The nature of the metal-ligand chemical bond and the electronic structure of Be, Mg, and Zn acetylacetonates and hetero- and β-substituted analogs

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Abstract. The effect of valence molecular orbitals on the nature of the chemical bond of the p-metal ion with chelate ligands in Be(acac)₂, Mg(acac)₂ and zinc Zn(acac)₂ was studied by theoretical methods. The effect of the substitution of atoms and functional groups in the ligands on the chemical bond was estimated. For beryllium, the bond is almost completely covalent with an insignificant ion component: the Coulomb potentials for complexes with beryllium are 1.37 and 1.08 eV for acetylacetonate and hexafluoroacetylacetonate, respectively. For Mg and Zn β-diketonates with a metal-oxygen bond, the calculations showed the essentially ionic nature of binding: about 8 eV for magnesium compounds and 12.3 and 11.3 eV for zinc. However, the O→S substitution significantly reduces the metal-ligand binding ionicity: to 2.8 and 0.9 eV for the thio- and dithio-substitution, respectively. The covalent bond of a metal with ligands is due to the overlapping of only some MOs with s- and p-orbitals of the metal. The covalence of the M–O bond in acetylacetonates decreases in the series Be→Mg→Zn due to an increase in the ionic radius of the metal, leading to two consequences.

1. Introduction

β-diketones are known for their ability to trap metal ions, forming the organometallic complexes. Such complexes have wide applicability: the f-elements compounds with luminescent properties can be used to create lighting devices and as luminescent probes and labels in biomedicine; transition d-metal complexes can be used as contrast agents for magnetic resonance therapy, to produce controlled molecular magnets. β-diketonates can be used to deposit thin metal films, to produce catalysts, and as precursors for the synthesis of new compounds, including polymers [1-5].

Beryllium compounds are used in industry, and beryllium acetylacetonate Be(acac)₂ is widely used to determine traces of beryllium ions in biological samples. Magnesium Mg(acac)₂ and zinc Zn(acac)₂ acetylacetonates are used to make MgO and ZnO films, respectively.

The nature of the chemical bond is defined by the electronic structure of the molecule and can be described in the orbital representation. An effective experimental method for studying the electronic structure is photoelectron spectroscopy, which makes it possible to obtain the binding energy of core and valence electrons [6-11]. The upper valence electron levels in the range of single-electron ionization and low density of states have been reliably determined experimentally [12-14]. However, deeper valence levels can be interpreted only with the help of quantum chemical modeling.
Gas-phase ultraviolet photoelectron spectra with a HeI radiation source of a beryllium (II) bis-acetylacetonate complex and a beryllium complex with ligands in which methyl groups are replaced by CF₃ groups were obtained by Evans and Co. in 1972 [12]. In the low-energy region, three intense bands are present in the spectra, which, in the approximation of the theory of molecular orbitals using the Koopmans approximation, were attributed by the authors to three MOs: π3, n- and n+. Based on the assignment of the Evans bands, the authors [13, 14] interpreted the spectra of magnesium and zinc bis-β-diketonates.

The effects of O→S and CH₃→CF₃ substitutions on the electronic structure of zinc β-diketonates were studied in [15–16] using a combination of quantum-chemical modeling and ultraviolet photoelectron spectroscopy.

The goal of this study is to theoretically determine the effect of valence molecular orbitals on the nature of the chemical bond of the p-metal ion with chelate ligands and to estimate the effect of the substitution of atoms and functional groups in the ligands on the chemical bond.

2. Methods

A series of calculations were performed using the B3LYP/Def2-TZVPP density functional theory method, as an easy-to-use and popular method that gives results of an acceptable quality.

The calculation results are compared with the literature experimental data on the structure of molecules (gas-phase electron diffraction) and on the electronic structure (UV PE spectra with a HeI radiation source).

