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Reactions of Coordinated Molecules. VII. A Theoretical Model for Intramolecular Bonding Within Metallo-β-diketonate Complexes

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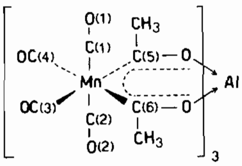
The observed tilting of the two trans *axial carbon monoxide ligands in complexes of the type* cis-$[(OC)_4M(CH_3CO)_2]_nM'$, *where* M *is Mn or Re and* M' *is Al or hydrogen, toward the metallo-β-diketonate side of the complex is interpreted as an intramolecular bonding interaction. This distortion results from the interaction of the filled and empty pi-molecular orbitals of the two carbonyl ligands with the filled and empty molecular orbitals of the pi-electron system of the metallo-β-diketonate ligand.*

Introduction

We reported the preparation and molecular structure of the first example of a coordination complex containing a metallo-acetylacetonate ligand, **1** [1].



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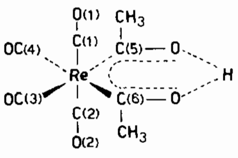

2

This complex is essentially isostructural to $Al(acac)_3$ and the coordination geometry about the manganese atoms is not unusual: the average value of the twelve Mn–C≡O angles of 175.6 (1.4)° indicates a linear coordination of the carbonyl ligands; and, the average value of the twelve Mn–C (1 to 4) bond distances of 1.842 (0.014) Å represents a normal Mn–CO bond length. However, the two "axial" CO ligands [C(1)O(1) and C(2)O(2)] on each manganese atom are leaning toward the Al ion so that the average value of the three C(1)–Mn–C(2) angles is only 166.3 (0.8)° while the average value of the six other angles which define the remaining two axes of the coordination octahedra [C(3)–Mn–C(5) and C(4)–Mn–C(6)] is 175.4 (0.8)°. This tilting of the six axial carbonyl ligands toward the Al ion by an additional 9.1° was assigned initially to a "long range Lewis acid–base interaction" between the carbonyl groups and the Al(III) ion.

Our recent report of the synthesis and molecular structure of the first enol tautomer of a metallo-acetylacetone molecule, **2**, has lead us to re-examine this interpretation [2]. The average values of the four Re–C≡O angles [177.1 (1.9)°] and of the four Re–C (1 to 4) bond distances [1.983 (0.023) Å] indicate normal bonding of the terminal carbonyl ligands to the Re atom. The *unexpected* feature is that the two axial carbonyl ligands are leaning toward the enol proton giving a C(1)–Re–C(2) angle of 170.6° which is nearly 8° more bent than the other two coordination axes [C(3)–Re–C(5) and C(4)–Re–C(6)] which are both 178.3°. This result is surprising since it is very unlikely that the enol proton could affect such a distortion by the above mechanism.

Several other explanations must be considered. Intermolecular packing forces are exclude since; (1) it seems rather unusual that two such different complexes should exhibit the same effect, (2) the distortion of the six axial CO ligands in **1** exhibits essentially D_3 symmetry whereas the crystallographic site symmetry of the molecule is only C_2 and, (3) in complex **2**, even though O(2) is involved in a very weak bifurcated hydrogen bond [3] with the enol proton (being 3.30 Å and 3.09 Å from the two acyl oxygen atoms of the adjacent molecule), the nearest intermolecular contact with O(1) is greater than 3.5 Å. Unequal strengths of the M–CO (axial) π bonds would lead to a bending of the M–C≡O angle rather than of the C(1)–M–C(2) angle. Also, a unique hybridization at the metal atom is another possibility although it seems highly coincidental that the eight such distortions observed in **1** and **2** should all be directed toward the same side of the molecule. Another explanation for a similar distortion was proposed recently by Hoffmann, Howell and Rossi [4]. The distortion of complexes of the type *cis*-A_2MB_4 from octahedral geometry toward the bicapped tetrahedron *via* σ-electronic effects presumably works well only where the capping ligands, A, are very strong σ-donors, such as with the hydride ligand. We propose that a pi-bonding interaction may cause such a distortion providing suitable orbital overlap is permitted by symmetry. It is the purpose of this paper to demonstrate that this type of interaction is possible for metallo-β-diketonate complexes.

