

SYNTHESIS AND SPECTROSCOPY OF TRANSITION METAL COMPLEXES

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Summary

In this chapter, the main synthetic strategies to obtaining transition metal complexes are presented. The principles of the main spectroscopic techniques used to investigate the electronic and geometrical structure of the complexes are presented and relevant examples of application are given.

1. Introduction

A great number of new compounds are created on purpose to address specific problems. Hence the required properties of a new compound are the actual objective of the

synthetic process, while the compound is a simple vehicle of such properties at the molecular level. The preparation of a new compound with predetermined properties is not a trivial process. Its successful accomplishment requires a combination of abilities, including recognition of a problem, a creative approach to its resolution, ability to envisage the molecular requirements needed, and last but not least, the ability to synthesize the designed compound.

A very large number of different synthetic strategies have been adopted to prepare the desired species, including very exotic processes designed for single compounds or for very small classes of compounds. Nevertheless, helpful general procedures are available to assist the chemist in transforming his thoughts into the concrete form of milligrams or grams of his/her designed compounds. This applies to all kinds of chemicals, including transition metal complexes for which a description of the principal and general synthetic methods is reported herewith.

Dealing with transition metal complexes the synthesis can not only focus on how to put together metals and ligands, but at least three important variables, defining the final complex and its specific properties, have to be considered: the oxidation state, the coordination number, and the coordination geometry of the complexed metal ion. In principle all these variables may change in a reaction and their changes can be controlled to a good extent but, in practice, there are several cases in which it is not possible to be confident with our expectations about the result of a synthetic procedure. For instance, metal ions like palladium(II) and platinum(II), with d^8 electronic configuration, form almost exclusively square planar complexes, while the octahedral geometry is the preferred ligands arrangement around rhodium(III) and iridium(III), having a d^6 configuration. Also chromium(III) (d^3) forms many complexes that, with a few exceptions, are all octahedral. Actually there are important relations between coordination geometry (and implicitly also the coordination number) of transition metal complexes and the electronic structure of the coordinated metal ion, the last feature being strictly correlated with the metal ion oxidation state. Such coordination tendencies determined by the electronic structure of metal ions can be enhanced by the ligands, as in the case of complexes with d^3 , d^6 and d^8 cations and ligands appearing at the end of the spectrochemical series, or partly/completely overcome by the ligand characteristics. Examples of the last type are offered by nickel(II). Nickel(II) gives rise to a variety of coordination geometries, including the square planar one as expected for a metal ion with a d^8 configuration. For instance, the $[(PPh_3)_2Ni(SCN)_2](PPh_3 = \text{triphenylphosphine})$ complex has a square planar geometry while the complex $[(PPh_3)_2NiBr_2]$ is tetrahedral due to greater steric repulsion brought about by the bulkier Br^- ligands. There are many cases in which the coordination geometry of a complex is the results of a subtle equilibrium of forces, including those deriving from packing interactions in the solid state. In general packing interactions are only responsible of modest distortions of a specific coordination geometry although, in some cases, they can lead to completely different geometries. A very representative example is offered by the pentacyanide complex $[Ni(CN)_5]^{3-}$. In $[Cr(pn)_3][Ni(CN)_5]$ ($pn = 1,3\text{-propanediamine}$) the complex anion displays the usual square pyramidal geometry, while replacing $[Cr(pn)_3]^{3+}$ with the very similar counterion $[Cr(en)]^{3+}$ ($en =$

ethylenediamine) affords the $[\text{Cr}(\text{en})][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$ product containing both square pyramidal and trigonal bipyramidal $[\text{Ni}(\text{CN})_5]^{3-}$ complex anions. However, when the complex is dehydrated the trigonal bipyramidal anions become square pyramidal.

It is quite clear from these examples that in a general sense the final complex of a synthetic procedure must be accurately characterized to ascertain its exact composition and its structural characteristics. In many cases also a particular electronic structure of the complex is one of the properties required to address the problem the complex has been designed for; hence also the attainment of such properties requires appropriate verification. A number of spectroscopic methods are available to help in this work of characterization. Accordingly, the present chapter describes both the principal synthetic methods for the preparation of transition metal complexes and the fundamental spectroscopic techniques employed for their characterization. Most of complexes presented here are Werner complexes, while only very few examples of organometallic complexes have been used. A more extensive description of the last type of compounds is reported in *Inorganic Synthesis*.

