

COORDINATION COMPOUNDS WITH METAL TO METAL BONDS: THE CONSTRUCTIVE INTERACTION OF THEORY AND EXPERIMENT

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Abstract - The weakness of the  $\delta$  component of a quadruple bond, resulting from the rather small overlap of the d orbitals concerned, leads to some interesting problems in reconciling theory and experiment. However, when all sides of the theoretical picture as well as sufficient experimental data are properly considered, a very satisfactory constructive interaction between theory and experiment is achieved.

INTRODUCTION

The desideratum for all scientific investigation is to achieve that maximally productive marriage of the noumenal and phenomenal aspects of the enterprise. When the optimal blend of theory and experiment exists, the two move forward in tandem, each sector stimulating progress in the other. In this lecture I shall show that in the investigation of metal atom cluster compounds and multiple bonds between metal atoms, there has been a high degree of mutually beneficial interaction between theory and experiment. By theory I do not necessarily always mean high-powered calculations on a big computer, though this will most often be the case.

From the outset, in the early 1960's, the field of transition metal compounds with metal-to-metal (M-M) bonds, of whatever order, has posed special and interesting challenges for bonding theory. Most simplified bonding models that have been successfully applied to transition metal complexes are so structured that they can apply only to Werner complexes - which in the broadest sense means one-center or mononuclear complexes. Thus we have the valence-bond hybridization model of Pauling, the crystal field theory, the ligand field theory and the angular overlap model, all of which emphasize - and, indeed, limit themselves to - the question of how the interaction of ligands with a metal atom (ion) may be represented.

When we turn to the new, non-Wernerian transition metal chemistry in which covalent bonds between metal atoms are the key feature, all models based on the symmetry properties of orbitals in a unicentric system, i.e., on the mathematics of spherical harmonics, become useless. We must turn back to fundamentals and develop new approaches suited to the new material.

There are also three additional difficulties.

(1) Many of the M-M bonded compounds are formed by the heavier transition elements and are rather large systems. Even today the computational capacity needed to treat them by the conventional Hartree-Fock (HF) method is often beyond practical reach.

(2) For the compounds formed by the third transition series it is necessary to introduce relativistic corrections if quantitative results are needed. Many interesting species, e.g.,  $[\text{Ta}_6\text{Cl}_{12}]^{n+}$ ,  $\text{W}_2\text{Cl}_4(\text{PR}_3)_4$ ,  $[\text{Re}_2\text{Cl}_8]^{2-}$ ,  $\text{Os}_2(2\text{-oxopyridine})_4\text{Cl}_2$ , are in this category.

(3) In all cases, even for compounds of 1st transition series metals (e.g., chromium, which will not be discussed in detail here) at least some of the components of the bonding are weak enough so that the HF result is inadequate and may even be qualitatively wrong. Electron correlation must be introduced, usually by the configuration interaction (CI) procedure.

In this lecture I shall focus on a few related problems, namely, difficulties associated with correctly assigning and calculating the energy and intensity of  $\delta \rightarrow \delta^*$  transitions.

THE NATURE OF  $\delta \rightarrow \delta^*$  TRANSITIONS

Multiple M-M bonds of orders 3 to 4 may be of the following five types:

Type	Bond Order	Configuration	Lowest Excited Configuration
<u>a</u>	3	$\sigma_{\pi}^2 \delta^4$	$\sigma_{\pi}^2 \delta^3 \delta$
<u>b</u>	3.5	$\sigma_{\pi}^2 \delta^4 \delta$	$\sigma_{\pi}^2 \delta^4 \delta^*$
<u>c</u>	4	$\sigma_{\pi}^2 \delta^4 \delta^2$	$\sigma_{\pi}^2 \delta^4 \delta \delta^*$
<u>d</u>	3.5	$\sigma_{\pi}^2 \delta^4 \delta^2 \delta^*$	$\sigma_{\pi}^2 \delta^4 \delta \delta^* \delta$
<u>e</u>	3	$\sigma_{\pi}^2 \delta^4 \delta^2 \delta^* \delta$	$\sigma_{\pi}^2 \delta^4 \delta^2 \delta^* \delta \delta^*$