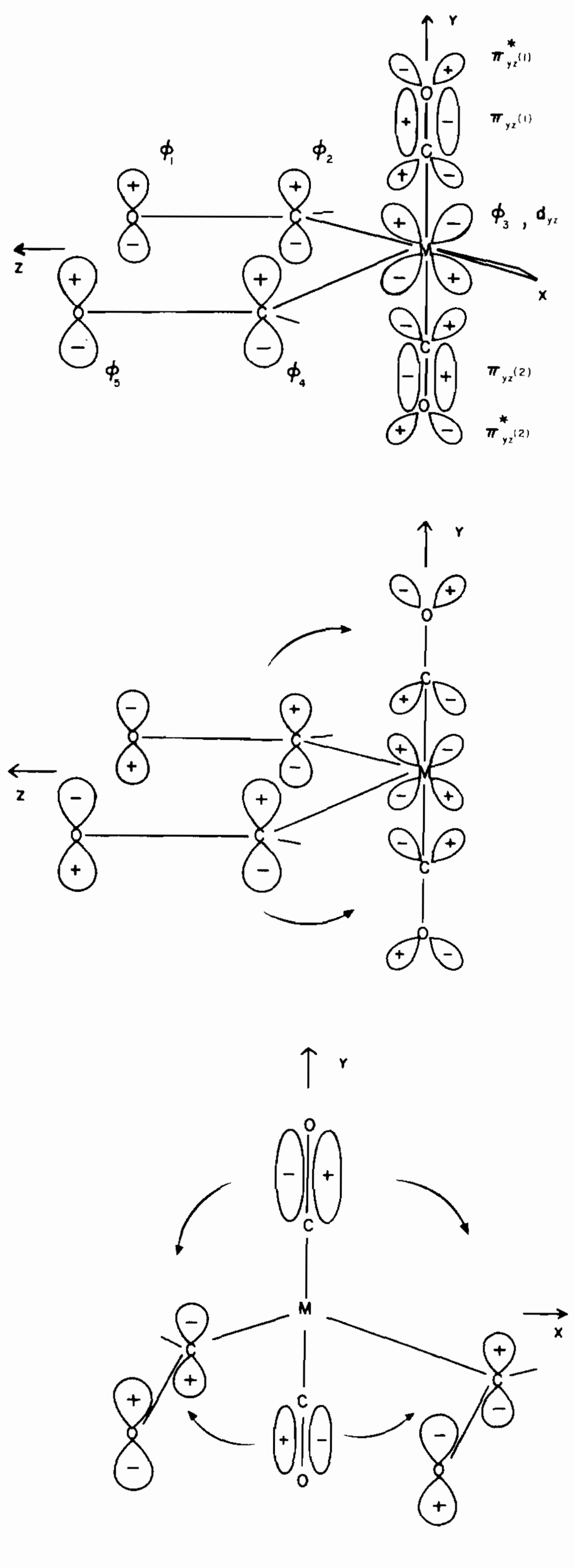

Figure 1. Top: the defined coordinate system and orbitals, the π_{xy} and π^*_{xy} orbitals are omitted for clarity. Middle: the ψ_3 to π^* overlap. Bottom: the π to ψ_4 overlap.

