MAGNETIC AND OPTICAL PROPERTIES

Lorenzo Sorace and **Dante Gatteschi**
UdR INSTM and Department of Chemistry, University of Florence, Italy

Keywords: coordination complexes, electronic structure, ligand field, magnetism, optical spectroscopy, exchange coupling, anisotropy, single molecule magnets, molecular switches

Contents

Summary

The magnetic and optical properties of transition metal ion molecular compounds will be treated highlighting the key factors which determine both of them, i.e. their electronic structure with special reference to the d orbitals splitting and the symmetry of the resulting electronic states. The UV-Visible spectra of the complexes will then be discussed with some example showing the most important piece of information one can draw from them. In the following sections, after a brief introduction to the fundamentals of magnetism, the magnetic properties of simple paramagnetic complexes of different transition series will be discussed. A further degree of complexity is then introduced by treating the magnetic properties of polynuclear clusters, both in terms of isotropic and anisotropic interactions. Finally a brief overview of some recent research topics in this field will be presented with peculiar attention to systems showing interplay of magnetic and optical properties.

1. Introduction

The complexes of transition metal ions have long attracted the interest of researchers for the variability of colors and magnetic behavior which characterizes them. The application of Quantum Mechanics showed that these properties are due to the fact that transition elements are characterized by having partially filled *d* shells, and the investigation of optical and magnetic properties provides information on the element involved, its oxidation number, its structural properties in terms of geometry and coordinating atoms in a given compound. It is then quite obvious that the deep understanding of the different factors which concur to determine magnetic and optical properties of compounds containing transition metal ions have been of paramount importance to disclose fundamental information about a large variety of molecular and bioinorganic systems.

The first successes in this field were obtained in the 30s, with the development of Crystal Field Theory by H. Bethe and its application to the rationalization of optical and magnetic properties of salts of transition metal ions by J. H. Van Vleck who was co-awarded the Nobel prize in 1977 for these studies. In the same period Linus Pauling showed that hemoglobin, a crucial protein for oxygen transport in blood, is diamagnetic when bound to O_2 or CO while it is paramagnetic when it is free, and was able to explain these results following an approach based on valence bond theory. This pointed out the need of inclusion of covalence effect in the description of both magnetic and optical properties of systems containing transition metal ions. This was subsequently carried out in the post war period which saw the development of Ligand Field theory which incorporated Molecular Orbital approach within the Crystal Field theory and formed, and still forms (notwithstanding the advent of Density Functional Theory based calculations) the basis for the understanding of magnetic and optic behavior of isolated transition metal complexes for chemists all over the world.

The following step concerned the rationalization of the optical and magnetic behavior of systems containing two or more interacting transition metal centers. In these systems, the interactions between ions strongly influence both magnetic and optical properties, and the type of interactions was showed to be again strongly dependent on the electronic and molecular structure of the whole system.

Magnetic and optic properties are not however to be regarded only as tools for elucidating the structure of systems containing transition metal ions, but can be exploited to build up new molecular based functional materials with tailored properties. The main advantage in using the molecular approach for the synthesis of functional materials is the possibility of obtaining crystalline materials in which all the functional units have identical and well defined properties and orientation, which in principle can be tuned using chemical approaches. Furthermore, it appears promising in order to develop materials showing novel association of physical properties. Using this approach chemists have been able to design more and more complex systems which are interesting both for fundamental studies, as they show novel properties, and for future applications like quantum computing or molecular optical switching.

In this essay we will try to give the reader some tools to understand both the fundamentals factors affecting the optical and magnetic properties of transition metal ion complexes, including polynuclear systems, resorting to well established theories. We will then provide some hints about the latest developments in this field concerning some exciting properties of newly synthesized systems. It is supposed that the reader is acquainted with some basic principles of quantum mechanics which is a fundamental tool for the elucidation of the electronic structure of transition metal ions.