For the quadruple bonds (c) and the two types of bond with a formal bond order of 3.5 (b,d) the lowest excited state derives from a configuration that is reached from the ground state by a  $\delta \rightarrow \delta^*$  promotion of one electron. As an optical transition, this is electric-dipole allowed in polarization parallel to the M-M bond axis. This transition has indeed been observed in all compounds containing bonds of types b, c and d, but in attempting to reconcile the observations with theory, two general problems have arisen.

First, in all cases the intensities are surprisingly low, considering that the transitions are orbitally allowed. Second, in the bonds of type c the transition is always observed at a far higher energy than that calculated despite the fact that the same calculation may give a rather accurate energy for all (or most) other electronic transitions in the same molecule. For cases b and d, however, the calculations predict the energy of the  $\delta \rightarrow \delta^*$  transition just as well as they do for the other transitions.

The intensity problem is actually not difficult to resolve. As Trogler and Gray<sup>1</sup> have observed, the overlap of the two d orbitals that form the  $\delta$  bond is quite small. Moreover, as Mulliken showed<sup>2</sup> many years ago, oscillator strength in a transition of this nature is approximately proportional to the square of the overlap integral. Thus, low intensity is a straightforward consequence of the weakness of the  $\delta$  bond, and using Mulliken's relation the correct order of magnitude of the intensity can be calculated. In this instance, available theory easily resolves an apparent experimental anomaly.

The accurate theoretical estimation of the energy of the  $\delta \rightarrow \delta^*$  transition has led to interesting theoretical developments. The first attempts to calculate this energy employed the SCF-X $\alpha$ -SW method and were quite unsatisfactory. For  $[\text{Mo}_2\text{Cl}_8]^{4-}$  the observed and calculated energies are<sup>3</sup>  $18.8 \times 10^3 \text{ cm}^{-1}$  and  $9.2 \times 10^3 \text{ cm}^{-1}$ , respectively, and for  $[\text{Re}_2\text{Cl}_8]^{2-}$  the band is observed at  $14 \times 10^3 \text{ cm}^{-1}$  and calculated<sup>4</sup> at  $4.5 \times 10^3 \text{ cm}^{-1}$ . On the other hand, for  $[\text{Tc}_2\text{Cl}_8]^{3-}$  the observed<sup>5</sup> and calculated<sup>6</sup> values,  $5.9 \times 10^3 \text{ cm}^{-1}$  and  $6.0 \times 10^3 \text{ cm}^{-1}$ , respectively, agree very well. In the closed shell species (type c) there are both singlet-singlet and singlet-triplet transitions possible, whereas for  $[\text{Tc}_2\text{Cl}_8]^{3-}$  only a doublet-doublet transition is possible. However, it has been shown that even when the type c species are treated entirely correctly as regards the spin multiplicity,<sup>3,7</sup> there is still a large discrepancy between observed and calculated energies, with the latter being far too low.

The difficulty with the  $\delta \rightarrow \delta^*$  energy calculation is now recognized to have its origin in the electron correlation phenomenon. It is not immediately obvious how to formulate this simply in the SCF-X $\alpha$ -SW formalism, but it is easily explained in terms of conventional LCAO MO theory. Considering only the  $\delta$  and  $\delta^*$  orbitals and two electrons, it is clear<sup>8</sup> that the four possible states can be expressed in the standard Slater determinantal form as follows, where normalizing factors are omitted.