Results and Discussion

The explanation we prefer is that the π and π^* molecular orbitals of the two axial carbonyl ligands interact in a synergistic manner with the filled and empty molecular orbitals of the metallo-β-diketonate ligand π system. This affords a much shorter range bonding interaction than the original explanation. In complex **1**, the Al–C(1) and Al–O(1) distances are 4.12 Å and 4.46 Å, respectively, which represents a very long distance for any interaction significant enough to cause the observed leaning of the two axial carbonyl ligands. If the π-electron system of these carbonyls were interacting with the π-electron system of the metallo-acetylacetonate ligand, then the C(1)–C(5) distance may approximate the distance between the closest interacting centers. This distance is only 2.63 Å for complex **1** and 2.77 Å for complex **2**. We wish to establish that this type of bonding interaction is permitted by symmetry, and that a qualitative and pictorial description of this intramolecular bonding is visualized readily *via* a synergistic mechanism.

The top diagram on Figure 1 defines the coordinate system and the orbitals to be considered. The second set of carbonyl π orbitals, π_{xy} and π^*_{xy}, are not shown for clarity. The symmetry is C_{2v} and the σ'_V plane is defined as the molecular plane, xz. The metallo–acac π system is composed of the atomic 2p orbitals (ϕ_1, ϕ_2, ϕ_4 and ϕ_5) and the metal d_{yz} orbital (ϕ_3). As for acac itself, this is a 6-electron π system. The relevant symmetry orbitals are:

$\psi_5 = \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5$	B_1	
$\psi_4 = \phi_1 - \phi_2 + \phi_4 - \phi_5$	A_2	
$\psi_3 = \phi_1 - \phi_2 - \phi_3 - \phi_4 + \phi_5$	B_1	↑↓
$\psi_2 = \phi_1 + \phi_2 - \phi_4 - \phi_5$	A_2	↑↓
$\psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$	B_1	↑↓
$\pi^*_{yz}(1) + \pi^*_{yz}(2)$	B_1	
$\pi_{yz}(1) + \pi_{yz}(2)$	B_1	↑↓
$\pi^*_{xy}(1) + \pi^*_{xy}(2)$	A_2	
$\pi_{xy}(1) + \pi_{xy}(2)$	A_2	↑↓

A second metal atomic d orbital, $d_{xy}(A_2)$, can interact with the metallo–acac π system. This orbital is assumed to be filled since both **1** and **2** are formally octahedral, d^6 complexes. It should be stressed that no attempt is made to evaluate the orbital coefficients.

Figure 2 shows a *schematic* orbital energy-level diagram of the bonding proposed when M is manganese. At the left, the Mn $3d_{xy}$ orbital is incorporated into the metallo–acac π system. At the right, the MO's of this π system are interacted with the π and π^* orbitals of the two axial carbonyl ligands. The relative energies of the orbitals were estimated from data available for acac ion [5] and for manganese carbonyl complexes [6].