2. Electronic structure of transition metal ions

The electronic structure of transition metal ions in complexes can be regarded as determined by different contributions:

- The kinetic energy of the electrons and the electrostatic electron nuclear attraction
- The electron-electron repulsion
- The spin-orbit coupling, i.e. the coupling between the orbital motion and the spin of the electrons
- The effect of the surrounding ligands

It is common practice to include 1 and an average of 2 in an unperturbed Hamiltonian, H_0, and the remaining part of 2 plus 3 and 4 are used to evaluate the energies of the states using perturbation theory.

$$\mathrm{H} = \mathrm{H}_0 + \mathrm{H}_{\text{el-el}} + \mathrm{H}_{\text{s-o}} + \mathrm{H}_{\text{CF}} \qquad (1)$$

where $\mathrm{H}_{\text{el-el}}$ is the electron-electron repulsion, $\mathrm{H}_{\text{s-o}}$ the spin-orbit coupling, and H_{CF} is the crystal field Hamiltonian.

Historically, subsequent perturbation treatments have been used to calculate the energy levels. For instance in many cases it is a good approximation that $\mathrm{H}_{\text{el-el}} > \mathrm{H}_{\text{CF}} > \mathrm{H}_{\text{s-o}}$. This is the so called weak field approximation for transition metal ions of the first series, where field is referred to Crystal Field. An alternative approach assumes $\mathrm{H}_{\text{CF}} > \mathrm{H}_{\text{el-el}} > \mathrm{H}_{\text{s-o}}$: this is the strong field approximation.

In the following we will briefly describe the energy levels of the $\mathrm{H}_{\text{el-el}}$ Hamiltonian, which correspond to the description of free ions, and later will introduce the H_{CF} Hamiltonian.

2.1. Free Ion

In zero order perturbation we consider each single electron moving in an average field due to the nucleus and to the remaining electrons and H_0 corresponds to the Hamiltonian of a hydrogen-like atom. For a free transition metal ion this yields five degenerate d orbitals, which are the product of a radial function R_{nl} defined by the quantum numbers n and l and of a spherical harmonic Y_l^m, depending on the quantum numbers l and m_l. Thus, by considering also the spin angular momentum, each electron is defined by 4 different quantum numbers:

- n = 1,2,3… indicating the energy and distance from the nucleus, i. e. what shell the electron is occupying
- l = 0, 1, 2… indicating what sort of orbital the electron is occupying: s, p, d…
- ml = -l…+l indicating the component of l, i.e. what kind of d orbital the electron is occupying: xy, xz…
- ms = ± ½ indicating the component of the spin angular momentum s (s =1/2 for an electron)

The l^n configuration corresponds to degenerate states whose number k is given by:

$$k = \frac{(4l+2)!}{(4l+2-n)!n!} \tag{2}$$

where $4l+2$ corresponds to the number of spin-orbitals functions each electron can occupy.

Introduction of the perturbation H_{el-el} removes this degeneracy, yielding states which can be labeled using total quantum numbers made up of contributions from all the electrons in the unfilled shells:

- S = maximum of Σm_s
- L = maximum of Σm_l for a given S.
- $M_L = L,\ldots,-L$
- $M_S = S,\ldots -S$

It is worth noting here that configurations with d^n and d^{10-n} give rise to the same set of free ion terms. Each term is labeled as $^{2S+1}$X, where X = S, P, D, F is related to the angular quantum number so that L = 0 is an S term, 1=P, 2=D, 3=F etc. 2S+1 is the spin multiplicity associated to the total spin quantum number S. This is the so-called Russell-Saunders coupling scheme. The ground term, i.e. the term with the lowest energy, is obtained through Hund's rules, i.e. the state with highest spin ,(2S+1), and orbital, (2L+1), multiplicity lies lowest (see Table 1).

Configuration	Ground state term	Excited state terms
d^1,d^9	^{2}D	-
d^2,d^8	^{3}F	^{3}P, ^{1}G, ^{1}D, ^{1}S
d^3,d^7	^{4}D	^{4}P, ^{2}H, ^{2}G, ^{2}F, ^{2}D, ^{2}D, ^{2}P
d^4,d^6	^{5}D	^{3}H, ^{3}G, ^{3}F, ^{3}F, ^{3}D, ^{3}P, ^{3}P, ^{1}I, ^{1}G, ^{1}G, ^{1}F, ^{1}D, ^{1}D, ^{1}S, ^{1}S
d^5	^{6}S	^{4}G, ^{4}F, ^{4}D, ^{4}P, ^{2}I, ^{2}H, ^{2}G, ^{2}G, ^{2}F, ^{2}F, ^{2}D, ^{2}D, ^{2}D, ^{2}P, ^{2}S

Table 1: Free ion terms for d^n configuration.

