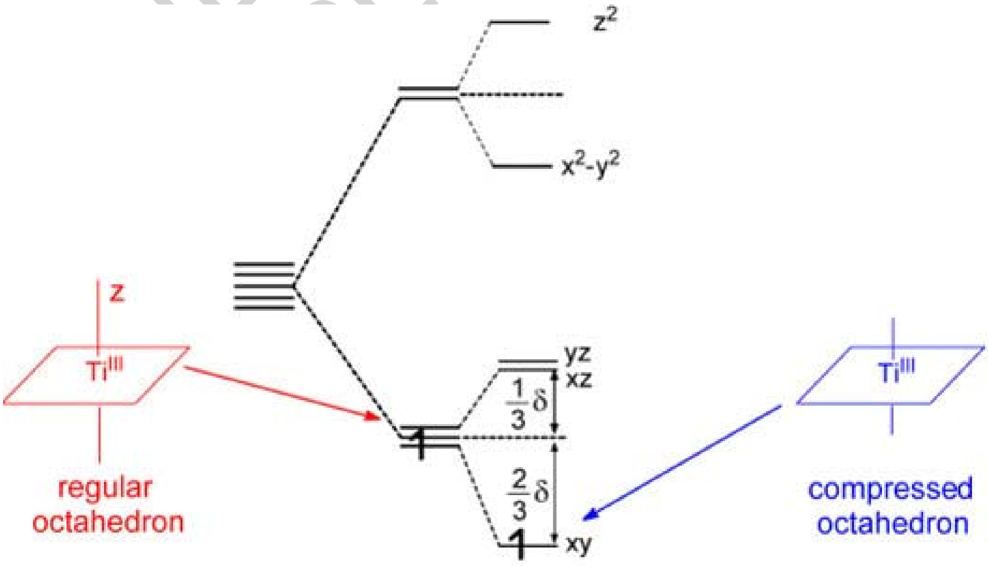

Figure 8: The effect of the axial compression (along the z axis) on the d levels of TiIII (d1), in an octahedral complex

Let us consider for instance the case of an octahedral complex of TiIII (d1), shown in Figure 8). The d electron can occupy whichever of the three degenerate orbitals dxy, dxz, dyz. Degeneracy can be removed if the two bonds along the *z* axis are made shorter and those along *x* and *y* axes are made longer. Following this geometrical modification (defined as axial compression), the orbitals which contain the *z* component are destabilized, those which do not contain the *z* component are stabilized (see Figure). Thus, in the compressed octahedron, the d electron of TiIII occupies the dxy orbital, which results in an additional CFSE contribution of 2/3 δ. Notice that elongation along the same *z* axis would not remove completely degeneracy. Indeed, even if no definite crystallographic support has been reported, yet, d–d spectra of the [TiIIICl6]3– complex clearly indicate a compressed octahedral stereochemistry.

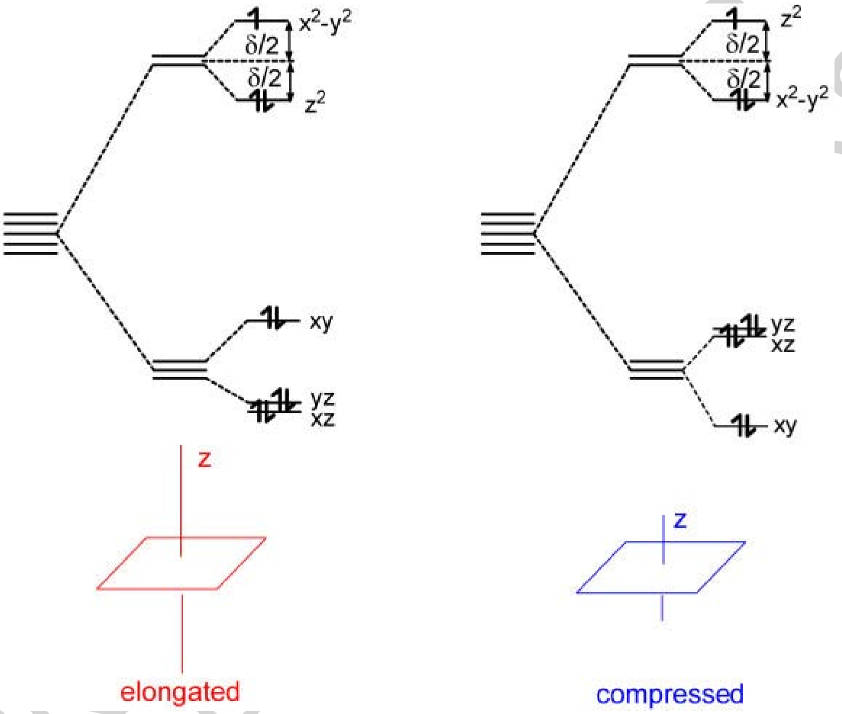

Figure 9: The effects of axial elongation and compression of the electronic structure of CuII (d9), in octahedral complexes

