

3 Radicals in metal complexes

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3.1 Introduction

3.1.1 Scope of the substances included and presentation

The coordination compounds listed in the following have unpaired electrons localized predominantly on the ligands. These ligands can be inorganic (e.g. $\text{NO}^\bullet$, $\text{O}_2^{\bullet-}$) or organic. The resulting ground state can be $S = 1/2$ or higher, depending on the number of paramagnetic ligands and on the state(s) of the metal(s). However, only those molecular complexes have been included which could be unequivocally analyzed in terms of meaningful EPR parameters. Materials with the main focus on bulk magnetism were excluded.

We have tried to present the literature data in a uniform manner, e.g. by using accepted abbreviations (see Sect. 3.1.4) and through conversion of units, whenever possible.

The statement referring to radical complex generation should be taken only as a first indication. Composition and structural formulae were adopted from the original references when appearing reasonable, however, there are still only a few radical complexes where this structural information has been independently confirmed, e.g. by diffraction methodology. The numbering of positions in the ligands is based on the original references and does not necessarily correspond to IUPAC nomenclature for organic molecules.

3.1.2 Arrangement

The ordering of this chapter follows the groups of the periodic table to which the metals of the complex belong in the following sequence: **1** (Li, Na, K, Rb, Cs), **2** (Be, Mg, Ca, Sr, Ba), **3** (Sc, Y, La), lanthanides and actinides, **4** (Ti, Zr, Hf), **5** (V, Nb, Ta), **6** (Cr, Mo, W), **7** (Mn, Tc, Re), **8** (Fe, Ru, Os), **9** (Co, Rh, Ir), **10** (Ni, Pd, Pt), **11** (Cu, Ag, Au), **12** (Zn, Cd, Hg), **13** (B, Al, Ga, In, Tl), **14** (Ge, Sn, Pb), **15** (Sb, Bi).

Within each group the complexes are ordered according to their molecular formula, so that closely related species with the same ligand but different metals are grouped together.

3.1.3 Literature

The literature has been covered starting from the end of 1984 to the end of 2001.

3.1.4 Index of abbreviations

Abbreviation	Name / chemical formula
Bpy	2,2'-bipyridyl
Cp	cyclopentadienyl
Cp'	methylcyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
DMF	N,N'-dimethylformamide
DMSO	dimethylsulfoxide
EFISH	Electric Field Induced Second Harmonic
EHMO	Extended Huckel Molecular Orbital
ESEEM	Electron Spin Echo Envelope Modulation
EXAFS	Extended X-ray Absorption Fine Structure
FT-ESR	Fourier-Transform-ESR
HMPTA	hexamethylphosphoric acid triamide
MCD	Magnetic Circular Dichroism
Mes	mesityl
MTHF	2-methyl-tetrahydrofuran
NaTPB	sodium tetraphenylborate
OEP	octaethylporphyrin
OETAP	octaethyltetraazaporphyrin
<i>o</i> Xyl	<i>o</i> -xylyl
Pc	phthalocyanine
Phen	1,10-phenanthroline
PMDTA	pentamethyldiethylenetriamine
<i>p</i> Xyl	<i>p</i> -xylyl
Py	pyridyl
pz	pyrazine
THF	tetrahydrofuran
THP	tetrahydropyran
TMP	tetramethylporphyrin
TPB	tetraphenylborate
TPP	tetraphenylporphyrin
TRIS	2-amino-2-hydroxymethyl-1,3-propanediol