In order to obtain the relative energies of the excited states it is necessary to solve the Schrödinger equation for the interelectronic repulsion term explicitly. The energies are expressed as a function of the Racah parameters *A*, *B*, *C*, which are related to two-centers radial integrals $< ab\left|1/r_{\kappa\lambda}\right|cd >$ where $< ab|$ and $|cd >$ are products of monoelectronic wavefunctions occupied by the two electrons λ and κ at distance $r_{\kappa\lambda}$ .. Of these parameters *A* is just shifting of a constant value the energies of all the states and does not affect the spectroscopic properties of the metal centers, *B* indicates the magnitude of the interelectronic repulsion between levels in the gaseous ions that have the same spin multiplicity, while *C* expresses the energy difference between terms of different spin multiplicity. The expression that one obtains for the energy for a given d^n configuration is then independent of the metal ion, but the magnitude of the Racah parameters depends on it.

If we now take into account also the spin orbit coupling term, this produces a splitting within each term, which in this approach is treated as a perturbation of the individual term energies. For each term, the resultant angular momentum L, and the resultant spin momentum S couple to give a resulting momentum $|L\text{-}S| < J < L+S$. The relative order of the states within a given ${}^{2S+1}L$ multiplet is given by solving the spin-orbit Hamiltonian $\mathbf{H}_{\text{s-o}} = \lambda\mathbf{L}\cdot\mathbf{S}$ for given values of L and S, where λ is the spin orbit coupling within a given Russell-Saunders multiplet and is related to the spin orbit coupling constant of the ion, ζ, by the relation $\lambda = \pm\zeta/2S$. The plus sign applies to configuration d^n with $1 \le n \le 4$ and the minus sign to $6 \le n \le 9$. For high spin d^5 ions no spin-orbit coupling is operative at first-order in the ground ^{6}S state.

The energies of the *J* states are given by:

$$E(J) = \lambda\left[J(J+1) - L(L+1) - S(S+1)\right]/2 \qquad (3)$$

and the energy difference between adjacent states is given by:

$$\Delta E_{J,\,J\text{-}1} = \lambda J \qquad (4)$$

Then for d^n configuration with $n < 5$ the ground term is the one with the lowest J, while for $n > 5$ the ground term is that with maximum J.

It is worth noting here that this approach considers the spin orbit coupling to be a perturbation with respect to the interelectronic repulsion and as such can be applied only to first row transition metal ions (3d^n shell). For second and third row *d* ions the situation is different, as spin orbit coupling magnitude increase with atomic number and overcome the interelectronic repulsion term. As a consequence spin orbit coupling is considered as dominant and a different coupling scheme applies, the so called *jj* coupling. In this scheme, the spin *s* of each electron is coupled with its orbital momentum *l* to give a resultant monoelectronic resulting moment *j*. These individual *j*'s are then coupled to give the resulting **J** for the system which is then perturbed by the effect of the interelectronic repulsion energy.

2.2. Coordination Complexes

When an ion is placed in a ligand environment with symmetry lower than spherical, the energies of its partly filled *d*- orbitals (and to a lower extent *f*-orbitals for lanthanides) are split by the electrostatic field of the ligands. It must be noticed that the presence of the ligands removes the orbital but not the spin degeneracy. This is an immediate consequence of the lowering of the symmetry as, even in the regular octahedral geometry, group theory tells us that the highest possible degeneracy is three, while L can be larger than 1. This is the basis of Crystal Field Theory, whose deeply symmetry based formalism was developed by Hans Bethe in 1929. Crystal Field Theory is a purely electrostatic, non-bonding approach, where the metal ion is placed in a field due to its ligands, which are approximated by negative point charges and thus assumed to be fixed and unpolarized. Thus in Hamiltonian (1), the $\mathbf{H}_{\mathrm{CF}}$ term is given by:

$$\mathbf{H}_{\mathbf{CF}} = \sum_i \frac{Z_i e}{r_{ij}} \tag{5}$$

It is worth highlighting here that Crystal Field theory is not treating each ligand separately but considers them as a whole, exploiting the total symmetry of the surrounding of the metal ion. This is accomplished by expanding each one-electron $\mathbf{H}_{\mathbf{CF}}$ in terms of spherical harmonics centered at the metal nucleus:

$$\sum_i \frac{Z_i e}{r_{ij}} = \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \frac{4\pi}{(2k+1)} \sum_i Z_i e Y_k^{q^*}(\theta_i, \varphi_i) \cdot \left(\frac{r_<^k}{r_>^{k+1}} \right) \cdot Y_k^q(\theta_j, \varphi_j) \tag{6}$$

here $r_>$ usually refers to electron-nucleus distance and $r_<$ to the nucleus-ligand distance. The first spherical harmonic, $Y_k^q(\theta_i, \varphi_i)$ refers to the ligands and the second to the electron, both defined by their polar coordinates. The problem thus reduces to the evaluation of matrix elements of (6), depending on radial integrals which are considered as parameters. It is evident that the use of a certain set of spherical harmonics critically depends on the geometry and the electron configuration of the system. Indeed, $\mathbf{H}_{\mathbf{CF}}$ must obviously transform as the totally symmetric representation in the symmetry group concerned, i.e. should not vary on transforming it by the symmetry operations of the groups. This introduces severe limitations on the use of given Y_k^q, and strongly simplifies (6). Thus, for the d electrons the sum over k is limited to $k = 0, 2, 4$ while it goes up to $k = 6$ for f electrons. Further, if the symmetry group possess a fourfold, a threefold or a twofold axis of symmetry (or a symmetry plane), only terms characterized by q values multiples of 4, 3 and 2 (including $q = 0$) respectively, can be retained. If the symmetry is octahedral only $k = 4$ and $q = 0$, ±4 terms are retained and thus only one parameter is needed to obtain the energy of the d orbitals in such configuration. This parameter is called Dq and the obtained energies for d orbitals in octahedral geometry are -6Dq for d_{xy}, d_{xz} and d_{yz} and +4Dq for $d_{x^2-y^2}$ and d_{z^2}. In this approach the quantization axis of the octahedron has been chosen to be the tetragonal one. The energy difference between the two subsets of d orbitals is then $10Dq$, and this can be accessed through electronic spectroscopy (see infra). This result translates in quantitative terms the intuitive expectation of a larger destabilisation of d_{z^2} and $d_{x^2-y^2}$ orbitals, which in octahedral symmetry directly point toward the negative charge of the ligands, with respect to the $d_{xy}, d_{xz},$ and d_{yz} ones.

The reverse splitting is obtained for purely tetrahedral complexes (see Figure 1). However, the corresponding energy difference is smaller, with $d_{xy}, d_{xz},$ and d_{yz} lying at 16/9Dq and $d_{x^2-y^2}$ and d_{z^2} at $-(8/3)\ Dq$, the total splitting amounting to -4/9 of the corresponding octahedral one.

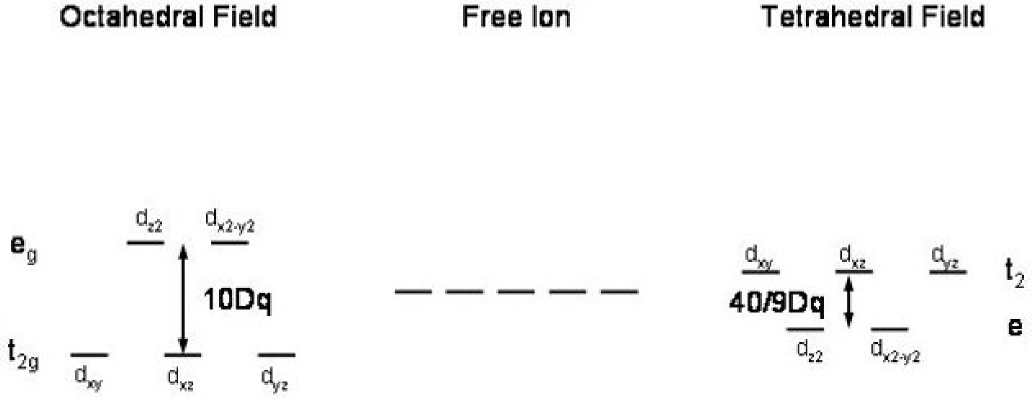


Figure 1: Splitting of the d orbitals in octahedral and tetrahedral ligand field.