Ground State:

$$\psi_1(^1A_{1g}) = |\delta\bar{\delta}| = |\delta\delta|\alpha\beta$$

Singly Excited States:

$$\psi_2(^1A_{2u}) = |\delta\bar{\delta}^*| + |\bar{\delta}\delta^*| = [\delta\delta^* + \delta^*\delta](\alpha\beta - \beta\alpha)$$

$$\psi_3({}^3A_{2u}) = |\delta\delta^*| \begin{matrix} (\alpha\alpha) \\ (\alpha\beta + \beta\alpha) \\ (\beta\beta) \end{matrix}$$

Doubly Excited State:

$$\psi_4({}^1A_{1g}) = |\delta^*\delta^*|\alpha\beta$$

The wave functions  $\delta$  and  $\delta^*$  are defined in terms of the two  $d_{xy}$  orbitals,  $\chi_A$  and  $\chi_B$ , as follows, where we neglect the overlap,  $S$ , which is  $\ll 1$ .

$$\delta = 2^{-1/2}(\chi_A + \chi_B)$$

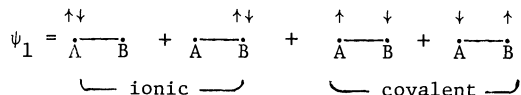
$$\delta^* = 2^{-1/2}(\chi_A - \chi_B)$$

From here the argument is essentially that given years ago by Coulson<sup>9</sup> with respect to the approach to the dissociation limit of  $H_2$ . Now, however, the  $\delta$  bond, even at the equilibrium internuclear distance of the ground-state, is subject to the same problems. Let us expand  $\psi_1$ , ignoring here, and later, normalizing factors.

$$\psi_1 = \{[\chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)] + [\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)]\} (\alpha\beta - \beta\alpha)$$

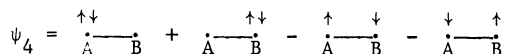
$\psi_{\text{ionic}} + \psi_{\text{covalent}}$

In pictorial terms we may write:



From this it is clear that  $\psi_1$  vastly overestimates the ionic contribution to the ground state; it is quite out of the question that the true electron density distribution could put both electrons at the same nucleus as much as half of the time.

We note, however, that  $\psi_4$  also defines a  ${}^1A_{1g}$  state and, analogously, this too will consist of equal contributions from ionic and covalent parts:



We note, though, that the algebraic signs are different so that  $\psi_1 + \psi_4$  is a pure ionic function while  $\psi_1 - \psi_4$  is purely covalent. This means that if instead of using simply  $\psi_1$  to represent the  ${}^1A_{1g}$  ground state we use  $\psi_1' = \psi_1 - \lambda\psi_4$  we can lessen the ionic character of the ground state to whatever degree we wish by choosing the magnitude of  $\lambda$ .

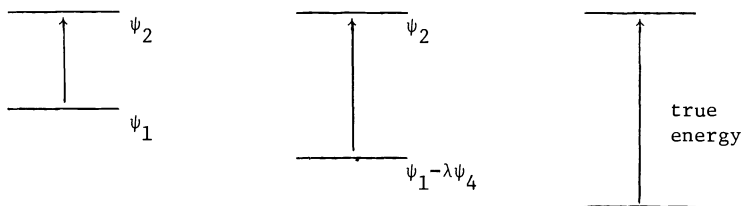
For the singlet excited state,  $\psi_2$ , we obtain, upon similar expansion, the results:

$$\psi_3 = [\chi_A(1)\chi_A(2) - \chi_B(1)\chi_B(2)](\alpha\beta - \beta\alpha)$$

$$\begin{array}{c} \uparrow\downarrow \\ \text{A} \text{---} \text{B} \end{array} - \begin{array}{c} \uparrow\downarrow \\ \text{A} \text{---} \text{B} \end{array}$$

Thus, this state is totally ionic.

The following diagram shows the relationship that all of this has to the calculation of the energy of the  $\delta^2 \rightarrow \delta\delta^*$  ( ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ) transition.