3. Results and Discussion

3.1. Geometry

According to experimental data obtained by gas phase electron diffraction [17–19], the geometry of Be(acac)₂, Mg(acac)₂ and Zn(acac)₂ complexes in the ground state has D₂d symmetry. The assumptions about the spatial structure of ligands, made in [17, 19], are confirmed by our calculations. The simulation results and the literature experimental geometrical parameters are presented in Table 1. The designations of the ligand atoms are shown in Figure 1.

In general, experimental geometry is satisfactorily reproduced by modeling. The optimal orientation of methyl groups in ligands according to calculated data is shown in Figure 1 and corresponds to the literature data for Mg(acac)₂ [18]. The difference between the total energy of Mg(acac)₂ with the optimal position of the methyl groups and the total energy of Mg(acac)₂ with one and two methyl groups turned 180 degrees is 0.08 eV and 0.16 eV, respectively. The energy of rotational vibrations of methyl groups is approximately 0.01-0.02 eV (99-174 cm⁻¹) according to calculated data.

Figure 1. Metal acetylacetonate structure and ligand atom designations
### Table 1 - Theoretical and experimental geometrical parameters of bis-acetylacetonates of beryllium (II), magnesium (II) and zinc (II).

| Bond length, Å | Be   | Mg   | Zn   | Be [8] | Mg [9] | Zn [10] |
|----------------|------|------|------|--------|--------|--------|
| M-O            | 1,624| 1,950| 1,963| 1,615(6)| 1,966(4)| 1,942(6)|
| O-Cβ           | 1,273| 1,272| 1,273| 1,270(4)| 1,279(3)| 1,261(9)|
| Cβ-Cγ          | 1,400| 1,405| 1,404| 1,397(4)| 1,408(3)| 1,418(21)|
| Cβ-Cγ          | 1,502| 1,507| 1,508| 1,499(5)| 1,534(4)| 1,516(30)|

### 3.2. Charges

The Mulliken’s effective atomic charges of the complexes are presented in Table 2. The atomic charges can be used to estimate the energy of the ionic bond of a metal with ligands through the potential energy of the Coulomb interaction. The value of $E_q$ is equal to the sum of the potential Coulomb energies affecting the metal ion from the side of O, Cβ, Cγ, Hγ atoms and methyl groups as the point charge of each ligand.

The Be→Mg→Zn substitution in the series of acetylacetonates shows an increase in the polarity of the M–O bonds due to an increase in the donor capacity of the heavier metal. A small charge on beryllium leads to a low value of $E_q$ (-1.37 eV), which is associated with a lower donor ability of the atom compared with other metals considered.

### Table 2 - Mulliken’s effective atomic charges of Be, Mg, Zn acetylacetonates. $E_q$(eV) is the potential energy of the Coulomb interaction of a metal ion with ligand atoms.

| Atom | Be(acac)₂ | Mg(acac)₂ | Zn(acac)₂ |
|------|-----------|-----------|-----------|
| M    | 0.263     | 0.892     | 1.172     |
| O    | -0.228    | -0.417    | -0.445    |
| Cβ   | 0.146     | 0.221     | 0.179     |
| Cγ   | -0.253    | -0.319    | -0.303    |
| Hγ   | 0.136     | 0.126     | 0.129     |
| CH₃  | 0.074     | 0.069     | 0.060     |
| $E_q$| -1.37     | -7.97     | -12.32    |

### 3.3. Orbital analysis

Analysis of the contributions of AOs to MOs allows us to estimate which MOs are responsible for the covalent binding of a metal ion to ligands. The change in the MO energy when the bonds are stretched (in this case, increasing the distance between the ligands and the metal ion), makes it possible to determine the nature of the binding of the orbitals (binding, antibonding character) and to estimate the energy of the influence of the orbitals mixing.