A fundamental consequence of this splitting is the resultant “quenching” of the magnetic contribution due to the angular orbital momentum: the removal of the degeneracy of d ions makes impossible for d electrons to freely circulate between orbitals of different symmetry. This was one of the most relevant results obtained by Crystal Field Theory as it explained why complexes of the first transition series usually present a magnetic moment value corresponding to that arising from the spin alone (the so-called spin-only value, see below). Another important point that is easily seen is that for very high Dq the levels may be split so much that the Hund rule asserting that the lowest energy state is that of maximum multiplicity permitted by the Pauli principle is not obeyed any more. This situation may occur for $d^4 - d^7$ ions and is shown schematically in Figure 2 for the configuration d^6. In the high spin configuration there are four unpaired electrons while in the low spin one there are no unpaired electrons: this clearly strongly affects both the optical and magnetic properties of the corresponding compounds.

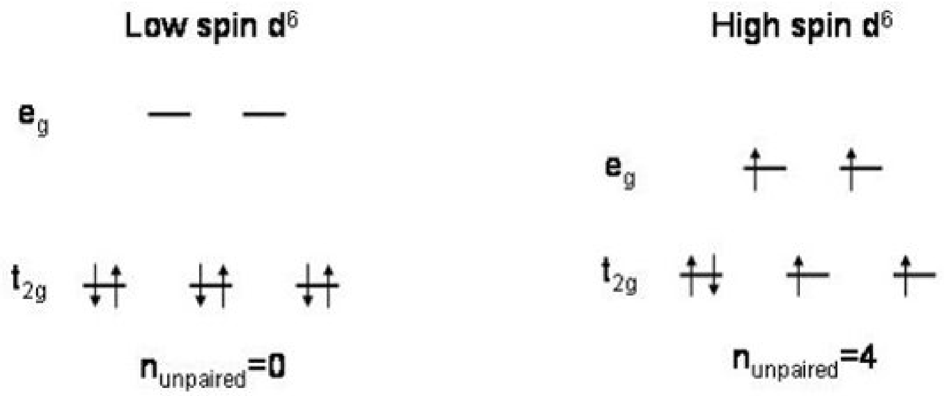


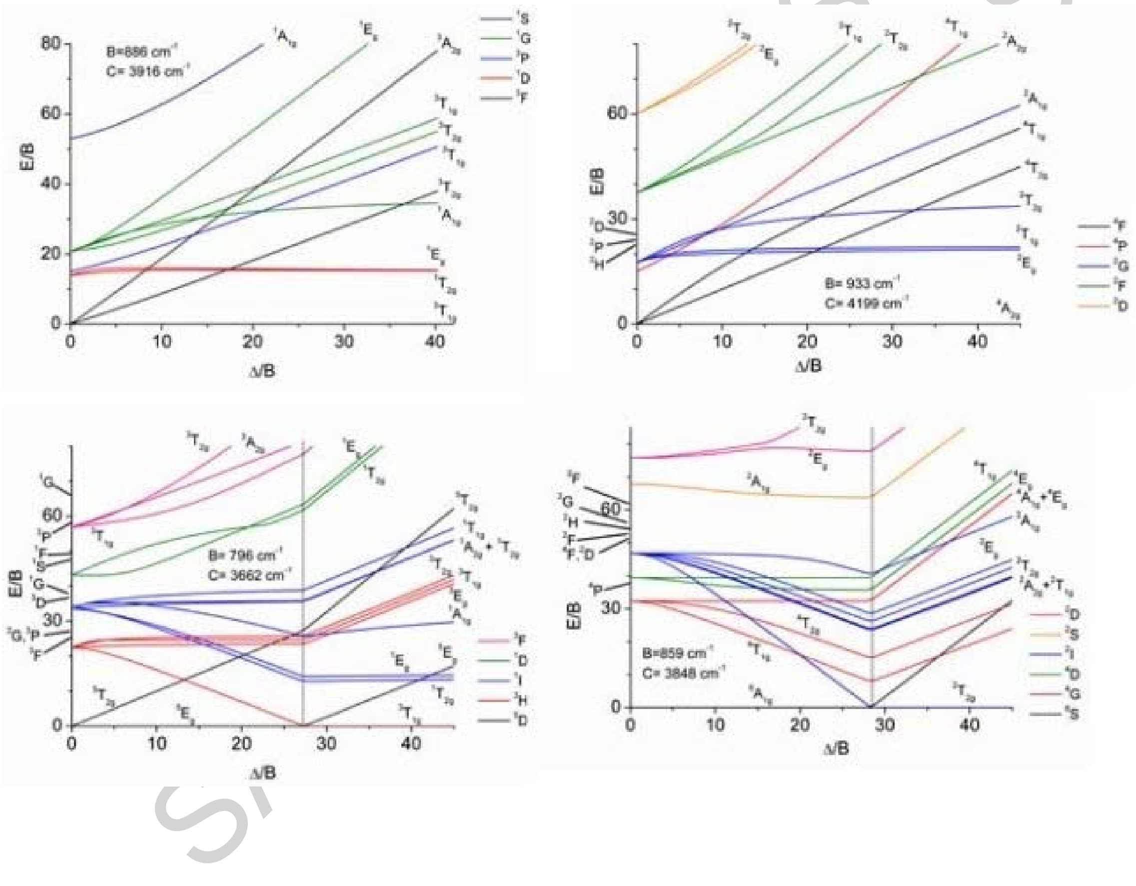
Figure 2. High- and low- spin electronic configuration for an octahedral d^6 complex

The treatment to be employed in the case of a Crystal Field energy which is large compared to the interelectronic repulsion is quite obviously different from what we have discussed up to now. Indeed, in this case the effect of the ligand over d orbitals is treated first and then the interelectronic repulsion is added as a perturbation. If we consider a d^n metal ion in a octahedral geometry as an example, the energy of a given configuration is then obtained by simply counting the number of electrons in the t_{2g} and e_g orbitals and multiplying it by the corresponding (de)stabilization energy, i.e. $-4Dq$ for t_{2g} and $+6Dq$ for e_g. The electron-electron repulsion energy is then added. On the other hand the symmetry of the state is determined on the basis of group theory techniques. The symmetry is identified by the Mulliken symbols, whose meaning is reported in Table 2.

