

Theoretical Studies on Structure of Acetylacetonates of Zn(II), Cd(II) and Hg(II)

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The molecular geometry of certain acetylacetonates of d^{10} metals are investigated through quantum mechanical studies. Using *ab initio* molecular orbital (MO) computations the studies on acetylacetonates of Zn(II), Cd(II) and Hg(II) are presented. The interesting feature of the present structural analysis is that it reflect delocalization in the chelate rings.

Key Words: Acetylacetonates, Huckel Calculation *ab initio* computations, Hartree-Fock-Consistent-Field MO calculations, Neutral bond orbital analysis-molecular geometries.

INTRODUCTION

A comprehensive understanding of a chemical system requires quantitative information regarding its electronic and molecular structures, properties and reactivities.

Quantum chemical techniques provide valuable tools to study quantitatively the electronic structures and properties in molecules. The advent of fast computers and developments in computational methods help in solving electronic structural problems with reliable accuracy even for molecules of moderately large size.

Earlier quantum chemical studies on the acetylacetonates of transition metals focussed mainly on the spectral and magnetic properties using Extended Huckel calculations and semiempirical Self-Consistent-Field (SCF) Molecular Orbital methods at CNDO, INDO, ZINDO, MNDO, AM1 and X-alpha levels. Application of the quantum chemical methods to determine the molecular geometries, electronic and structural changes in the chelating unit, the nature of bonding between the metal and chelating unit *etc.* are rather limited. Burton *et al.*¹ performed *ab initio* pseudopotential calculations on palladium(II) acetylacetonate at the Restricted Hartree-Fock level and determined the molecular geometry and ionization energies. Recently, Reynolds *et al.*² studied the structure of *tris*(acetylacetonato) Ru(III) by X-ray

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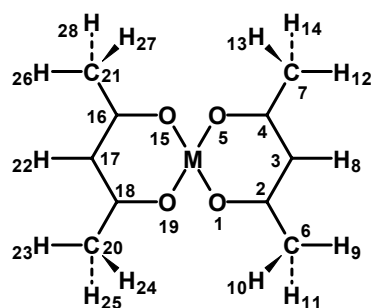
and polarized neutron diffraction and also by *ab initio* computations. Ustinov *et al.*³ obtained the equilibrium geometries in some *bis*- β -diketonates of zinc and their thio-analogues using the MNDO method and examined their electronic structures. The metal-oxygen lengths obtained in the above theoretical studies show a deviation of about 0.06 Å from the crystal structures of Pd(acac)₂⁴ and Zn(acac)₂·H₂O^{5,6}. In Ru(acac)₂, the calculated Ru-O distance deviates by 0.05 Å. These studies show that more accurate *ab initio* methods including correlation correction are necessary to get reliable molecular and electronic structures in the metal acetylacetonates.

Although β -diketonates of transition metals have been investigated extensively by different spectroscopic techniques, spectroscopic probes of those with d^{10} configuration are rare. In order to gain better understanding of the electronic structure and bonding in d^{10} systems, the *bis*-acetylacetonates of zinc, cadmium and mercury are subjected to quantum chemical analysis with a view to get the molecular geometries, the structural changes in the chelate ring responsible for electrophilic substitution in the γ -position, nature of interactions between the metal and the chelate *etc.* This paper describes the study on *bis* acetylacetonates of Zn(II), Cd(II) and Hg(II) using *ab initio* molecular orbital (MO) computations.

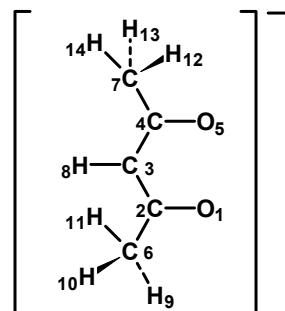
COMPUTATIONAL ASPECTS

The molecular and electronic structures in the *bis*acetylacetonato metal(II) complexes of Zn(II), Cd(II) and Hg(II) were examined by *ab initio* quantum chemical computations. The computations were performed using the GAUSSIAN 94 software⁷ in DEC PC Celebris XL 590 computer upgraded with 192 MB RAM. The molecular geometries of the complexes were initially defined for planar structure using standard structural parameters, namely, the bond lengths, bond angles and dihedral angles. They were then subjected to complete structural optimization using Berni algorithm incorporated in GAUSSIAN 94 package⁷ to yield the geometries with lowest energies. At the optimized geometries, the energetics and electronic properties involving the nature of bonding, net atomic charges, population of different atomic orbitals, *etc.* were examined. The labelling of atoms in the molecules studied are shown in structures **1** and **2**.

