On the Origin of Electronic Term Splittings in Trigonally Distorted Metal Complexes

R. DINGLE

Chemical Laboratory IV, Department for Physical Chemistry, H. C. Ørsted Institute, The University of Copenhagen, Copenhagen, Denmark

Trigonally distorted octahedral complexes of $3d$ metals have been a popular field of study.[1-3] Generally, these systems are generated by chelation of the metal ion by three bidentate ligands. In addition, certain hard crystals, such as Al_2O_3, provide trigonally distorted sites for trivalent ions substituted in the lattice at, or nearly at the aluminium ion site.

The subsequent splitting of degenerate states of the octahedron and the changes in frequency of absorption in mutually perpendicular planes of polarized light have been interpreted.[1,2,4,5] For splittings measured at the absorption band maxima, Δ_{max}, there are several competing effects that should be resolved before the experimental results are compared with the theory. Firstly (a), if the distortions are large, then the measured splittings may not represent, even approximately the actual displacement of the electronic energy levels and, in some cases, even the sign of the splitting may be altered. These effects are shown in Fig. 1.

Secondly (b), in these complexes it is usually assumed that the absorption band intensity is allowed by the static asymmetric field and thus can be represented as $(0,0) + nv'$, where v' is the frequency of a totally symmetric upper state vibration. If this is true, and the same frequency applies to say both components of a split T state of O_h, then assuming that (a) has been resolved,* the true electronic splitting, measured at (0,0), should correspond to the vibronic splitting measured at v_{max}. We have recently demonstrated[6] that, when vibronic contributions are significant and

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* This requires that the equilibrium configuration of the excited states are the same for the vibration v' and that the potential surfaces at low to medium n are very similar. This is likely for rather small distortions[6] as well as for intraconfigurational transitions.
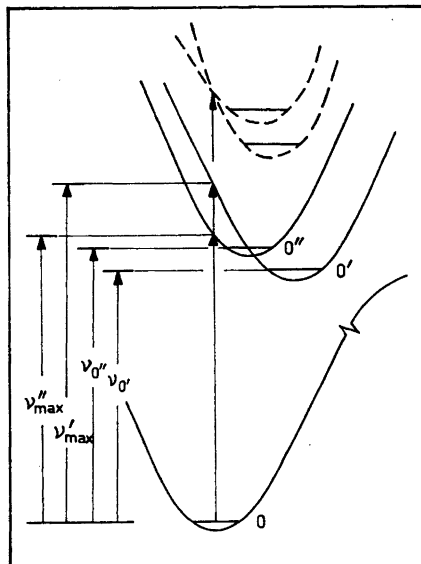
Fig. 1. Two possible situations that may arise when upper state trigonal distortions are considerable. The solid curves show $v_0'' > v_0'$ and $v''_{max} < v'_{max}$ whereas the broken curves show $v''_{max} \simeq v'_{max}$; $v_0'' \neq v_0'$.

there is a violation of the electronic selection rules, these conditions are not likely to be met and Δv_{max} values do not give a true measure of the electronic splitting. This does not appear to be a problem in hard crystals[2] but it should certainly be an important feature in most tris bidentate complexes (tris-oxalato complexes appear to be an exception[7]).

When these preliminary matters are resolved, probably best done by measuring crystals at low temperatures and observing the vibrational fine-structure, the origin of the electronic distortion may be considered.

The so-called ionic model[1,2] treats the problem from the electrostatic, point charge point of view and as such determines the absorption band splittings entirely from the relative dispositions of the ligand nuclei. This model, which is equivalent to considering the splittings as arising from a distortion of the σ bonding framework, has met with only partial success.[1,2]

An alternative model, treated by Orgel,[4] describes the splittings in terms of π

interaction between the ligand and the metal t_{2g} orbitals (in the ionic model these latter orbitals are nonbonding). In the covalent approach, the nature of the interaction is determined by molecular orbitals constructed from appropriate ligand and metal orbitals. The extent of the interaction is determined by overlap and other considerations. In a qualitative sense there will be ligands with no π bonding capacity, one type of π bonding orbitals or with two, non-equivalent sets of π bonding orbitals. If to these is added the variable ionic radius of the central metal ion it should be possible, in favorable cases, to describe the spectral splittings. Orgel [4] has used more quantitative arguments to describe the magnetic properties of tris-1,1-bipyridyl titanium in which, from energetic considerations, the ligand π system is expected to be nearly degenerate with the metal t_{2g} orbitals.

From recent spectral analyses there seems to be a basis for extending this point of view. Experiments in this laboratory [6] have shown, from measurements of $\Delta\nu_{0,0}$ in crystals at low temperatures, that the electronic splitting of the $A_1 \rightarrow {}^1A_2$; ${}^1E$ ($^1T_{1g}$) transition of the Coen$_3{}^{3+}$ ion is very small (0 ± 4 cm^{-1}). Available crystal structures [8,9] show that the CoN$_6$ octahedron is somewhat distorted and, since the ligand has no π orbitals available to the metal, any splittings must be a function of nuclear displacement. This may be termed a σ bonding effect. The absence of any splitting indicates that the spatial distribution of the electron density on the ligand nitrogen is such that the small displacements seen in the X-ray results, do not influence the central metal ion to any large extent.

Apparent splittings, measured from $\Delta\nu_{max}$ values, indicate sizeable interactions in tris oxalates ($\Delta\nu_{max} \sim 500$ cm^{-1}) and in tris-1,1-dipyridyls ($\Delta\nu_{max} \sim 600$ cm^{-1} in, for instance (bipyr$_3$Ni)$^{2+}$). In both cases considerable nuclear distortions are thought to be present [10,11] and π bonding effects are possible and likely.

At the opposite extreme to the tris-ethylenediamine complexes are the tris acetylacetone complexes. These are thought to be covalent and to show strong π bonding properties.[12,13] It is reasonable to expect that the in-plane and out-of-plane π orbitals of this ligand will interact differently with the t_{2g} set when in trigonal symmetry. In addition, the larger the central metal ion the greater should be the splitting of the t_{2g} orbitals. Of the tris acetylacetonato complexes that have been studied, the Ti(III) and Os(III) central metal ions have the largest ionic radii and these two complexes are believed to show very large "trigonal-field" splittings.[14,15] These complexes are only slightly distorted from a regular octahedron and the π bonding model has to be invoked in order to provide a satisfactory explanation of these observations. This is especially obvious when it is observed that other isomorphous, and presumably isostructural, metal complexes with acetylacetone show very much smaller splittings.[16]

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