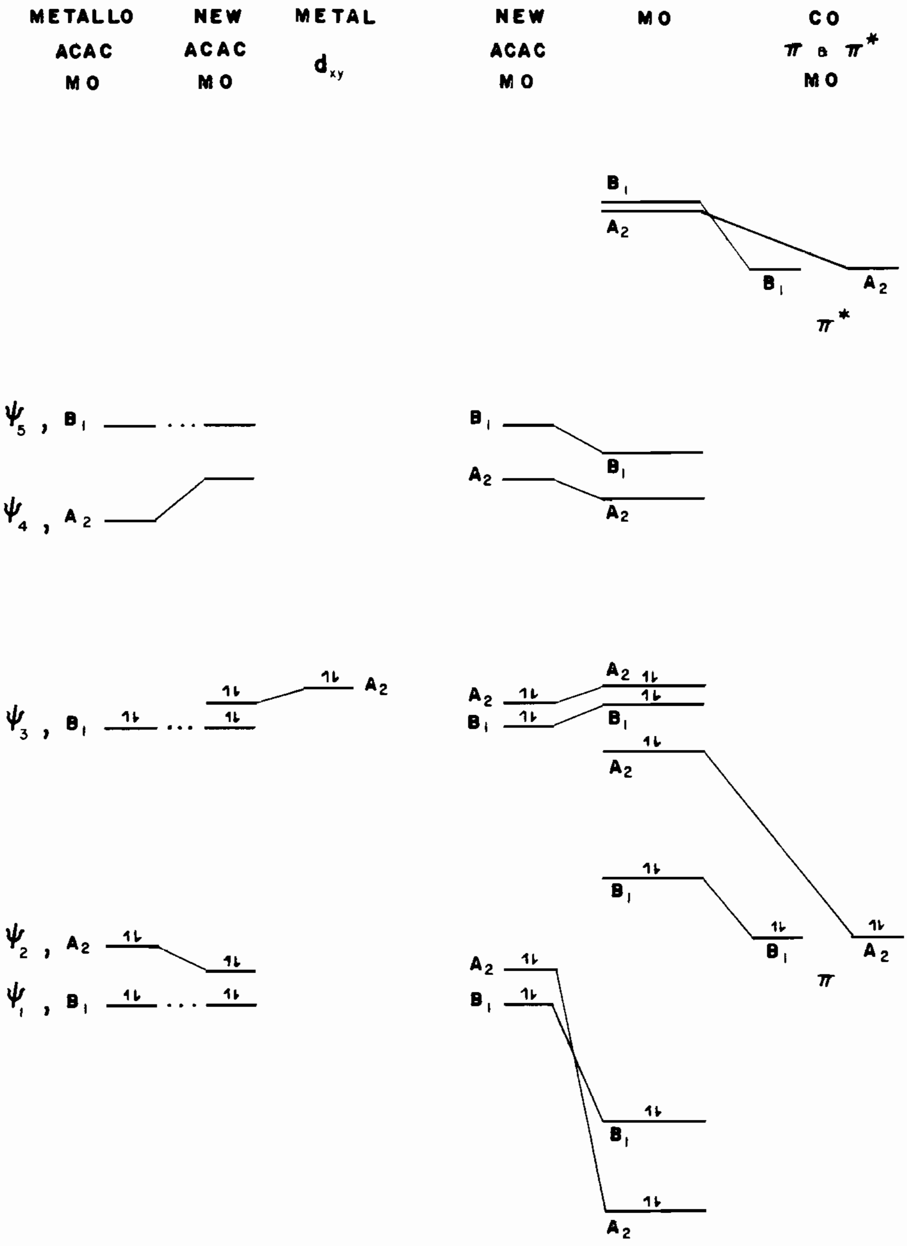

Figure 2. A schematic orbital energy-level diagram of interacting the metallo–acac π-electron system with a Mn $3d_{xy}$ orbital and with the π and π* orbitals of the two axial carbonyl ligands.

Figure 1 also shows a pictorial representation of what may be the predominant bonding interactions leading to the observed tilting of the axial carbonyl ligands. The middle diagram depicts the flow of electron density from the highest occupied predominantly metallo–acac orbital (HOMO, ψ_3) into the empty π* orbitals of the two carbonyl ligands, while the bottom diagram depicts electron flow from the filled π orbitals of the carbonyl ligands into the lowest unoccupied metallo–acac orbital (LUMO, ψ_4). As seen from Figure 2 several other similar interactions are possible.

The quantitative verification of this bonding interaction must await a detailed MO calculation since this effect is expected to be very weak. Although we do not anticipate performing such a calculation, some interesting chemical reactivity may be predicted. For example, this may be a new way in which a ligand can both stabilize a complex and become activated intramolecularly. This realization suggests that other ligands possessing low lying filled π orbitals, such as isocyanides, may preferentially substitute in the axial positions of metallo-β-diketonate complexes, and that the axial carbonyl ligands may be more reactive, perhaps more easily reduced, than normal terminal carbonyl ligands.

Also, this type of pi-interaction might be extended to other complexes containing unsaturated metallocyclic systems where such a distortion is observed. This may account for the similar tilting of the two axial carbonyl ligands of tetracarbonyl(2-methyl-3-prop-1-ynylmaleoyl)iron [7].

Acknowledgement

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