The present *ab initio* study explicitly treats all electrons in the atoms of acetylacetonates excepting in the metal atoms. In the case of the metal atoms effective core potentials (ECPs) are used to simulate the effect of chemically inert core electrons on the reactive valence electrons. The ECPs evaluated analytically using gaussian functions by Hay and Wadt⁸ were used in this work. It has been shown that the ECPs provide accurate results for transition metal compounds comparable to all electron *ab initio* calculation at a small fraction of the computational cost⁸.



Structure 1



Structure 2

The relativistic mass-velocity and Darwin effects on the valence electrons are incorporated in the ECPs of heavier elements with atomic number greater than 36. Thus in $\text{Cd}(\text{acac})_2$ and $\text{Hg}(\text{acac})_2$, the relativistic ECPs on the metal centres were used in computation. In addition, the small-core approximation denoted by the keyword LANL2 is used in this study. Accordingly the calculations take into account explicitly the electrons in the following orbitals including the sub-valence orbitals.

Zn : 3s, 3p, 3d, 4s and 4p

Cd : 4s, 4p, 4d, 5s and 5p

Hg : 5s, 5p, 5d, 6s and 6p

For the elements in the first row of the periodic table, all electrons are taken into account in the basis set. Both the minimal basis set denoted by the keyword LANL2MB and double zeta basis set denoted by LANL2DZ were used in the present calculations. The LANL2MB calculations use STO-3G basis on first row atoms and the outer orbitals of the metal centre. Hay and Wadt's ECPs are used for describing the "small core" of the metal atoms. The LANL2DZ calculations invoke Dunning/Huzinaga full double-zeta basis on first row atoms. "Small core" potentials are used to describe the inner electrons of the metal and the valence metal orbitals are described by Dunning/Huzinaga double-zeta basis set. It has been found earlier that LANL2DZ level calculations yield reliable results on transition metal compounds⁹.

The Hartree-Fock Self-Consistent-Field MO calculations were carried out on the metal acetylacetonates at the LANL2MB and LANL2DZ levels. The molecular geometries were obtained by energy minimization technique. The Hartree-Fock calculation does not take into account the electron correlation effects as it is based on the relatively inflexible single determinantal wave function. In the present study, electron correlation is incorporated by Møller-Plesset second order perturbation theory (MP2) and also by Becke's three parameter hybrid density functionals (B3LYP). Structural optimization

is also performed with the MP2 and B3LYP techniques at the LANL2DZ level.

At the optimized geometries obtained by the different levels of computation, the electronic structures of the complexes were analyzed. Mulliken population analysis¹⁰ (MPA) was performed to characterize the net charges on the atomic centres. Since atomic charge is not a quantum chemical observable, the MPA charges are rather arbitrary and do not always yield reliable results in systems, which have significant ionic character. In addition, they are highly sensitive to the basis set employed⁹. Hence, natural population analysis (NPA)¹¹⁻¹³ was also carried out in terms of localized electron pair bonding units to get reliable estimates of net charges on atoms.

To understand the nature of bonding between the metal and chelating moiety, the natural bond orbital (NBO) analysis was performed and the covalent bond orders between the atoms in the complexes were calculated. The natural bond orbital (NBO) program¹⁴, incorporated in the GAUSSIAN 94 package was used to do natural population and natural bond orbital analyses. The extent of covalent bonding is calculated using Wiberg's bond orders in terms of natural atomic orbital basis set. The Wiberg bond order is the sum of squares of off-diagonal density matrix elements between atoms.

RESULTS AND DISCUSSION

Molecular geometries

Acetylacetonate anion: The geometry of acetylacetonate anion is obtained in the present study by complete structural optimization in order to understand the structural changes accompanied by complex formation. Since no experimental structure is available for this species, the geometry at B3LYP/6-31G* level is also examined by structural optimization in addition to the LANL2MB, LANL2DZ, B3LYP/LANL2DZ and MP2/LANL2DZ levels studied in the complexes. It may be mentioned that the structural optimization at B3LYP/6-31G* level, in general, yields structure very close to the experimental geometry⁹.