2. Synthesis of Transition Metal Complexes

A classification of synthetic procedures for the preparation of transition metal complexes may be rather restrictive since different stages, involving different mechanisms, may be necessary to obtain the desired final compound. However it is useful and instructive to distinguish between reactions in which the metal maintains or changes its oxidation state. When the metal oxidation state is maintained, complexes are commonly obtained by transforming a complex into another one through substitution of ligands (substitution reaction). Alternatively, when the metal centre is coordinatively unsaturated further ligands can be added in the first coordination sphere of the metal, increasing its coordination number (addition reaction). The opposite reactions (dissociation reactions) are also possible and useful for synthetic purposes; they may occur with decrease of the metal coordination number upon elimination of coordinated ligands, or through replacement of the leaving ligands, in general with a counterion of the original complex. The coordinated ligands may be reacted without detachment from the metal leading to many new complexes. Such reactions of coordinated ligands can be very spectacular as in the case of template syntheses which make it possible to prepare complicated new ligands through easy reactions performed on simple complexes. Reactions involving a change of the metal oxidation state (oxidation/reduction reactions) are generally used when suitable precursors with the metals in the desired oxidation state are not available for the preparation of a complex, or when the metals are too inert in those specific oxidation states. Complexes are not isolated systems and may further interact with other species forming a second coordination sphere. In such complexes, the metal is coordinated by ligands which, in turn, bind further molecules or ions by means of weak forces. Examples of similar synthetic procedures are reported in this chapter.

All these types of reactions have found useful application in the designed preparation of complexes of relatively small dimensions. When the sizes of the desired complexes are very large, like those required by many new materials, the use of such reactions without any additional criterion is commonly unfruitful, or at least not convenient. A criterion,

based on typical reactions, which makes use of molecular building blocks that spontaneously bind together to construct very large structures, the self-assembly criterion, is presently moving its first steps, enlarging the horizons of synthetic transition metal complexes towards new frontiers. Also this type of reactions, which are more comprehensively described in *From Simple to Complex Compounds*, is presented herewith.

The comprehension of this overview of synthetic procedures can be facilitated and complemented by prior reading of *Inorganic Synthesis* and *Inorganic Reaction Mechanisms*.

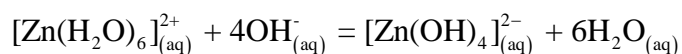
2.1. Synthesis by Substitution Reactions

Most of transition metal complexes can be prepared by substitution reactions. Almost all complexation reactions in solution take place through substitution reactions. In solution metal ions are coordinated by solvent molecules, defining a first coordination sphere which is surrounded by further interacting solvent molecules to form a solvated cation. In complexation reactions all solvent molecules in the first coordination sphere, or part of them, are replaced by the ligand(s), and further changes are likely to occur in the successive shells of solvation. In order to have a complete picture of the thermodynamic solvent effect on a specific complexation reaction, all solvation and desolvation processes involving the metal ion, the ligand(s) and the complex should be considered. In a general sense, however, we can say that the solvent competes with the ligand(s) in metal ion complexation and consequently more favorable complexation reactions are observed in solvent displaying lower solvation energies for that metal ion. The same applies for anions which are the counterions accompanying metal cations. Counterions may compete with the ligand(s) in metal cations complexation in solution, which means that the metal ion salt employed as a reactant does not dissociate completely in solution. Hence, metal ion salts containing anions with poor coordinating ability towards the specific cation must be employed to favor the complexation reactions. Such considerations, however, deal with the thermodynamic effects that coordinated solvent molecules or anions may have on the substitution equilibria. Further effects can operate in determining the substitution mechanisms. In order to get further information about this aspect we address the reader to the chapter on *Inorganic Reaction Mechanisms*.

Another general aspect deserving consideration is that it may be possible to isolate a solid complex from a solution where a completely different complex is the principal species. On the other hand, there are also complexes displaying incongruent solubility. For example, both phenomena are observed with the blue $\text{Cs}_2[\text{CoCl}_4]$ compound, containing tetrahedral $[\text{CoCl}_4]^{2-}$ complex anions, which crystallizes from pink aqueous solutions containing the octahedral aquo ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and CsCl , and dissolves in water to form the pink solution.

