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MODERN DEVELOPMENTS OF THE THEORY OF COMPLEX COMPOUNDS

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## MODERN DEVELOPMENTS OF THE THEORY OF COMPLEX COMPOUNDS

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The absorption spectra of transition group complexes in solution, in molten salts, in glasses and crystalline solids are frequently determined by the composition of inorganic chromophores  $MX_N$  (cf. "Inorganic Complexes", Academic Press, London 1963) consisting of the  $N$  nearest neighbour atoms  $X$  of the ligands surrounding the central atom  $M$ . Thus, the octahedral chromophore  $Cr(III)O_6$  occurs in ruby, tourmaline, emerald,  $Cr(H_2O)_6^{+3}$ ,  $Cr(OC(NH_2)_2)_6^{+3}$ ,  $Cr\text{ oxalate}_3^{-3}$ , in borate, silicate and phosphate glasses, etc. In all cases, the narrow absorption lines are caused by transitions from the ground-state having the total spin quantum number  $\underline{S} = 3/2$  to other states having  $\underline{S} = 1/2$  and belonging to the same M.O. (molecular orbital) configuration and hence having nearly the same electronic density in our three-dimensional space. On the other hand, the broad absorption bands are caused by transition to other M.O. configurations, modifying the most favourable internuclear distances and consequently co-exciting many vibrational quanta, which are not normally resolved

at room temperature. If the number of electron in the partly filled shell is different in the excited M.O. configuration, we talk about electron transfer bonds. The electron usually comes from a filled M.O. mainly localized on the ligand atoms, and the wave-number is the smaller, the more oxidizing M and the more reducing X.

It is worth emphasizing that the oxidation state of M, indicated by Roman numerals is defined on the basis of the number of electrons in the partly filled shell of the preponderant M.O. configuration of the groundstate, e.g. five in Mn(II) and three in Mn(IV). It is not argued that the fractional charge is as high as in the corresponding gaseous ions  $Mn^{++}$  and  $Mn^{+4}$  though it must be remembered that the interelectronic repulsion parameters derived from the absorption spectra observed indicate, in most cases, fractional charges in the interval 1 to 25 (Progress Inorg. Chem. 4 (1962) 73) rather larger than the higher limit 1 suggested by Pauling's electroneutrality principle.

Actually the transition group complexes are good examples, as is the oxygen molecule, of the tendency of partly filled shells or sets of necessarily (of group-theoretical reasons) degenerate orbitals to have groundstates having the maximum value for  $S$ . The energy differences can then be characterized by a spin-pairing energy parameter  $P$ , and the total expression for the interelectronic repulsion contains a contribution  $-DS(S+1)$ . Since  $P$  is known from isoelectronic series of gaseous ions to be inversely proportional to the average radius of the partly filled shell and

to be a linear (not a proportional) function of the ionic charge, it is argued that the decrease of  $\underline{D}$  always found in compounds relative to the gaseous ions can be ascribed to an expansion of the radial function (due to decreased effective charge, corresponding to an intermediate situation between the neutral atom and a positive ionic charge as large as the oxidation state) and a delocalization, forming M.O. This phenomenon is called the nephelauxetic effect from the Greek word for cloud-expanding. The conditions for a pronounced nephelauxetic effect are roughly the same as for low-energy electron transfer bands: highly oxidizing M and highly reducing X. Recently, J. Sugar (J. Opt. Soc. Amer. 55 (1965) 1058) has extended Ephraim's observations from 1926 of the nephelauxetic effect in praseodymium (III) compounds by finding the expected, slightly larger, term distances in gaseous  $\text{Pr}^{+3}$ .

Whereas the transitions inside partly filled d and f shells certainly have the largest interest for spectroscopists, the optical electronegativities derived from electron transfer spectra may actually be of greater interest to chemists. A theoretical introduction is given in "Orbitals in Atoms and Molecules", Academic Press, London 1962, and several review papers exist, e.g. Advances Chem. Phys. 5 (1963) 33 and 8 (1965) 47 and one in French to appear shortly in Journal de Physique.