The geometries obtained at the various levels of calculation are listed in Table-1 (see structure 2 of numbering). The species is found to possess C_{2v} symmetry at all levels of calculation. Though the bond lengths are sensitive change. The inclusion of correlation correction at the B3LYP/LANL2DZ and MP2/LANL2DZ levels leads to carbonyl C=O bond lengths 1.282 and 1.302 Å, respectively. These values reflect that the carbon-oxygen bond is longer than the typical double bond length of 1.22 Å in the carbonyl group and shorter than the standard C-O single bond of 1.43 Å. However the elongation of C-O bond is less marked in the LANL2MB, LANL2DZ and B3LYP/6-31G* calculations. The C₂-C₃ lengths at the different levels are in the range 1.422-1.446 Å and are closer to the delocalized aromatic bonds

of *ca.* 1.4 Å. Comparison of the structures at different levels shows that the B3LYP/LANL2DZ optimized geometry is very similar to the B3LYP/6-31G* structure, giving a clue that the geometry in the complexes obtained at the B3LYP/LANL2DZ level should be reliable.

Acetylacetonates of Zn(II), Cd(II) and Hg(II): Optimized geometries of acetylacetonates of zinc, cadmium and mercury are presented in the Tables 1-4, respectively. The theoretical geometries are also compared with the available experimental geometries of related zinc and cadmium chelates^{5,6,15,16}. Bisacetylacetonate of mercury is unknown experimentally¹⁷ although monodentate complexes such as *bis*(dipivaloyl)mercury¹⁸ and 2,2,6,6-tetramethyl-3,5-heptanedione¹⁹ are characterized.

Complete structural optimization leads to D_{2h} symmetry for all the three metal chelates. Analysis of the structures given in Tables 1-4 shows that the chelating ligand fragment possesses nearly identical bond lengths in the three complexes for a given method of calculation. Thus the carbon-oxygen bond lengths are 1.308, 1.308 and 1.309 Å respectively in the acetylacetonates of Zn, Cd and Hg according to B3LYP/LANL2DZ calculations. The corresponding chelate ring bond lengths for C₂-C₃ are respectively 1.417, 1.418 and 1.417 Å. The above C-O and C-C bond lengths are intermediate between those of the standard single and double bond lengths and characterize delocalization in the chelate ring. The O-C-C bond angle of the chelating unit increases in the different complexes as the atomic number of the metal increases. The B3LYP/LANL2DZ calculations yield the values 124.1, 125.0 and 129.9° respectively for O₁-C₂-C₃ in the Zn, Cd and Hg complexes. Even the ring angle C₂-C₃-C₄ shows a similar trend. As compared to the geometry of acetylacetonate anion, the C₂-O₁ bond in the complex is elongated by about 0.02 Å leading to bond lengths in the range 1.28 to 1.33 Å at the various levels of computation. The carbon-carbon bonds C₂-C₃ and C₂-C₆ are shortened in the complexes compared to the values in the free ligand.

The structural parameters in the ligand fragments in the acetylacetonates of Zn, Cd and Hg are found to be similar to those observed in a number of *bis*acetylacetonates of transition metals^{4-6,17,20}. The observed O-C bond lengths in the chelate vary in the range 1.27-1.31 Å. The C-C bond length in the ring vary from 1.38-1.42 Å while the C-C bond length outside the ring, *i.e.*, C₂-C₆ is found to be a single bond having bond length in the range 1.48 to 1.52 Å. A comparison between these crystal structures and the present theoretical results in Tables 2-4 reveals that the geometries of the ligand in the *d*¹⁰ zinc, cadmium and mercury *bis*acetylacetonates remain very similar to those of the transition metals. This leads to the inference that the ligand fragment in the different metal acetylacetonates retain similar electronic structure irrespective of the electronic configuration of the central