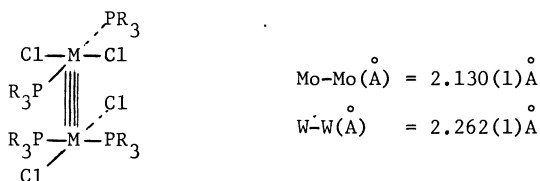
When we use the simple, heavily ionic wave function,  $\psi_1$ , we obtain too high an energy for the ground state and hence too low an energy difference between  $\psi_1$  and  $\psi_2$ . Mixing in some of  $\psi_4$  to make the ground state less ionic increases its stability and gives a better approximation of the true energy difference. This mixing is an example of using configuration interaction (CI) to correct a simple LCAO wave function for electron correlation. However, there are other CI contributions to the ground state wave function and also CI contributions to the wave function for the excited state, and the argument just given is greatly oversimplified from a quantitative point of view. Nevertheless, it probably deals with the principal effect, and shows the way to making improved calculations.

It is to be noted that the above argument is consistent with the fact that for  $\delta \rightarrow \delta^*$  ( ${}^2B_{1u} \leftarrow {}^2B_{2g}$ ) and  $\delta^2 \delta^* \rightarrow \delta \delta^* {}^2$  ( ${}^2B_{1u} \leftarrow {}^2B_{2g}$ ) good results can be obtained without CI. These are either actually or effectively one-electron systems and no correlation problems exist.

While the foregoing analysis does not apply directly to the SCF-X $\alpha$ -SW approach, it is in the nature of any one-electron MO theory that it will, for reasons of electron correlation, describe a pair of electrons improperly in the limit of weak coupling between them.<sup>10-12</sup> It was with the problem of treating the weak  $\delta$  interactions as one specific objective that several interesting new approaches to handling the correlation problem have been devised. The classical method of allowing for electron correlation is to mix appropriate excited state wave functions into the ground state (just as we did above in the almost trivial case of mixing the  $|\delta^* \delta^*| \alpha \beta$  wave function,  $\psi_4$ , with  $|\alpha \alpha| \alpha \beta$ ,  $\psi_1$ . While in principle this is always possible and in the limit this configuration interaction (CI) treatment will converge to give an accurate result, its full implementation is extremely cumbersome and expensive.

#### SOME RECENT RESULTS

Let us now look at some recent experimental results concerning  $\delta \rightarrow \delta^*$  transitions and see how they compare with theoretical expectation at either a qualitative or a quantitative level. We turn first to a situation that allows us to examine, rather simply, the effect of decreasing the d-orbital overlap in a  $\delta$  bond while keeping other factors essentially the same. This is done using data for a type of quadruply-bonded ditungsten compound<sup>13,14</sup> that has only recently been made and characterized. The availability of the dimolybdenum homolog makes possible an informative comparison. The molecules in question, which have been studied structurally and spectroscopically in detail<sup>15</sup> are:



The basis of the argument in comparing the two compounds is that the outer d orbitals of the molybdenum and tungsten atoms are very similar in size, but because of the presence of an additional 32 electrons in the tungsten core, two tungsten atoms cannot approach as closely as two molybdenum atoms. As indicated above, the actual difference in bond lengths is  $\sim 0.13\text{\AA}$ . This difference causes the  $\delta$ - $\delta$  overlap to be appreciably smaller for the tungsten compound and we should expect this to be reflected clearly in both the energies and intensities of the  $\delta \rightarrow \delta^*$  transitions. As shown in Fig. 1, the observations are in excellent accord with these expectations. The  $\delta \rightarrow \delta^*$  transition lies at much lower energy and is considerably weaker for the tungsten compound.