A further general consideration is that we must be very cautious in assessing that a complexation reaction takes place by a substitution reaction, even when reaction stoichiometry and thermodynamics are indicative of a similar mechanism, unless also

the kinetics of reaction gives the same indication. A familiar example of this type is the formation of a hydroxo complex from an aquo complex, such as



The reaction $\text{M-OH}_2 + \text{OH}^- = \text{M-OH}^- + \text{H}_2\text{O}$ could be erroneously interpreted as the substitution of a metal coordinated water molecule by a free OH^- anion. Actually, the formation of the hydroxo complex takes place *via* the acidic dissociation of the coordinated water molecule ($\text{M-OH}_2 = \text{M-OH}^- + \text{H}^+$) which is much faster than the substitution reaction.

From a practical point of view synthetic inorganic chemists make a distinction between substitution reactions of labile and inert complexes.

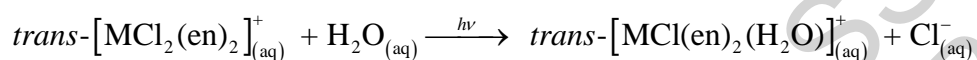
Reactions with labile complexes are almost instantaneous upon mixing of the reactants. An example of substitution reaction with a labile complex is the preparation of the hexamminenickel(II) complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$ from the hexaquaonickel(II) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion. When an excess of aqueous ammonia is added to a bright green solution containing $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the solution turns deep blue due to the formation of the hexammine complex. The reaction takes place through the stepwise substitution of the coordinated water molecules and working with appropriate metal ion to ammonia molar ratios all complexes from $[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O})_5]^{2+}$ to $[\text{Ni}(\text{NH}_3)_6]^{2+}$ are formed in solution although the concentrations of some may be low. Solid $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ can be easily isolated from aqueous solution containing nickel(II) chloride and excess of ammonia.

Substitution reactions of inert complexes need more complicated procedures or, at least, longer times to obtain the desired complex with a satisfactory yield. To accelerate such reactions energy may be supplied to the system by heating or by light irradiation, otherwise a catalyst may be adopted. Such expedients to accelerate sluggish reactions may have drawbacks.

A simple example of this type of reactions is found in the synthesis of $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ performed in water by reacting $\text{K}_2[\text{PtCl}_4]$ with 2,2':6,2''-terpyridine (terpy). The reaction is slow even at high temperatures. The suspension obtained upon addition of terpy to the solution of $\text{K}_2[\text{PtCl}_4]$ is heated at reflux until a clear red solution is evident, a process which takes from 20 to 100 hours. A typical good yield is about 65%. Halting the reaction before the reaction mixture clarifies significantly lowers the product yield. On the other hand, prolonged heating of the clear solution may result in product disproportionation as shown by metallic platinum plating out onto the sides of the reaction flask. The trihydrated salt of the product crystallizes from the aqueous solution and is converted in the dihydrated $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ compound upon drying in a vacuum desiccator. The basic reaction of this synthetic procedure consists in the substitution of three out of the four chloride ions of the square planar $[\text{PtCl}_4]^{2-}$ by terpy to form the square planar $[\text{Pt}(\text{terpy})\text{Cl}]^+$

complex. Actually $[\text{PtCl}_4]^{2-}$ undergoes extensive, although slow, hydrolysis in water with formation of $[\text{PtCl}_3(\text{H}_2\text{O})]^{2-}$ and $[\text{PtCl}_2(\text{H}_2\text{O})_2]^{2-}$ species which become important components, along with $[\text{PtCl}_4]^{2-}$, of the reaction mixture.

Another way to favour exchange reactions is to destabilize inert metal complexes by supplying them with internal energy by photon absorption. Accordingly, photochemical reactions have been exploited to yield coordination compounds that are otherwise difficult to prepare. For instance, mixed-ligand complexes of the type *trans*- $[\text{MClX}(\text{en})_2]^+$ (M(III) = Rh(III), Ir(III); $\text{X}^- = \text{Br}^-, \text{I}^-$) can be obtained in high yields by photosubstitution of a single chloride ion of aqueous *trans*- $[\text{MCl}_2(\text{en})_2]^+$ with a water molecule according to the equation



followed by precipitation of free Cl^- with Ag^+ and successive reaction with stoichiometric amounts of X^- at high temperature (100°C) for relatively short times (ca. 30 min). In contrast to this successful procedure, thermal routes to these complexes are less advantageous due to the long reaction times required at high temperatures and the propensity to yield doubly substituted products.