According to Mulliken’s populations, the upper valence orbitals π₃, n, π₁ (e symmetry), n₁ (a₁ and b₂ symmetries), π₂ (b₁ symmetry), and MO O2s, σ (CO), σ (a₁ symmetry) from the deeper valence region are occupied molecular orbitals participating in covalent bonding. They have the most noticeable contribution of the metal AO (Fig. 2). The energies and compositions of these molecular orbitals for the Be(acac)₂, Mg(acac)₂, Zn(acac)₂ complexes are in Table 3.
Figure 2. Some molecular orbitals of Mg(acac)2, characteristic of all the considered $D_{2d}$ symmetry complexes

Under substitution in the series Be→Mg→Zn, the n+ and π2 MOs have the most significant change in the transition from Be to Mg. According to the simulation of ligands without metal ion, the proximity of the ligands in Be(acac)2 causes strong anti-binding overlapping of oxygen AOs in n and π-type orbitals, and the largest one in n+ (8b2) orbitals. The binding overlap with the 2p orbital of beryllium leads to a stabilization of the n+ (8b2) orbital by 0.54 eV, due to which the order of the n+ (8b2) and n- (8a1) orbitals is inverted in the Be(acac)2 complex.

Increasing the distance between the ligands in complexes of Mg and Zn leads to stabilization of the n+ (8b2) ligand orbitals by 0.25-0.30 eV; and n-type orbitals become ligand-ligand binding. Due to changes in the orbital energies, n-type MOs are mixed with the asymmetric p-orbital wave function of the metal, and the metal-ligand interaction becomes anti-binding for n-type orbitals in the Mg(acac)2 and Zn(acac)2 complexes.

Table 3 - Energy of valence molecular orbitals (eV), Mulliken’s AOs contributions to MOs (%) and estimated metal-ligand covalent binding energy for MOs $E_{cov}$ (eV) of Be(acac)2, Mg(acac)2 and Zn(acac)2 complexes. A negative $E_{cov}$ value means binding, a positive - anti-binding.

| MO          | $\epsilon_r$, eV | Ir.Rep. | Sym. | Be / 4O / 4Cp / 2(Cp+H) / 4CH3 | $E_{cov}$, eV |
|-------------|------------------|---------|------|-------------------------------|--------------|
| π3          | -6,45            | 10e     | $\pi_1$ | 1 / 33 / 14 / 49 / 3          | -0,11        |
| n-          | -7,43            | 9e      | n-   | 4 / 63 / 12 / 8 / 13          | -0,02        |
| n-          | -8,68            | 8a1     | n-   | 4 / 67 / 7 / 13 / 9           | +0,01        |
| n-          | -8,84            | 8b2     | n-   | 9 / 59 / 11 / 9 / 12          | -0,54        |
| n+          | -9,33            | 2a2     | $\pi_2$ | 0 / 60 / 18 / 0 / 22          | 0            |
| n+          | -9,79            | 2b1     | $\pi_2$ | 2 / 57 / 13 / 0 / 28          | -0,46        |
| n-          | -10,13           | 8e      | $\pi_1$ | 1 / 34 / 13 / 5 / 47          | -0,04        |
| n-          | -11,39           | 6a1     | $\sigma$ | 3 / 14 / 23 / 33 / 27        | -0,20        |
| n-          | -15,33           | 4a1     | $\sigma$(CO) | 7 / 51 / 19 / 8 / 15    | -1,05        |
| n-          | -28,63           | 1a1     | O2s  | 1 / 72 / 23 / 2 / 2           | -0,21        |

Be(acac)2

Mg(acac)2

Zn(acac)2
The different nature of molecular orbitals allows us to estimate the covalent binding energy \( E_{\text{cov}} \) for MOs in various ways. For the \( O2s \) (1\( a_1 \), \( \sigma \) (CO) (4\( a_1 \)), \( \sigma \) (6\( a_1 \)) and \( \pi \) (2\( b_1 \)) orbitals, the covalently bonding MOs can be used to take the difference in the energies of \( \epsilon_i - \epsilon_j \) molecular orbitals of the same nature, the \( i\)-th of which is the orbital with the binding (anti-binding) contribution of the metal, \( j\)-th - orbital without the contribution of the metal or with non-binding contribution. In general, pairs of such orbitals degenerate in energy in the absence of a metal contribution. In particular, for the \( \pi \) (2\( b_1 \)) \( i\)-th orbital, the pair is \( \pi \) (2\( a_2 \)), and the covalent bonding energy for them is \(-0.14\) eV (the “-” sign indicates a decrease in the total energy of the system, that is, the binding character metal contribution).