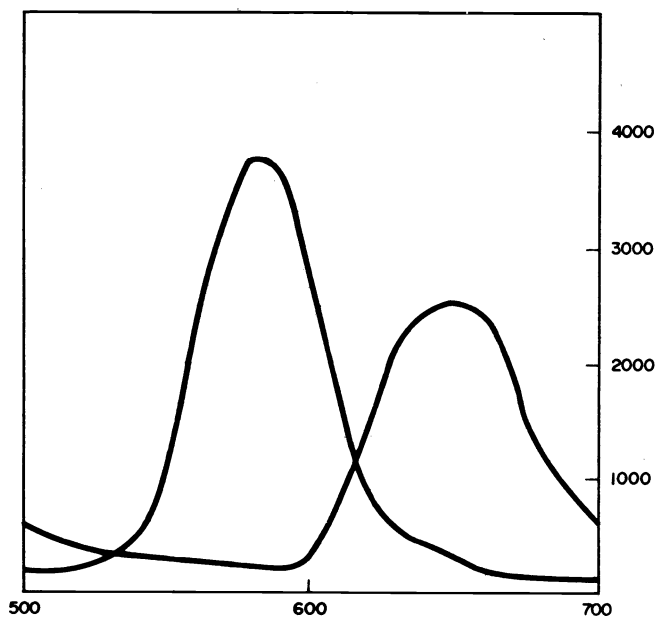


Fig. 1. The  $\delta \rightarrow \delta^*$  absorption bands for the homologous  $M_2Cl_4(PMe_3)_4$  molecules. The abscissa scale is in nanometers and the ordinate gives molar extinction.

In the preceding example, we have not attempted to justify the assignment of the bands as  $\delta \rightarrow \delta^*$  transitions. In view of the fact that a direct calculation of the energy may, for the reasons discussed earlier, be expected to give a prediction far below the experimental value, how do we know, in general as well as in this particular case, that the assumption is correct? A complete answer to that question is beyond the scope of this article, but one type of evidence will be discussed since it adds further to our theme of the interaction of theory and experiment.

When a  $\delta \rightarrow \delta^*$  transition is measured at low temperature and in an oriented single crystal theory predicts that it should consist of a resolved vibrational progression in the M-M stretching frequency and that it should have a well-defined polarization parallel to the metal-metal bond; both of these features are observed in certain simple cases and such observations provide powerful evidence for the correctness of the assignment.<sup>1</sup> However, in other cases far more complex behavior has been observed and this has called for a more sophisticated extension of theory. It is pertinent to the theme of this paper that this extension is based, qualitatively, on the fact that the  $\delta \rightarrow \delta^*$  transition, though formally an orbitally allowed transition, has an intrinsically small dipolar contribution to its transition moment because the  $\delta$ - $\delta$  overlap is small.

To understand how this affects the appearance of the absorption band (other than making it very weak) we must consider in detail the following expression for the transition moment:

$$M_{fg}(Q) = M_0 + m_i Q_i \text{ where } m_i = \left( \frac{\delta M}{\delta Q_i} \right)_{Q_i=0} = 0$$

This expression takes account of vibronic coupling to first order and must be squared to give the intensity values for each vibrational component. When this is done using the adiabatic Born-Oppenheimer approximation we obtain:

$$M_{g_0, f_{v_1'}}^2 = [M_0^2 \langle g_0 | |f_{v_1'} \rangle|^2 + 2M_0 m_i \langle g_0 | |f_{v_1'} \rangle \langle g_0 | Q_i | f_{v_1'} \rangle + m_i^2 \langle g_0 | Q_i | f_{v_1'} \rangle^2] \prod_{j \neq i} \langle g_0 | |f_{v_j'} \rangle|^2$$

The functions  $\langle g_0 |$  and  $|f_{v_1'} \rangle$  denote the 0th vibrational level of the electronic ground state and the  $v_1$ th vibrational level of the upper electronic state, respectively.

As a normal rule, when a transition is orbitally dipole-allowed,  $M_0$  is so large that  $M_0^2 \gg M_0 m_i \gg m_i^2$  and we see only the vibrational progression in a totally symmetric frequency

represented by the first term on the RHS of the equation. Moreover, this occurs only in parallel polarization. For dipole-forbidden transitions ( $M_0 = 0$ ) only the third term survives; we then see vibronic progressions in one or both polarizations, but not in the totally symmetric frequencies. The curious situation we have with the weaker  $\delta \rightarrow \delta^*$  transitions is that  $M_0 \approx m_1$  so that all three terms in the equation are of similar importance.