However, the best defined evidences of Jahn-Teller effect in metal complexes are observed with the CuII ion (d9). In a regular octahedral arrangement, the unpaired electron of CuII can choose to stay either in the dz_2 or in the $dx_2–y_2$ level, as shown in Figure 9. Both elongation and compression along the *z* axis remove degeneracy and induce the same energy gain in term of CFSE (of δ/2, in this case). As a consequence, both axially elongated and compressed octahedral geometries should be observed in CuII coordination chemistry. In solution, CuII experiences a so pronounced elongation that it beahaves as a square solvo-cation, e.g. [CuII(H2O)4]2+, and, on crystallization, gives salts of the square tetra-solvated cation.

Octahedral elongation can be also induced by the set of the ligands. This is the case of the NiII complexes of the cyclic tetramine *cyclam* (**7**). Cyclam has a tendency to include transition metal ions placing its secondary amine nitrogen atoms at the corners of a square, a favorable arrangement, in terms of CFSE contribution. Complex of NiII can be isolated as salts of formula NiII(cyclam)X2, where X– represents a mononegative anion. When the anion presents distinct coordinating tendencies (e.g. Cl–, N3–, NO3–), the metal complex displays an octahedrally elongated geometry, in which the equatorial NiII–N bonds are shorter than the axial NiII–X bonds. Figure 10a shows the crystal structure of the [NiII(cyclam)(NO3)2] complex salt. The complex shows an octahedrically elongated geometry: the NiII–N distance is 2.05–2.06 Å, whereas the distance between NiII and the oxygen atom of each coordinate nitrate ion is 2.17 Å.

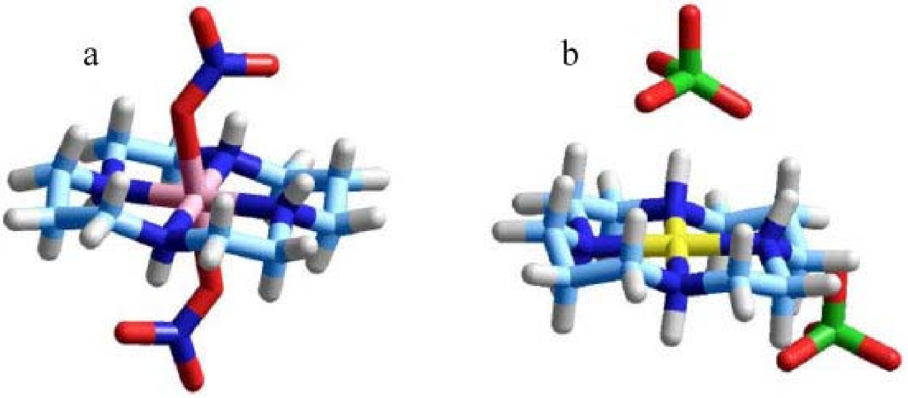

Figure 10: The crystal and molecular structure of NiII(cyclam)X2 complex salts (cyclam = 7): (a) X– = NO3–, octahedral, high-spin complex; (b) X– = ClO4–, square, low-spin complex

The complex salts is purple and is paramagnetic for two unpaired electrons, as expected for a d8 metal ion in a moderately elongated octahedral geometrical arrangement (see Figure 11). On the other hand, the analogous complex salt [NiII(cyclam)](ClO4)2 shows a yellow-orange color and is diamagnetic. Strucural studies (see Figure 10b) indicated that the two ClO4– anions are well far away from the coordinating environment of the complex. In particular, the closest oxygen atom of perchlorate anions lies at 3.55Å from the NiII center. Moreover, the NiII–N distance in the [NiII(cyclam)](ClO4)2 salt is distinctly smaller than observed in the [NiII(cyclam)(NO3)2] complex: 1.96 ± 0.03 Å. Such a drastic change in geometry and electronic properties depends upon the difference in the coordinating properties of the anion: ClO4– is a weaker ligand than NO3–, due to the fact that the negative charge is distributed over 4 rather than 3 oxygen atoms. The NiII center, therefore, is no longer interested to interact with the anions and moves to a square geometry. The octahedral-to-square geometrical change induces a drastic rearrangement of the d levels, which ultimately leads to a spin-paired electectronic configuration (see Figure 11). In such a situation, NiII has lost the two NiII–O bonds, but profits from reinforced NiII–N interactions. The same behavior is observed for [NiII(cyclam)]2+ complexes with other poorly coordinating counterions: BF4–, PF6–, CF3SO3–.

