281.   *On the Use of Metal Outer* s- *and* p-*Orbitals for Bonding in Transition-metal Complexes.*

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Optical and magnetic data for silver atoms in sodium chloride are discussed in terms of σ-bonding between the six equivalent nearest-neighbour chloride ions and the $5s$- and $5p$-atomic orbitals of silver.

ALTHOUGH there is a wealth of information pertaining to the participation of metal d-orbitals in σ- and π-bonding with ligands, especially the halide ions in octahedral complexes, very little is known about the degree of involvement of metal s- and p-orbitals in such bonds.   The concept of d^2sp^3-hybridisation seems to be unnecessarily rigid and is not demanded by symmetry.   Equally, the concept that only d-levels contribute significantly to the bonding, although satisfactory for the understanding of most properties of such complexes, is likely to prove an oversimplification in many instances.   (It is sometimes supposed that the participation of metal s- and p-levels is a necessary outcome of molecular orbital theory; this is not the case, since the ligand a_{1g} and t_{1u} σ-levels can be treated as being non-bonding, this description having the advantage of revealing in a simple way the markedly ionic character of these bonds.   Although both the metal outer s- and p-orbitals will have considerable extension over the regions occupied by the ligands, this does not necessarily imply significant covalent bonding.   Thus, covalent involvement of the outer s-level will be small because of the large energy-gap between this level and the a_{1g} σ-orbitals.   In addition, extension beyond the chlorine nuclei will diminish the effective bonding with the a_{1g} ligand level.)

Since there is a great dearth of experimental information relating to this question, the construction of energy-level diagrams such as those depicted in the Figure must be somewhat arbitrary.   However, it is now very common to find scheme (a) used for qualitative discussions of structure.   This frequent, uncritical reproduction is dangerous in that it gives the general reader the impression that these matters are decided, and that the order a_{1g}, t_{1u}, and e_g for the σ-bonding levels is the normal arrangement.   The purpose of this Paper is to suggest that the level-scheme (b) may often be more appropriate for qualitative discussion, and to examine methods for probing this problem experimentally.   In particular, it is shown that recent spectrophotometric and magnetic data for silver " atoms " trapped in sodium chloride are pertinent and informative.[1]

One way to probe the nature of the upper levels is to study the ultraviolet spectra of suitable complexes, but this task is difficult because transitions of interest, such as $e_g{}^* \longrightarrow t_{1u}{}^*$ (Figure), are expected to occur in the ultraviolet region normally dominated by intense and broad charge-transfer bands such as ligand $\pi \longrightarrow e_g{}^*$.   Some of these problems can be surmounted by studying complexes having a " filled " d-shell, such as those of Cu^+, Zn^{2+}, etc.   These are not always considered in this context because there can be no " crystal-field " stabilisation (the bonding and antibonding e_g and t_{2g} levels being completely occupied), but if interaction between ligand σ-orbitals and metal s- and p-levels is important, as implied in the Figure, there should still be significant σ-bonding, since the antibonding a_{1g} and t_{1u} levels are unoccupied.   Transitions to these antibonding levels should be both more readily detected and interpreted.

This approach has been discussed in detail by Jörgensen,[2] who stresses the many confusing issues which arise.   Perhaps the only firm conclusion is that the $a_{1g}{}^*$ level lies well below the $t_{1u}{}^*$ level.   If an extra electron could be added to d^{10} complexes, in such a way that a symmetrical octahedral ligand environment were retained, the electron spin

¹ Delbecq, Hayes, O'Brien, and Yuster, *Proc. Roy. Soc.*, 1963, *A*, **271**, 243.
² Jörgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

resonance spectrum would distinguish clearly between the $a_{1g}*$ and $t_{1u}*$ levels. This situation has been achieved for silver " atoms " in potassium chloride crystals, formed by irradiation of crystals doped substitutionally with silver cations.[1]

The significant data for silver " atoms " in potassium chloride (taken from ref. 1) are as follows. (i) The hyperfine coupling to ^{109}Ag, which was purely isotropic, was 649 $\pm$ 2 gauss. (ii) The isotropic part of the hyperfine coupling to six equivalent chloride ions was 13·3 $\pm$ 0·2 gauss, and the anisotropic component, estimated from the variation in line-width with orientation, was approximately 1 gauss. (iii) There were intense optical absorption bands at 23,500 and 50,750 cm.$^{-1}$, attributable to the trapped silver " atoms." The electron spin resonance spectrum of this centre shows clearly that the unpaired electron is in an orbital having very large s-character on silver. Thus, the hyperfine coupling for ^{109}Ag atoms is 707·3 gauss,[3] and that for ^{109}Ag in sodium chloride is 649 $\pm$ 2 gauss.[1] Thus the a_{1g} level is shown to be predominantly $5s$ on silver.