TABLE-1
OPTIMIZED GEOMETRY OF ACETYLACETONATE ANION

Parameters	LANL2MB	LAN2LDZ	B3LYP/ LANL2DZ	MP2/ LANL2DZ	B3LYP/ 6-31G
Bond length (Å)					
O ₁ -C ₂	1.244	1.258	1.282	1.302	1.245
C ₂ -C ₃	1.425	1.422	1.432	1.446	1.424
C ₂ -C ₆	1.578	1.537	1.554	1.571	1.554
C ₃ -C ₈	1.072	1.074	1.090	1.097	1.089
C ₆ -C ₉	1.084	1.083	1.098	1.106	1.098
C ₆ -C ₁₀	1.088	1.086	1.100	1.108	1.099
C ₆ -C ₁₁	1.088	1.086	1.100	1.108	1.099
Bond angle (°)					
O ₁ -C ₂ -C ₃	128.8	128.9	128.6	128.6	128.9
C ₂ -C ₃ -C ₄	124.1	128.4	128.7	128.4	127.4
O ₁ -C ₂ -C ₆	116.5	115.4	115.8	116.1	115.7
C ₂ -C ₃ -H ₈	118.0	115.8	115.7	115.8	116.3
C ₂ -C ₆ -H ₉	112.3	113.2	113.3	112.6	114.5
C ₂ -C ₆ -H ₁₀	110.5	108.8	108.9	109.0	109.1
C ₂ -C ₆ -H ₁₁	110.5	108.8	108.9	109.0	109.1

TABLE-2
OPTIMIZED GEOMETRY OF *BIS*(ACETYLACETONATO) Zn(II) [Ref. 5]

Parameters	HF/ LANL2MB	HF/ LANL2DZ	B3LYP/ LANL2DZ	MP2/ LANL2DZ	Expt.
Bond length (Å)					
Zn-O ₁	1.927	1.992	2.000	2.010	2.02
O ₁ -C ₂	1.276	1.285	1.308	1.326	1.29
C ₂ -C ₃	1.403	1.406	1.417	1.429	1.40
C ₂ -C ₆	1.544	1.507	1.516	1.532	1.51
C ₃ -H ₈	1.073	1.069	1.083	1.091	-
C ₆ -H ₉	1.089	1.080	1.094	1.102	-
C ₆ -H ₁₀	1.087	1.083	1.097	1.104	-
C ₆ -H ₁₁	1.087	1.083	1.097	1.104	-
Bond angles (°)					
Zn-O ₁ -C ₂	131.8	132.4	130.3	129.4	127.0
O ₁ -C ₂ -C ₃	124.4	123.8	124.1	124.3	124.0
C ₂ -C ₃ -C ₄	120.6	122.6	123.7	124.0	126.0
O ₁ -C ₂ -C ₆	115.9	115.8	115.6	115.4	117.0
O ₁ -Zn-O ₅	86.8	85.1	87.5	88.7	88.0
O ₅ -Zn-O ₁₅	93.2	94.9	92.5	91.3	-
C ₂ -C ₃ -H ₈	119.7	118.7	118.2	118.0	-
C ₂ -H ₆ -H ₉	111.0	112.5	112.3	111.7	-
C ₂ -C ₆ -H ₁₀	109.7	109.0	109.3	109.3	-
C ₂ -C ₆ -H ₁₁	109.7	109.0	109.3	109.3	-

TABLE-3
OPTIMIZED GEOMETRY OF *BIS*(ACETYLACETONATO) Cd(II) [Ref. 15]

Parameters	HF/	HF/	B3LYP/	MP2/	Expt.
	LANL2MB	LANL2DZ	LANL2DZ	LANL2DZ	
Bond length (Å)					
Cd-O ₁	2.088	2.169	2.184	2.180	2.23
O ₁ -C ₂	1.275	1.284	1.308	1.326	1.28
C ₂ -C ₃	1.404	1.407	1.418	1.431	1.39
C ₂ -C ₆	1.546	1.510	1.519	1.535	1.53
C ₃ -H ₈	1.073	1.069	1.084	1.091	-
C ₆ -H ₉	1.084	1.080	1.094	1.102	-
C ₆ -H ₁₀	1.087	1.083	1.097	1.104	-
C ₆ -H ₁₁	1.087	1.083	1.097	1.104	-
Bond angles (°)					
Cd-O ₁ -C ₂	131.8	133.4	131.0	129.8	128.6
O ₁ -C ₂ -C ₃	125.6	124.6	125.0	125.2	126.2
C ₂ -C ₃ -C ₄	122.4	124.1	125.6	125.9	127.8
O ₁ -C ₂ -C ₆	115.5	115.6	115.3	115.9	115.2
O ₁ -Cd-O ₅	82.6	79.9	82.4	84.2	80.4
O ₅ -Cd-O ₁₅	97.2	100.1	97.6	95.8	-
C ₂ -C ₆ -H ₈	118.8	117.9	117.2	117.1	-
C ₂ -H ₆ -H ₉	111.0	112.5	112.4	111.8	-
C ₂ -C ₆ -H ₁₀	109.7	109.0	109.4	109.3	-
C ₂ -C ₆ -H ₁₁	109.7	109.0	109.4	109.3	-