Quite interestingly, the two forms – octahedral and square – coexist in solution, according to a spin crossover equilibrium. In particular, in a solution of a polar solvent S (H2O, MeCN), the following equilibrium takes place (L = cyclam):

[NiII(L)S2]2+ $\rightleftharpoons$ [Ni(L)]2+ + 2S (1)

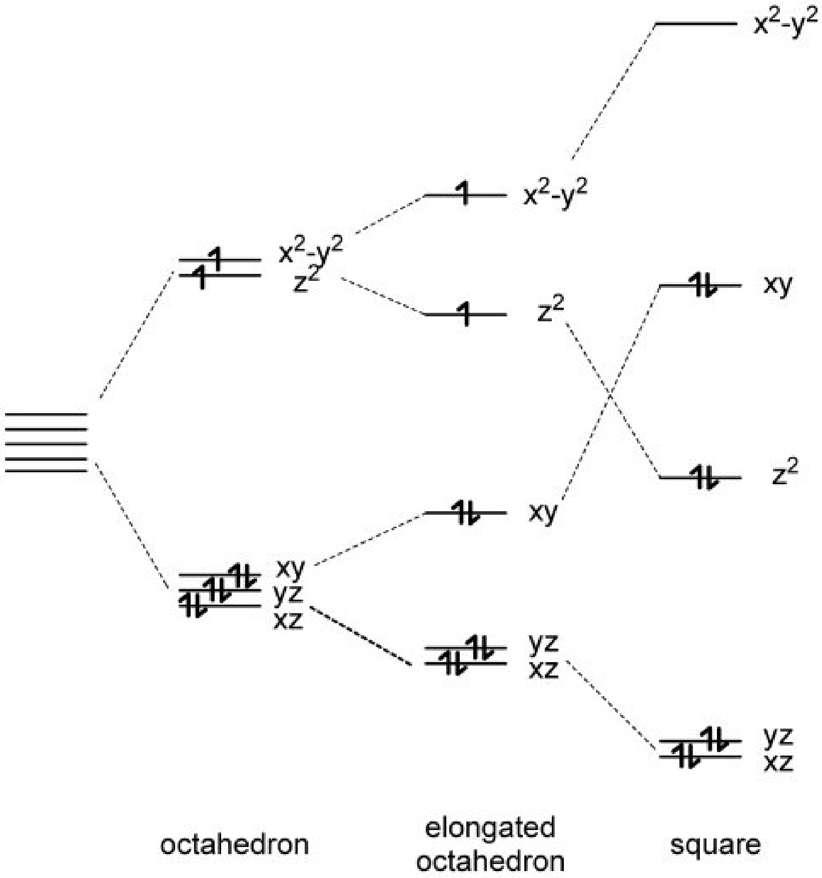

Figure 11: Energy of d orbitals, when moving from a regular octahedron to an elongated octahedron, to a square. In the case of a d8 metal (e.g. NiII), the passage from an octahedrally elongated geometry (as observed in the [NiII(cyclam)(NO3)2] complex) to a square geometry (as observed in the [NiII(cyclam)](ClO4)2 complex) induces spin pairing

The equilibrium is endothermic (Δ*H*° = 5.4 kcal mol–1) and characterized by a largely positive entropy change (Δ*S*° = +16 cal mol–1 K–1). The endothermicity of eq. (1) points forward the breaking of the two NiII–OH2 axial bonds, an event which is not fully compensated by the strengthening of the equatorial NiII–N(amine) bonds, which follows spin pairing. On the other hand, the positive entropy change reflects the increase of translational entropy associated to the liberation of two water molecules. Such a very favorable contribution more than compensates the intrinsically negative entropy contribution associated to the reduction of spin multiplicity, when moving from a triplet to a singlet electronic state: Δ*S*°spin = Rln3 – Rln1 = –2.18 cal mol–1 K–1 [Sabatini L., 1979].

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Biographical Sketch

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