Delbecq *et al.*[1] briefly discussed the observed 8% reduction relative to the atomic value in terms of the theory developed by Adrian[4] for atoms trapped in rare-gas matrices, and concluded that it is primarily due to an increase in the radius of the $5s$-orbital. The
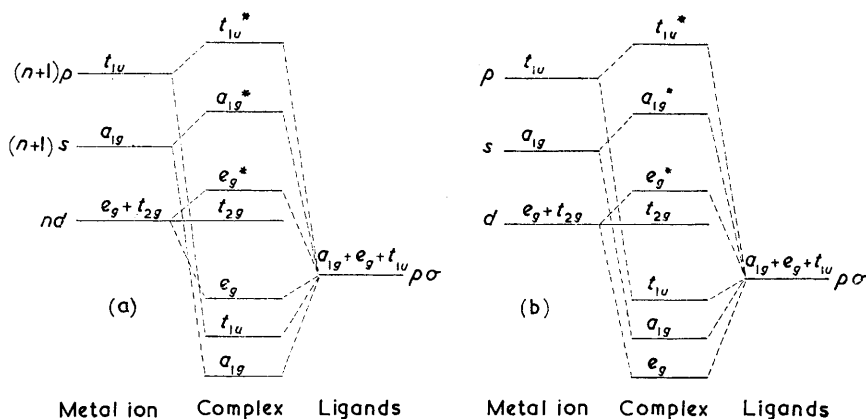
Energy-level diagrams for an octahedral transition-metal complex, MHal$_6$, with appreciable σ- and π-bonding, (a) as commonly given in current texts, and (b) an alternative and possibly preferable arrangement, relevant to the case of Ag^0 in alkali-metal halides.

present representation implies that this reduction is largely a result of delocalisation on to the ligands, which naturally arises from an electron in the a_{1g} $\sigma*$-level. This can be checked approximately by considering contributions from the $3s$- and $3p$-(σ)-levels on the six chloride ligands. In calculating this contribution from the isotropic and anisotropic hyperfine coupling constants, values for $\psi(0)^2$ and $\langle r^{-3} \rangle$ recently calculated for chlorine atoms[5] have been employed, and, since the contributions from ^{35}Cl and ^{37}Cl were not resolved in the spectra,[1] a weighted average has been used. It should be stressed that, since the purely anisotropic coupling was estimated from the variation in line-width,[1] the error in the estimated p-character may be quite large. The results of calculations similar to those discussed previously[6] are that there is about 0·8% chlorine $3s$-character and 0·8% chlorine $2p$-character in each σ-bond, that is, about a 10% contribution from the chlorine atoms.

In view of these approximations, the agreement with the observed 8% reduction in

[3] Wessel and Lew, *Phys. Rev.*, 1953, **92**, 641.
[4] Adrian, *J. Chem. Phys.*, 1960, **32**, 972.
[5] Mayers, personal communication.
[6] Atkins, Brivati, Keen, Symons, and Trevalion, *J.*, 1962, 4785.

5s-character on silver is satisfactory, and it is concluded that the main cause of the reduction in the [109]Ag hyperfine coupling from the free-atom value is delocalisation on to the six chloride " ligands " through slight σ-bonding. This conclusion is reinforced by the observed [1] reduction of about 6500 cm.$^{-1}$ in the energy of the $5s^2 \longrightarrow 5s^1 5p^1$-transition relative to that for the free atom. In terms of the present scheme, the transition at 23,500 cm.$^{-1}$ is $a_{1g}{}^* \longrightarrow t_{1u}{}^*$, and the reduction arises because of a greater destabilisation of the 5s-level than of the 5p-level. If one makes the crude approximation that the extent of stabilisation of the a_{1g} and t_{1u} components of the ligand σ-levels is equal to the destabilisation of the metal levels, then the a_{1g} σ-bond is below the t_{1u} bond by about 6500 cm.$^{-1}$.

Unfortunately it is not possible to make a similar calculation for the e_g level unambiguously. However, if one assigns the intense band at 50,750 cm.$^{-1}$ to the allowed $e_g \longrightarrow t_{1u}$-transition, and uses results for Ag$^+$ in the gas phase [7] to estimate a separation of about 31,000 cm.$^{-1}$ for the atomic 4d- and 5s-levels, then an argument similar to that for the t_{1u} and a_{1g} levels places the e_g σ-bonding level about 4000 cm.$^{-1}$ below the a_{1g} level.

These approximate considerations lead to the order of σ-bonding levels given in Figure (b), and are in accord with the concept stressed here that this arrangement is likely to prove to be of more general applicability than that shown in Figure (a).

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[7] Shenstone, *Phys. Rev.*, 1940, **57**, 894.