Cobalt(III) is another transition metal cation whose complexes are generally inert towards substitution reactions. A successful method to prepare complexes with this metal ion is based on the use of its tricarbonato complex $[\text{Co}(\text{CO}_3)_3]^{3-}$ as starting material. Stepwise substitution of the bidentate CO_3^{2-} coordinated anions in aqueous $[\text{Co}(\text{CO}_3)_3]^{3-}$ can be performed by using ligands of higher ligand field (L = monodentate ligand, L-L = bidentate ligand) leading first to dicarbonato-complexes such as $[\text{Co}(\text{CO}_3)_2\text{L}_2]$ or $[\text{Co}(\text{CO}_3)_2\text{L-L}]$, then to monocarbonato-complexes such as $[\text{Co}(\text{CO}_3)\text{L}_4]$ or $[\text{Co}(\text{CO}_3)(\text{L-L})_2]$, and finally to complex of the type $[\text{CoL}_6]$ or $[\text{Co}(\text{L-L})_3]$ (complex charge not specified). Similarly, complexes containing both mono- and bi-dentate ligands can be prepared. In general such reactions are performed under mild conditions. When the ligands are 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) the first substitution reaction takes place at room temperature upon addition of stoichiometric amounts of the ligands in ethanol to the green aqueous solutions of $[\text{Co}(\text{CO}_3)_3]^{3-}$ affording the $[\text{Co}(\text{CO}_3)_2\text{bpy}]$ and $[\text{Co}(\text{CO}_3)_2\text{phen}]$, respectively. Also the other complexes $[\text{Co}(\text{CO}_3)(\text{bpy})_2]^+$, $[\text{Co}(\text{CO}_3)(\text{phen})_2]^+$, $[\text{Co}(\text{bpy})_3]^{3+}$ and $[\text{Co}(\text{phen})_3]^{3+}$ are obtained by the reaction of $[\text{Co}(\text{CO}_3)_3]^{3-}$ with the ligands in stoichiometric amounts, but activated charcoal is necessary to prepare the three-substituted species.

Activated charcoal is commonly employed as a catalyst in substitution reactions of inert complexes containing metal ions that can be reduced to more labile oxidation states. Charcoal has occasional non-bonded single electrons scattered on its surface that may reduce complexes temporarily adsorbed onto its surface. Hence, the substitution

reaction takes place on the charcoal surface by the reduced complex in the labile oxidation state (cobalt(II) in the present case) and re-oxidation occurs upon desorption from the charcoal.

Substitution reactions of square planar platinum(II) complexes and, to a lesser extent, of similar complexes with palladium(II) and gold(III) (all d^8 cations) follow an important role that makes it possible to predict with confidence the main reaction product. This role, referring to the so-called “trans effect”, is determined by the different ability of ligands bound to such metal ion to labialize the ligand coordinated *trans* to it. Accordingly, ligands can be arranged in a series, depending on the relative magnitude of the trans effect they exert, that can be used to predict the product of a substitution reaction. More details regarding the *trans* effect can be found in *Inorganic Synthesis* and *Inorganic Reaction Mechanisms*.

2.2 Synthesis by Oxidation/Reduction Reactions

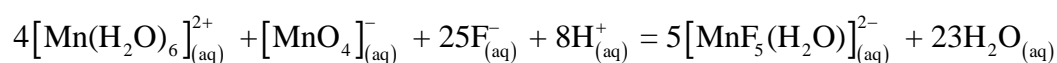
In the previous section we have shown that substitution reactions involving inert metal complexes may be rather problematic. For this reason it is commonly preferred to prepare such complexes by using the metal in a labile oxidation state and oxidize or reduce it in the presence of the chosen ligands or after complexation with these ligands.