To estimate the covalent binding energy \( E_{\text{cov}} \) of \( \pi_1 \) and \( \pi_3 \) orbitals, a series of calculations was performed with increasing the distance between ligands and a metal ion with preservation of optimal geometry and the dependence of the energy of all MOs on this distance was determined. It was suggested that for orbitals of a similar type (for example, \( \pi_1 \), \( \pi_2 \), \( \pi_3 \)) the interaction energy between the two ligands is the same, and the difference in the change of MO energy under increase in bond length is determined only by overlapping with the metal AO.

Molecular \( \pi \)- and \( n \)-type orbitals are characterized by high overlap of oxygen AOs. The stretching of the ligands shows the strong binding character of \( n \)-MOs. To estimate \( E_{\text{cov}} \), the energies of ligand MOs with frozen complex geometries were determined. This allowed us to take into account the inter-ligand interaction.

### 3.4. Photoelectron spectra

The ionization energies of the three bands in the low-energy range of the spectra of beryllium, magnesium, and zinc acetylacetonates and MO energy are presented in Table 4. Figure 3 shows HeI spectra of beryllium (II), manganese (II) and zinc (II) acetylacetonates [12, 13].
The theoretical and experimental energy shift for metal acetylacetonates is approximately 2.0 eV. The sequences of the levels of the upper valence range correspond to the results of calculations; the ionization energy intervals between the bands are approximately reproduced by calculations.

**Table 4** - Vertical ionization energies and calculated energies of molecular orbitals of bis-acetylacetonates of beryllium (II), manganese (II) and zinc (II).

| Compound/Ref. | Ionization energies, eV | MO energies B3LYP/Def2-TZVPP, eV |
|---------------|-------------------------|----------------------------------|
| Be(acac)$_2$  | $\pi_3$, n. n. n. n. | $\pi_3$ e n. e n. $a_1$, $b_2$  |
| (12)          | 8.41, 9.67, 10.86, 11.13| -6.45, -7.43, -8.68, -8.84, -9.33, -9.79 |
| Mg(acac)$_2$  | $\pi_3$, n. n. n. n. | $\pi_3$ e n. e n. $a_1$, $b_2$  |
| (13)          | 8.42, 9.44, 10.48     | -6.46, -7.20, -8.20, -8.36, -9.51, -9.65 |
| Zn(acac)$_2$  | $\pi_3$, n. n. n. n. | $\pi_3$ e n. e n. $a_1$, $b_2$  |
| (13)          | 8.46, 9.22, 10.39, 10.72| -6.46, -7.16, -8.37, -8.55, -9.56, -9.60 |

**Figure 3.** Ultraviolet photoelectron HeI spectra of beryllium [12], manganese and zinc [13] acetylacetonates.

4. **The effect of substitution in ligands**
In order to study the effect of substitution in ligands on the nature of the chemical bond, bis-β-diketonate complexes of Be, Mg, Zn were studied with the substitution of methyl groups of ligands on trifluoro-groups, as well as thio- and dithio-substituted (O→S) Zn acetylacetonates.

4.1. **Geometry**
According to calculated data (Table 5), the substitution of CH$_3$ on CF$_3$ groups in the ligands did not cause a change in the metal-oxygen inter-nuclear distance in the complex of beryllium. This can be explained by the high degree of covalent binding of beryllium with ligand orbitals. In compounds with Mg and Zn, the metal-oxygen bonds increased by less than 0.01 Å. The lengths of other bonds of the
O–C–C–O chelate cycle are slightly reduced (less than 0.01 Å) in all the complexes. The bond of carbonyl carbon Cβ to carbon of the substituted CF3 group increased by 0.03 Å.

