

# CHAPTER 7

## Coloured Glasses

Glass is usually coloured by dissolving transition-metal ions in it. In this chapter we shall discuss the elementary principles of *ligand field* and *molecular orbital* theory with which the absorption bands produced by different transition-metal ions can be interpreted.

### 7.1 ATOMIC STRUCTURE AND THE PERIODIC CLASSIFICATION OF TRANSITION METALS

In a modified Bohr atom, the electrons are arranged in shells ( $n = 1, 2$ , etc.) within which there are a number of sub-shells (s, p, d, f) comprising respectively 1, 3, 5 and 7 orbitals, characterized by the same energy. Each orbital can accommodate two electrons which according to *Pauli's exclusion principle* should be of opposite spin.

The first eighteen electrons fill successively the 1s, 2s, 2p, 3s and 3p levels. In potassium the 19th electron goes not to the 3d, but into the 4s sub-shell and the 20th electron in Ca also goes to the 4s sub-shell. After this the electrons continue to fill up the incomplete 3d sub-shell. In the elements from Sc to Ni the 3d sub-shell is only partly filled and associated with it are some characteristic properties of these metals such as variable valency and the formation of coloured paramagnetic ions. Copper may be included in the first series of transition elements because in the divalent state it has an incomplete 3d shell and the characteristic properties of a transition metal. In the next set of transition elements, Y to Pd, the filling of the 4d sub-shell takes place. The filling of the 4f level does not begin, however, until Ce is reached, where the 4th shell expands from 18 to 32 electrons in the elements from Ce to Lu inclusive. Since the two outer sub-shells are similarly constituted in all of these fourteen elements (the rare-earths) their chemical properties are very similar. It is likely that the filling of the 5f sub-shell in the elements from Th or Pa onwards leads to a second series of chemically similar elements analogous to the rare-earths. Thus there are four series of transition elements of general electronic structure as follows:

Sc to Ni	1st series	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^n 4s^2$
Y to Pd	2nd series	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^n 5s^{1-2}$
Ce to Lu	3rd series	(1s to 4d – complete) $4f^n 5s^2 5p^6$
Pa to —	4th series	(1s to 4f – complete) $5s^2 5p^6 5d^{10} 5f^n 6s^2$

## 7.2 THEORIES OF CHEMICAL BONDING IN TRANSITION METAL COMPLEXES

The beginning of coordination chemistry is usually dated from the discovery of the cobaltamines by Tassaert (see Graddon [1]) in 1798. Tassaert observed that ammoniacal solutions of cobalt chloride deposited the orange compound  $\text{CoCl}_3 \cdot 6\text{NH}_3$  on standing overnight, and recognized in this a new type of chemical substance, formed by the combination of two already fully-saturated compounds, but possessing properties quite different from either. In 1890 Werner [2-4] published the first of his papers on complex compounds in which he suggested the concept of *Primary* and *Secondary* valencies. According to Werner the primary valencies are those involved in satisfying the chemical equivalence of the atoms and the secondary valencies are those by which the coordinated molecules are attached. From experimental evidence with different luteo-cobaltic chlorides precipitated with  $\text{AgNO}_3$  solutions it is apparent that one of the differences between primary and secondary valencies is that the primary valency allows ionization of the bound atoms whereas the secondary valency does not.

The presence of six groups attached by secondary valencies to the metal atom in a complex compound raised a similar stereochemical problem to that posed to organic chemists by the benzene molecule. However, it has been confirmed by numerous X-ray analysis results, and from the number of possible isomers of different compounds, that these six groups are arranged at the apices of an octahedron.

There are three major approaches to the study of bonding in transitional metal complexes:

- (1) Ligand field theory, which is a modified form of crystal field theory in which allowance is made for orbital overlap.
- (2) Valency bond theory.
- (3) Molecular orbital theory.

Since valency bond theory has not yet been widely used in interpreting absorption spectra of coloured glasses, only ligand field and molecular orbital theories will be described here.

### 7.2.1 Crystal field and ligand field theory

The s, p and d orbitals of a free ion are shown in Figure 7.1. In the crystal field theory the salt of a transition-metal ion is considered as an aggregate of ions and/or dipolar molecules which interact with each other electrostatically but do not exchange electrons.

Let us consider a metal ion  $\text{M}^{n+}$  having one 3d electron, lying at the centre of an octahedral set of anions  $x^-$ . In the free ion, this d-electron would have had equal probability of being in any one of the five degenerate 'd' orbitals, but in the electric field created by the ligands the five d orbitals split into two groups, as shown in Figure 7.2(a).

As the ligands present a negative charge (ligands are always negative ions or oriented dipoles) towards the central ion, it follows that an electron will tend to avoid the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals the lobes of which point towards the ligand, and