We therefore see more than one progression in parallel polarization with different Franck-Condon factors and one or more vibronic progressions in perpendicular polarization of intensity comparable to those in parallel polarization. Beautiful examples of this

phenomenon have recently been reported for  $[\text{Mo}_2(\text{O}_2\text{CCHNH}_3)_4]^{4+}$ ,<sup>16</sup>  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ ,<sup>17</sup>  $\text{Mo}_2[(\text{CH}_2)_2\text{P}(\text{CH}_3)_2]_4$ <sup>18</sup> and  $[\text{Mo}_2(\text{L-leucine})_4]^{4+}$ .<sup>19</sup>

Our final example concerns a  $\delta^2\delta^* \rightarrow \delta\delta^*$  transition in a bond of order 3.5 (type d).

R. A. Walton<sup>20</sup> has observed that compounds of the type  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  are spontaneously oxidized by oxygen and in further electrochemical and synthetic studies<sup>21</sup> he has shown that the product is a +1 cation, presumably with the same stoichiometry and structure. The oxidized species has a weak absorption band in the near infrared. Using a powder sample of  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]\text{PtF}_6$  provided by Walton, we have recorded the spectrum<sup>22</sup> shown in Fig 2 at 5K.

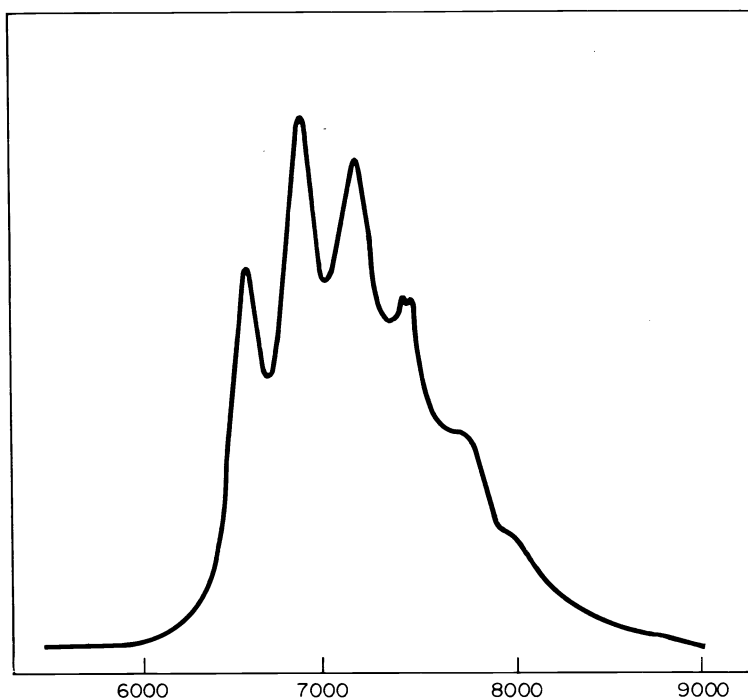


Fig. 2. The  $\delta \rightarrow \delta^*$  band at 5 K for  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^+$  recorded on a powder sample.

The vibrational spacing averages  $275 \pm 5 \text{ cm}^{-1}$ , consistent with expectation for an Re-Re stretching mode.

A complete calculation for  $\text{Re}_2\text{Cl}_4(\text{PH}_3)_4$  by the SCF-X $\alpha$ -SW method of the ground state electron configuration and the energies of the first 18 expected electronic transitions gives an excellent fit of the entire spectrum of  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^+$  from 4000 to 30,000  $\text{cm}^{-1}$ . In particular, for the  $\delta \rightarrow \delta^*$  ( ${}^2\text{B}_{1u} \leftarrow {}^2\text{B}_{2g}$ ) transition we obtained an energy of 5,650  $\text{cm}^{-1}$ , which compares very well with the 0-0 transition in Fig. 2 at 6,653  $\text{cm}^{-1}$ .

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