Classical examples of oxidation reactions involving inert transition metal complexes are found in the preparation of cobalt(III) complexes. The synthesis of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, for instance, can be performed in aqueous solution according to the stoichiometry

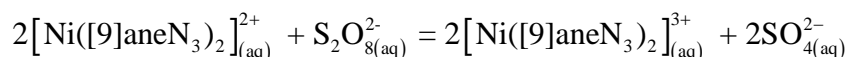


The synthesis takes place, through different steps, in the presence of activated charcoal as a catalyst. The labile $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ aquo-ion, formed in solution upon dissolution of CoCl_2 , reacts with ammonia to give the hexamminecobalt(II) $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex, which is successively oxidized by H_2O_2 to $[\text{Co}(\text{OH})(\text{NH}_3)_5]^{2+}$. The last complex is quite inert and substitution of the coordinated OH^- group by NH_3 occurs thanks to the activated charcoal, whose catalytic action was described in the previous section. The ammoniac buffer prevents the pH increase that would be produced by the release of OH^- ions in the substitution step. In a more general sense, oxidation/reduction reactions are used when a suitable precursor with the metal in the desired oxidation state is not available for the preparation of a complex.

Complexes of manganese(III) can be prepared by oxidation of the hexaquomanganese(II) cation or by reduction of $[\text{MnO}_4]^-$ in presence of the ligand(s). In some case the two reactions can be combined as in the preparation of $[\text{MnF}_5(\text{H}_2\text{O})]^{2-}$:

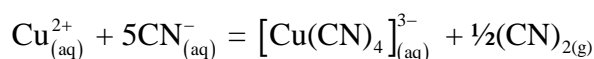


Nickel (III) can be stabilized in aqueous solution by complexation with polyamine macrocyclic ligands. Such complexes can be conveniently prepared by oxidation of the corresponding nickel(II) compounds. For instance, $[\text{Ni}([\text{9}]\text{aneN}_3)_2]^{3+}$ ($[\text{9}]\text{aneN}_3 = 1,4,7\text{-triazacyclononane}$) can be prepared by oxidation of $[\text{Ni}([\text{9}]\text{aneN}_3)_2]^{2+}$ with $\text{S}_2\text{O}_8^{2-}$ in acidic aqueous solution at room temperature:

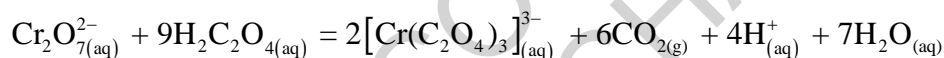


The reaction develops with a change of color from red-violet to brown. From the oxidized solution, the nickel(III) complex can be easily isolated as $[\text{Ni}([\text{9}]\text{aneN}_3)_2](\text{ClO}_4)_3$ by addition of solid sodium perchlorate.

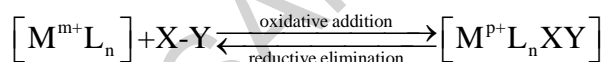
The ligands itself may act as the reactant that modify the oxidation state of the metal. This is the case, for instance, of the reaction of cyanide with copper (II) in the preparation of $[\text{Cu}(\text{CN})_4]^{3-}$:



or of the reaction of dichromate with oxalic acid to form the trisoxalatochromium(III) complex:



In the previous reactions, changes of metal oxidation state may be accompanied by changes of coordination numbers. Although such modifications of coordination numbers are determined by the oxidative or reductive process, there is not a clear correlation between the two changes. Conversely, there are two classes of reactions, known as *oxidative addition reactions* and *reductive elimination reactions*, for which the link between the two changes is substantial. These types of reactions generally described by the equation



have been most thoroughly studied for complexes with metal centers with d^6 , d^8 and d^{10} configurations, and in particular for $\text{Pd}^{2+}/\text{Pt}^{2+}/\text{Rh}^+/\text{Ir}^+/\text{Fe}^0/\text{Ru}^0/\text{Os}^0$ (d^8) and $\text{Ni}^0/\text{Pd}^0/\text{Pt}^0$ (d^{10}). Most common X-Y molecules are

H-H, Hal-Hal (Hal = halogen),

RS-SR, H-Y (Y = Hal, OR, Oac, SR, NR_2 , CN, C_5H_5 , SiR_3 , etc.),),

R-I, Ac-Cl, NC-CN, $\text{R}_3\text{Si-Cl}$, $\text{Ph}_2\text{B-Cl}$, Cl-HgCl

and similar molecules of the type $X=Y$, such as $O=O$, $O=SO$, $S=CS$, $RN=CNR$, $O=C(CF_3)$ and $RC=CR$, forming, at least in the initial stage of complexation, a three-membered MX_Y chelate ring.