Changes in the geometry at thio- and dithio-substitutions are due to the larger ionic radius of the S atom. Increase in the C–S interatomic distances relative to C–O by 0.42–0.44 Å and Zn–S relative to Zn–O by 0.35–0.39 Å are accompanied by an increase in the angle X1–Zn–X2. The Cγ–Zn–Cγ angle between the ligands in the Zn(Sacac)2 complex decreases from 180° to 156° as a result of repulsion of the sulfur atoms of two ligands while the planes of the two ligands are orthogonal.

Table 5 - Theoretical bond lengths and angles of Be, Mg, Zn hexafluoroacetylacetonates, and thio- and dithio-acetylacetonates of Zn.

| Compound: | Be(hfac)2 | Mg(hfac)2 | Zn(hfac)2 | Zn(Sacac)2 | Zn(SSacac)2 |
|-----------|-----------|-----------|-----------|------------|-------------|
| Symmetry: | D2d       | D2d       | D2d       | C2         | D2d         |
| Bond, Å   |           |           |           |            |              |
| M–X1      | 2,001     | 1,624     | 1,957     | 1,967      | 2,001        |
| M–X2      | 2,314     | 1,626     | 1,980     | 2,012      | 2,349        |
| X1–Cβ     | 1,257     | 1,260     | 1,257     | 1,260      | 1,257        |
| X2–Cβ     | 1,714     | 1,397     | 1,396     | 1,397      | 1,398        |
| Cβ1–Cγ    | 1,422     | 1,397     | 1,396     | 1,397      | 1,398        |
| Cβ2–Cγ    | 1,381     | 1,075     | 1,075     | 1,075      | 1,084        |
| Cγ–Hγ     | 1,082     | 1,051     | 1,105     | 1,105      | 1,102        |
| Cβ1–Cβ1   | 1,510     | 1,544     | 1,546     | 1,546      | 1,513        |
| Cγ1–Cβ2   | 1,511     | 1,135     | 1,130     | 1,130      | 1,129        |

4.2. Charges

Substitution of the CH3 groups on CF3 in the ligands reduces the polarity of the M–O, O–Cβ and Cβ–Cγ bonds by decreasing the electron density from the entire complex to fluorine atoms. Eq decreases approximately 20% in accordance with the charges.

Analysis of the effective charges of the atoms (Table 6) showed that the substitution of O by S leads to the most significant redistribution of electron density on Zn and X1–Cβ1, X2–Cβ2 bonds, mainly due to the difference in O and S electronegativity. Under decrease of the bond polarity of Zn–S and S–C, the bond order according to the calculated data increased accordingly for Zn–S from 0.48 to 0.69 and decreased from 1.56 to 1.47 for S–C.

The change in the electron density distribution under thio- and dithio-substitution significantly reduces the electrostatic potential affecting on the metal ion (4.4 and 14 times, respectively).

Table 6 - Mulliken’s effective atomic charges of Be, Mg, and Zn β-diketonates. Eq (eV) is the potential energy of the Coulomb interaction of a metal ion with atoms of one ligand.

| Atom   | Be(hfac)2 | Mg(hfac)2 | Zn(hfac)2 | Zn(Sacac)2 | Zn(SSacac)2 |
|--------|-----------|-----------|-----------|------------|-------------|
|        | R=CF3     | R=CF3     | R=CF3     | R=CH3      | R=CH3       |
|        | X1=X2=O   | X1=X2=O   | X1=X2=O   | X1=O, X2=S | X1=X2=S     |
| M      | 0.244     | 0.926     | 1.145     | 0.523      | 0.275       |
| X1     | -0.163    | -0.358    | -0.381    | -0.329     | -0.186      |
| X2     | 0.043     | 0.121     | 0.074     | 0.230      | 0.070       |
| Cβ1    | -0.189    | -0.257    | -0.227    | -0.270     | -0.223      |
| Hγ     | 0.196     | 0.181     | 0.181     | 0.122      | 0.115       |
### 4.3. Orbital analysis