Mulliken Symbol	
a	Non-degenerate and symmetric with respect to the principal symmetry axis
b	Non-degenerate and unsymmetric with respect to the principal symmetry axis
e	Doubly degenerate
t	Triply degenerate
subscript g	Symmetric with respect to inversion
subscript u	Unsymmetric with respect to center of inversion
subscript 1	Symmetric with respect to a binary symmetry axis perpendicular to the principal symmetry axis.
subscript 2	Unsymmetric with respect to a binary symmetry axis perpendicular to the principal symmetry axis.
superscript: '	Symmetric with respect to a plane perpendicular to the principal symmetry axis.
superscript: "	Unsymmetric with respect to a plane perpendicular to the principal symmetry axis.

Table 2: Symmetry properties of orbitals (small caps) and states (capital letters) associated with Mulliken symbols.

The two situations of “strong” and “weak” fields have to be considered as a simplified view, which helped much in the treatment of electronic energy structure in a period where computation facilities were limited. The actual situation encountered in real systems is often an intermediate one and the correct solution is obtained only by complete diagonalization of the matrix of the Hamiltonian (1), which is now easily feasible by using modern computers. The variation from weak fields to strong fields is normally described, for different d^n configurations, by means of Tanabe-Sugano diagrams (Figure 3). Here, the changes in the energies (expressed as E/B) of the states of each configuration as one goes from “no field” or “Free Ions” (far left on the x axis) to Strong Field ligands is plotted as a function of Δ (equal to the $10Dq$ value) in unit of the Racah Parameter B.