Two representative examples of oxidative addition reactions are the reactions of the Vaska's complex $[Ir(CO)(PPh_3)_2Cl]$ with H_2 and O_2 , respectively (Figure 1). In these reactions the oxidation state of iridium changes from +1 to +3 while its coordination number increases from 4 to 6. The opposite reactions, in which H_2 and O_2 are eliminated from the complex, iridium(III) is reduced to iridium(I) and the coordination number decreases from 6 to 4, is a reductive elimination reactions. Further details regarding these type of reactions can be found in *Inorganic Synthesis*.

All oxidation/reduction processes presented here are based on the use of appropriate chemical reagents. Another way to perform similar reactions consists in the use of electrochemical methods. One of the most used techniques for the electrochemical generation of transition metal complexes in solution is the Controlled Potential Electrolysis (CPE). If only the reduced/oxidized species is initially present, the oxidation/reduction electrolysis can be performed by setting the potential at a constant value sufficiently positive/negative to cause rapid oxidation/reduction and maintaining it at this value until only the oxidized/reduced species is present in solution. In the case that different oxidation states of the complex can be reached or when other electroactive materials are present in solution, the potential can be set at a value that allows only the desired electrochemical reaction to occur. In such a case, the potential required for the CPE experiment is determined by the redox potential of the complex measured by means of cyclic voltammetry or other electrochemical methods.

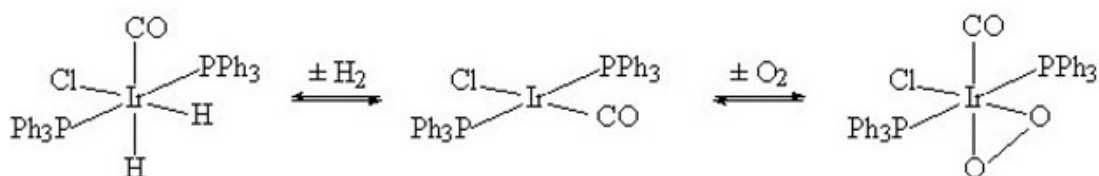


Figure 1. Oxidative addition of H_2 and O_2 to the Vaska's complex $[Ir(CO)(PPh_3)_2Cl]$.

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Bibliography

Abragam A. and Bleaney B. (1970). *Electron Paramagnetic Resonance of Transition Metal Ions*. Oxford: Oxford University Press. [The classical treatise on the EPR of transition metal complexes].

Black D.StC. (1987). Reactions of Coordinated Ligands (*Comprehensive Coordination Chemistry*), Vol. 1 (eds. G. Wilkinson, R.D. Gillard and J.A. McCleverty), pp. 415-462. Oxford: Pergamon Press. [A review of the most typical synthetic procedures for the preparation of metal complexes via the reaction of coordinated ligands].

Constable E.G. (1996). *Metals and Ligand Reactivity*, 2nd edition. 308 pp. VCH: Weinheim. [This is an introduction to the reactions of coordinated ligands, including reactions with nucleophiles and electrophiles, oxidation and reduction of coordinated ligands, cyclic and encapsulating ligands, template effect and supramolecular chemistry].

Davies J.A., Hockensmith C.M., Kukushkin V.Yu and Kukushkin, Y.N. (1996). *Synthetic coordination chemistry: principles and practice*. 472 pp. Singapore: World Scientific. [The book reports a systematic classification of synthetic reactions].

Fujita M. (2000). Molecular Paneling Through Metal-Directed Self-Assembly (*Structure and Bonding*), Vol. 96 (ed. M. Fujita), pp. 177-201. Berlin: Springer. [A description of the criteria for the preparation of metal complexes *via* self-assembly with references for the relevant synthetic procedures].

Gibbs, T.C. (1976). *Principles of Mössbauer Spectroscopy*. London: [Classical treatise on MB spectroscopy].

Griffith J.S. (1961). *The theory of Transition Metal Ions*. Cambridge: Cambridge University Press. [The classical textbook on the electronic structure and spectroscopy of transition metal complexes].