Substitution of the CH$_3$ groups on CF$_3$ in the ligands leads to stabilization of all the orbitals considered by 1.7–2.1 eV, while maintaining their sequence (Fig. 4). For three pairs of $\pi$, n., n. levels, a stabilization in all compounds differs by no more than 0.1 eV; however, for $\pi$ orbitals (localized by 15–30% on carbonyl carbon atoms), the shift is 0.3–0.4 eV higher. The reason for the stabilization of MOs is the change in the polarity of intra-ligand bonds. According to the results of calculations in unsubstituted acetylacetonates, the C$_R$ atoms of methyl groups have a negative charge of about $-0.2$ e. Fluoridation leads to a shift of the electron density C $\rightarrow$ F and the C$_R$ atom has a positive charge of about $+0.5$ e. The polarization of the electron density of the atoms of the cycles, caused by a change in the polarity of the substituents, leads to a decrease in the positive charges on the carbon atoms of the C$_b$ bonds, as the negative charge decreases on O(S) and C$_\gamma$ (Table 6). The inductive effect of the CF$_3$ groups remains positive, but the transfer of electron density leads to a decrease in the total charge of the groups by approximately 0.02 e. The main influence of the fluorination on the $\pi_b$ orbitals confirms the main influence of the field effect on the stabilization of the valence levels in the fluorinated complexes.

![Graph](image)

**Figure 4** - Correlation diagram of the MO energies (eV) of bis-acetylacetonates of beryllium (II), manganese (II), zinc (II) and their hexafluoro-substituted analogues (the MO energy scale for acetylacetonates is on the right, for hexafluorinated acetylacetonates - on the left)

Substitution of a single O atom on S in Zn(Sacac)$_2$ reduces the symmetry of the complex, which leads to the removal of the degeneracy of the $e$-orbitals. However, for $\pi$-type MOs, the differences in the energies of the $a$ and $b$ levels do not exceed 0.1 eV, and they are 0.3 eV for n.. The splitting of n. orbitals (degenerated under $D_{2d}$ symmetry) is due to three reasons. First, the contributions of S3p and O2p to n ($b$) and n ($a$) are different, secondly, the prevailing S3p orbitals contribution to both MOs enhances the antibonding for n ($b$), and binding for n ($a$) ligand–ligand interaction; third, the contributions of 4s-AO zinc to n ($a$) and 4p-AO to n ($b$) cause more significant covalent stabilization of n ($a$).
For Zn(Sacac)<sub>2</sub>, with a slight destabilization (from 0.1 to 0.4 eV) of three upper pairs of MO (π<sub>3</sub>, n<sup>–</sup> and n<sup>+</sup>), the energies of two π<sub>2</sub> orbitals changed by 1.3 eV (Fig. 4). The multiple difference in the π<sub>2</sub> shift is due to the energies of the π- and n-orbitals of the carbonyl and thio-carbonyl groups.

The symmetry of the complex is restored to D<sub>2d</sub> under dithio-substitution; the upper π<sub>3</sub> and n<sup>–</sup> orbitals are degenerate, their preferential localization on sulfur atoms (74% and 72%) caused an increase in the energy of the orbitals in comparison with Zn(acac)<sub>2</sub> by 0.4 eV (Fig. 4). Significant destabilization of two π<sub>2</sub> MOs is 1.9 and 1.8 eV relative to similar levels of the oxygen analogue. More complex changes under the substitution of all oxygen atoms on sulfur are observed for n<sup>–</sup> (b<sub>2</sub>) and n<sup>+</sup> (a<sub>1</sub>), localized on sulfur atoms according to the calculated results (76 and 72%, respectively). The energy change for the n<sup>–</sup>(b<sub>2</sub>) orbitals with anti-binding inter-ligand overlapping of sulfur AOs is 0.98 eV, whereas for the binding n<sup>–</sup>(a<sub>1</sub>) MO the energy change is much lower (0.11 eV). The observed qualitative differences in the shifts of two n<sup>–</sup> levels are due to the sum of the interaction of the inter-ligand and binding interactions of the n<sup>–</sup> orbitals with zinc AO.