TABLE-4
OPTIMIZED GEOMETRY OF *BIS*(ACETYLACETONATO) Hg(II)

Parameters	HF/	HF/	B3LMP/	MP2/
	LANL2MB	LANL2DZ	LANL2DZ	LANL2DZ
Bond length (Å)				
Hg-O ₁	2.179	2.249	2.283	2.261
O ₁ -C ₂	1.278	1.284	1.309	1.327
C ₂ -C ₃	1.404	1.407	1.417	1.430
C ₂ -C ₆	1.547	1.511	1.520	1.536
C ₃ -H ₈	1.073	1.069	1.084	1.091
C ₆ -H ₉	1.084	1.080	1.094	1.102
C ₆ -H ₁₀	1.087	1.083	1.097	1.04
C ₆ -H ₁₁	1.087	1.083	1.097	1.04
Bond angle (°)				
Hg-O ₁ -C ₂	130.7	133.3	129.9	128.5
O ₁ -C ₂ -C ₃	126.7	125.1	126.0	126.1
C ₂ -C ₃ -C ₄	123.6	124.9	127.0	127.2
O ₁ -C ₂ -C ₆	114.8	115.3	114.7	114.5
O ₁ -Hg-O ₅	81.7	78.1	81.1	83.5
O ₅ -Hg-O ₁₅	98.3	101.9	98.9	96.5
C ₂ -C ₆ -H ₈	118.2	117.5	116.5	116.4
C ₂ -H ₆ -H ₉	111.0	112.5	112.4	111.8
C ₂ -C ₆ -H ₁₀	109.7	109.0	109.3	109.3
C ₂ -C ₆ -H ₁₁	109.7	109.0	109.3	109.3

metal ion. This is evidenced by the property exhibited by all these complexes towards electrophilic substitution at the C₃ (γ)-position.

Major changes in the structures of the complexes are centered around the metal atoms. The metal-oxygen distance is found to increase in the order.



as expected from the atomic radii of the metals concerned. In zinc acetylacetonate, the various methods yield the Zn-O bond lengths in the range 1.927 to 2.010 Å. It may be mentioned that the mean Zn-O bond length of 2.02 Å in the crystal structure of Zn(acac)₂·H₂O^{5,6} is close to the predicted values of 2.000 and 2.010 Å in Zn(acac)₂, by B3LYP/LANL2DZ and MP2/LANL2DZ calculations. The present theoretical Zn-O bond lengths show better agreement with the mean value of 2.03 Å observed by Lippert and Truter¹⁴. The theoretical Zn-O bond lengths obtained by the post-Hartree-Fock methods, particularly the B3LYP/LANL2DZ method, deviate from the experimental values by less than 0.02 Å. Thus the present *ab initio* calculations with correlation correction are more suitable to study the metal acetylacetonates than those reported earlier^{3,8} which showed a deviation of 0.05-0.06 Å in the metal-oxygen bond lengths. Comparison of the theoretical results at different levels shows that the minimal basis set LANLZMB calculation deviate significantly from the experimental structure, particularly in the M-O bond lengths and is not suitable to study the metal acetylacetonates. Cd-O bond length is predicted to be in the range of 2.088-2.180 Å by the present investigation while the experimental length in the crystal of catena-di-m-acetonato cadmium(II)¹⁵ is longer with a value of 2.23 Å. The Hg-O bond length is found in the range 2.179-2.283 Å. The analysis of bond angles around the metal centre shows that the angle O₁-M-O₅ decreases in the order.



The results at the different levels for Zn(acac)₂ show that the above angle is in the range 85.1 to 88.7° which is in good agreement with the experimental value of 88.0° in Zn(acac)₂·H₂O. In the cadmium complex the above angle is in the range 79.9 to 82.6° while in Hg(acac)₂ it is 78.1-83.5°. Analysis of the different theoretical structures for zinc and cadmium complexes show reasonable agreement with the available experimental structures. The overall agreement is better with the available B3LYP/LANL2DZ calculations even though the C-O and C-C ring bonds deviate from the experimental value by about 0.03 Å. An interesting feature of the present structural analysis is that it reflect delocalization in the chelate rings.

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