Inorganic Electronic Structure and Spectroscopy, Vol. 1, 732 pp. and Vol. 2, 658 pp. (1999) (eds. E.I. Solomon and A.B.P. Lever). New York: John Wiley & Sons. [These books contain the principles (Vol. 1) and selected applications (Vol.2) of the spectroscopic techniques most commonly used in inorganic chemistry as well as some methods of calculation of the electronic structure of inorganic systems].

Inorganic Synthesis [A series started by McGraw Hill in 1939 and now published by Wiley. This series provide all users of inorganic substances with step-by-step, tested procedures for the preparation of important and timely inorganic compounds].

Lever A.B.P. (1986) *Inorganic Electronic Spectroscopy*. 864 pp. New York: Elsevier. [The most comprehensive treatise on the electronic spectra of transition metal compounds].

Mabbs F.E. and Collison D. (1992). *Electron Paramagnetic Resonance of d Transition Metal Compounds*. 1326 pp. Amsterdam: Elsevier. [A comprehensive treatise on EPR of transition metal complexes].

Stephen S. J. (1996). Second-sphere coordination, (*Comprehensive Supramolecular Chemistry*), Vol. 1, (ed. G.W. Gokel), pp. 733-753. Oxford: Elsevier. [This chapter is a reviews on second-sphere coordination of transition metal complexes including references to the relevant synthetic procedures].

Tobe M.L. (1987). Substitution Reactions (*Comprehensive Coordination Chemistry*), Vol. 1 (eds. G. Wilkinson, R.D. Gillard and J.A. McCleverty), pp. 281-384. Oxford: Pergamon Press. [A review of the most typical substitution reactions for the preparation of metal complexes].

Biographical Sketches

Antonio Bianchi was born in Pistoia, Italy, in 1956. He graduated in Chemistry from the University of Florence, Italy, in 1981. After a post-graduation appointment at the ISSEC Institute of the Italian National Research Council in Florence he received his PhD in Chemical Sciences at the University of Florence in 1989. His major field of study are inorganic chemistry, supramolecular chemistry, macrocyclic chemistry, and anion coordination chemistry.

He is presently Professor of General and Inorganic Chemistry at the Faculty of Science of the University of Florence, where he had previous positions as Tenure Researcher and Associated Professor.

He is author of more than 200 publications in international journals and coeditor of the book "The Supramolecular Chemistry of Anions" (New York, Wiley-VCH, 1997).

Professor Bianchi is a member of the Italian Chemical Society.

Alessandro Bencini was born in Fauglia (Pisa) in 1951. Got the "Laura in Chimica" at the University of Florence in 1975, under the supervision of Prof. Dante Gatteschi and Prof. Luigi Sacconi. From 1977 to 1987 he was researcher at the National Research Council of Italy (CNR), and is actually Professor of General and Inorganic Chemistry at the Faculty of Science of the University of Florence.

He is co-author of publications on international journals on the following topics:

a) Electron Paramagnetic Resonance and Single Crystal Polarized Electronic Spectroscopy of Transition Metal Complexes. b) Development and Application of Ligand Field (AOM) and Molecular Orbital Models to Compute the Spectro-magnetic Properties of Transition Metal Complexes in Low Symmetry Environments. c) Polynuclear Complexes of First-Row Transition Metals: Synthesis, Structural Characterization and Interpretation of their Magnetic and Spectroscopic Properties (UV-Vis, ESR, Mössbauer). d) Application of Density Functional Theory to the Description of the Electronic Structure, Magnetism and Reactivity of Transition Metal Compounds.

Selected publications are:

"Nickel" in *"Comprehensive Coordination Chemistry"*, edited by G. Wilkinson, R.D. Gillard e J.A. McCleverty, Pergamon Press, Oxford, vol. 5, p. 1-350 (1987). Co-authors: Luigi Sacconi and Fabrizio Mani.

Electron Paramagnetic Resonance of Exchange Coupled Systems, Springer-Verlag, Heidelberg, 1990. Co-author: Dante Gatteschi.

"Electron Paramagnetic Resonance Spectroscopy" in *"Inorganic Electronic Structure and Spectroscopy"*, edited by E.I. Solomon and A.B.P. Lever, John Wiley & Sons, vol. I, p. 93-160 (1999). Co-author: Dante Gatteschi.