### 4.4. Photoelectron spectra

The shift in theoretical and experimental energies for metal hexafluoroacetylacetonates is approximately 2.1 eV. The sequences of the levels of the upper valence region are reproduced by calculations for fluorine-substituted complexes. The ionization energy intervals between the bands are close to theoretical.

#### Table 7 - Vertical ionization energies and calculated energies of molecular orbitals of the substituted analogs of beryllium (II), manganese (II) and zinc (II) bis-acetylacetonates.

| Compound/Ref. | Ionization energies, eV | MO energies B3LYP/Def2-TZVPP, eV |
|---------------|------------------------|----------------------------------|
|               | π<sub>3</sub> | n<sup>–</sup> | n<sup>+</sup> | π<sub>1</sub> | n<sup>–</sup> | n<sup>+</sup> | a<sub>1</sub>, b<sub>2</sub> |
| Be(hfac)<sub>2</sub> [12] | 10.39 | 11.66 | 12.96 | -8.29 | -9.28 | -10.49 | -10.60 |
| Mg(hfac)<sub>2</sub> [13] | 10.28 | 11.18 | 12.31 | -8.18 | -8.94 | -9.94 | -10.08 |
| Zn(hfac)<sub>2</sub> [13] | 10.25 | 11.17 | 12.53 | 12.78 | -8.19 | -8.92 | -10.11 | -10.26 |
| Zn(SSacac)<sub>2</sub> [20] | 7.68 | 8.37 | 9.11 | 10.73 | -6.06 | -6.77 | -7.39 | -8.44 |
Figure 5 - Ultraviolet photoelectron HeI spectra of beryllium [12], manganese and zinc [13] hexafluoroacetylacetonates

5. Conclusion
The calculation results showed that the nature of the bond between the metal ion and the ligands in the Be, Mg and Zn β-diketonate complexes differs depending on the ion. For beryllium, the bond is almost completely covalent with an insignificant ion component: the Coulomb potentials for complexes with beryllium are 1.37 and 1.08 eV (132 and 104 kJ/mol) for acetylacetonate and hexafluoroacetylacetonate, respectively.

For Mg and Zn β-diketonates with a metal-oxygen bond, the calculations showed the essentially ionic nature of binding: about 8 eV (770 kJ/mol) for magnesium compounds and 12.3 and 11.3 eV (1190 and 1100 kJ/mol) for zinc. However, the O→S substitution significantly reduces the metal-ligand binding ionicity: to 2.8 and 0.9 eV (85 and 270 kJ/mol) for the thio- and dithio-substitution, respectively.

According to calculations, the covalent bond of a metal with ligands is due to the overlapping of only some MOs with s- and p-orbitals of the metal. The orbital σ (CO), located in the middle of the valence range of the complexes, makes the largest contribution to the binding. The covalence of the M–O bond in acetylacetonates decreases in the series Be→Mg→Zn due to an increase in the ionic radius of the metal, leading to two consequences. The first is an obvious decrease in the overlap of metal orbitals with ligands. Secondly, the nature of the overlapping of the metal p-AO with the n-MO of ligands (from binding to anti-binding), which is caused by some stabilization of n-MO with increasing the distance between the ligands due to the repulsion of oxygen p-AOs.

Comparison of MO energies with UV PE spectra showed a satisfactory quality of the B3LYP/Def2-TZVPP method application for all studied compounds.
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