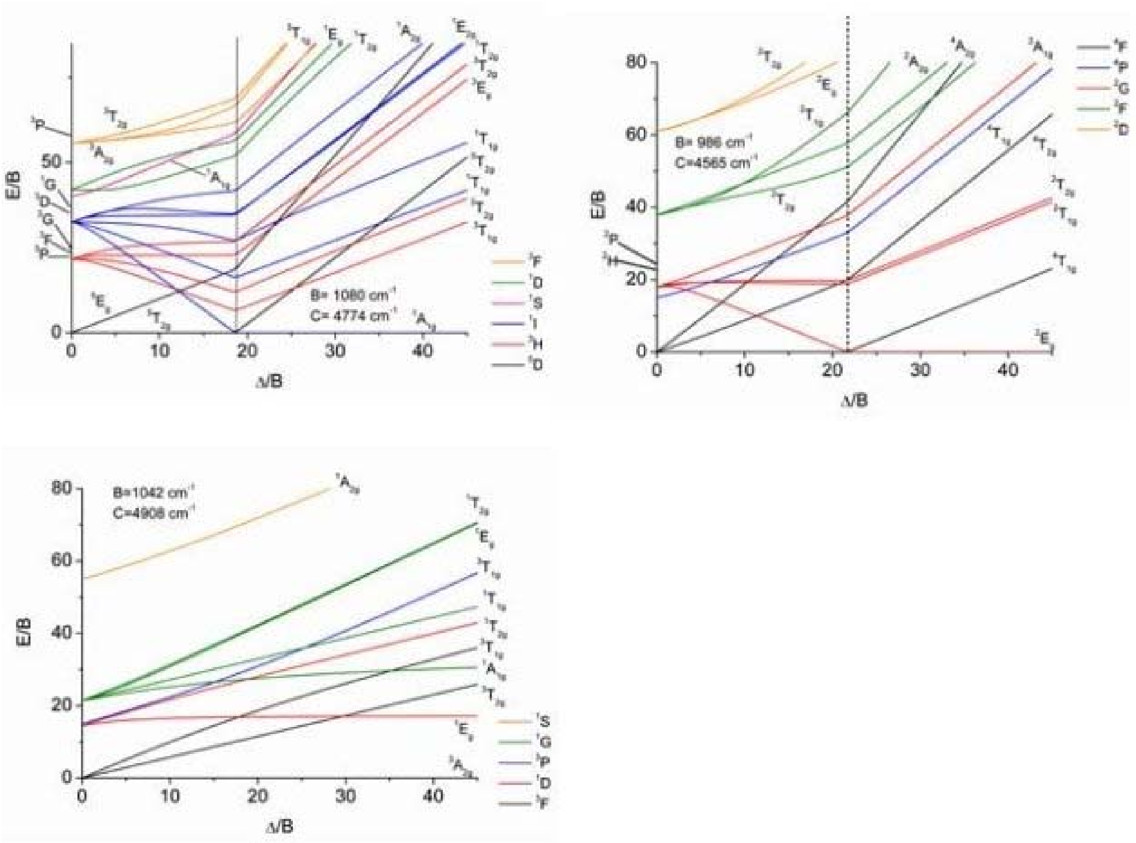


Figure 3 Tanabe Sugano diagrams for octahedral d^2 - d^8 configurations. For clarity reasons some of the states have not been included in the graphs. Their parent free ion terms are indicated on the left of ordinate axis. The vertical dotted lines for d^4 - d^7 evidences the high spin low spin transition on increasing the ligand field.

-
-
-

Bibliography

Abragam, A.; Bleaney, B. (1986). Electron paramagnetic resonance of transition ions, Dover Publications, New York [A comprehensive treatise making deep use of spin Hamiltonian formalism]

Ballhausen, C. J. (1962). Introduction to Ligand field theory McGraw-Hill New York [The first comprehensive book dealing with quantitative aspect of ligand and crystal field theory]

Boudreaux, E. A.; Mulay, L. N. (1976). Theory and application of molecular paramagnetism, Wiley-Interscience New York [A collection of essays on different paramagnetic systems, with a particular emphasis on anisotropic properties]

Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. (1984). *Chemical Physics Letters***, 13**, 1 [The first report of the observation of LIESST effect which paved the way to the use of molecular complexes as magnetooptical switches]

Drago, R. S. (1992). Physical methods for Chemists, Saunders, Philadelphia [A book for pre-graduate chemists containing a good introduction to the factors determining electronic configuration and to magnetic properties and Uv-Vis spectroscopy of transition metal ions]

Gatteschi, D.; Bencini, A. (1990). EPR of Exchange coupled systems, Springer Verlag Berlin [A book where the problem of the anisotropy of exchange coupled systems is systematically treated in relation to the experimental results of Electron Paramagnetic Resonance spectroscopy]

Gatteschi, D.; Sessoli, R.; Villain, J. (2006). Molecular Nanomagnets, Oxford University Press; Oxford, [The first book devoted to a peculiar branch of molecular magnetism, written together by chemists and physicists, which accounts for the impressive development of this field in past 10 years]

Griffith, J. S. (1961). Cambridge University Press, Cambridge, [A book developed around a deeply mathematical-based formalism which deals, among other aspects, on the relation between crystal field theory and spin Hamiltonian approach.]

Herrera, J. M.; Marvaud, V.; Verdaguer, M.; Marrot, J.; Kalisz, M.; Mathoniére, C. (2004). Reversible Photoinduced Magnetic Properties in the Heptanuclear Complex $[Mo^{IV}(CN)_2(CN\text{-}CuL)_6]^{8+}$: A Photomagnetic High-Spin Molecule, *Angewandte Chemie; International Edition*, **43**, 5467 [The report of the first reversible photoinduced high-spin molecule]

Kahn, O. (1993). Molecular Magnetism, Wiley-VCH, New York-Weinheim [The first book on molecular magnetism, written in a very clear way by a pioneer of the field. Contains many interesting examples of different problems which can be encountered when dealing with magnetic properties of molecular complexes]

Lever, A. B. P. (1986). Inorganic Electronic Spectroscopy, Elsevier, Amsterdam [A book collecting electronic spectra and parameters of hundreds of complexes, together with a detailed exposition of the theoretical background needed for their interpretation]

Morrish, A. H. (1965). The Physical Principles of Magnetism, John Wiley & Sons, New York [A book which is mainly devoted to solid state systems and can be used as a very useful introduction to magnetic properties of the matter].

Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. (1993). Magnetic bistability in a metal-ion cluster, *Nature*, **365**, 141. [The communication of the first observation of slow relaxation of the magnetization in a molecular compound, i.e. the first single molecule magnet ever reported]

Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. (1996): Macroscopic quantum of magnetization in a single crystal of nanomagnets, *Nature*, **383**, 145; Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. (1996)**.** Macroscopic Measurement of Resonant Magnetization Tunneling in High-Spin Molecules *Physical Review Letters*, **76**, 3830 [The first two independent reports on the unequivocal observation of Quantum Tunneling of the magnetization, which opened the way for a large wealth of studies on this issue]

Van Vleck, J. H. (1977). Quantum Mechanics: the key to understanding magnetism, Nobel Lecture http://www.nobelprize.org [A very interesting historical account of the importance of the development of quantum mechanics in the explanation of magnetic properties of simple paramagnets. Can be found also as *Review of Modern Physics* (1978), **50**, 181]

Biographical Sketches

Lorenzo Sorace, born in 1974, he received the Degree in Chemistry from the University of Florence in 1998. In 2001 he received the Ph. D. in Chemistry at the same University under the supervision of Prof. D. Gatteschi with a thesis on “Magnetism and magnetic anisotropy of spin clusters”. After a post-doctoral period in Grenoble with Dr. A.L. Barra and Dr. W. Wernsdorfer devoted to the study of spin dynamics of single molecule magnets under microwave irradiation he came back to University of Florence where he is currently a temporary researcher at the Dipartimento di Chimica. He is mainly interested in the use of EPR spectroscopy for the analysis of the properties of molecular magnets.

Dante Gatteschi is Professor of Inorganic Chemistry at the University of Florence since 1980. His initial research interests have been in the investigation of coordination compounds using several different techniques and in particular EPR spectroscopy. Since the ‘80s he has focused on molecular magnetism where he contributed to the development of metal-radical approaches to molecular magnets and of the field of single molecule magnets, i.e. molecules whose magnetization relaxes slowly at low temperature, behave as nanomagnets.