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Complexation of luteolin with lead (II): Spectroscopy characterization and theoretical researches

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ABSTRACT

The interactions of $(CH_3COO)_2Pb{\cdot}3H_2O$ (lead acetate trihydrate) with luteolin, 5,7,3′,4′-tetrahydroxyflavone, were investigated in methanol solution. The spectroscopy (UV–Vis, FT-IR, HPLC-MS, ^{1}H NMR) and elemental analysis were adopted to assess the interaction of luteolin and Pb(II). The results show that luteolin reacts with Pb(II) through the chelating sites of 4-carbonyl and 5-hydroxy in two luteolin molecules. The structures, energies, CDA (charge decomposition analysis) and orbitals analysis of the ligand and complex have been analyzed according to quantum-chemical calculation, which is further proofed that luteolin molecule can effectively chelate Pb(II) by 5-hydroxyl-4-oxo chelating site. It is speculated that luteolin has a high potential of becoming a health care product to eliminate lead cation in the future.

1. Introduction

Lead is ubiquitous, especially in industrialized societies. Because of its high vapor pressure and low melting point, industrial uses of lead may cause extensive local environmental pollutions [1,2]. It is reported that lead poisoning is taken by intake, inhalation, prenatal and skin exposure [3,4]. Lead is absorbed through the respiratory and digestive tract, into the blood, and distributed to tissues of the body. Also it is a cumulative toxicant that adversely affects the neurologic, hematologic, gastrointestinal, cardiovascular, renal and reproductive systems [5–7]. It is considered that lead and its inorganic compounds are probable carcinogens for humans [8]. Recent studies have shown that the chemical factors in natural foods can remove the lead ions from the body [9–11]. Thus, it is very important to use natural foods with small side effects to eliminate or avoid lead poisoning.

Luteolin (5,7,3′,4′-tetrahydroxyflavone, Scheme 1) is one of the most common flavonoids presented in honey, pollen and so on. It has been shown to treat a wide range of diseases in the traditional medicine [12]. Recently, luteolin has been investigated in antioxidant properties [13], antimicrobial activity [14,15] as well as its anti-inflammatory [16]. In addition, it is also one of the effective metal chelators [17]. As metal chelators, the flavonoids play an important role in both bioavailability [18] and toxicity of a variety of metals [19]. For instance, the divalent lead ion has been implicated to be involved in neurological and bone disorders [20,21], however, the damage resulted from lead ion can be reduced through the complexation of quercetin.

Luteolin possesses two possible chelating sites in complexation: the 5-hydroxy-4-oxo and 3′,4′-dihydroxyl (catechol) groups (Scheme 1). The 5-hydroxy-4-oxo group is superior to 3′,4′-dihydroxyl group in the complexation process [17,22]. Complexation of metal cations and luteolin has been reported [23–26], but almost no information is known on the interaction between Pb(II) and luteolin.

In this work, spectroscopy and quantum-chemical calculations can be used to study the complexation between luteolin and Pb(II). The aims of this present work are (i) to examine the chelation property of the luteolin with Pb(II) in ethanol-water solution and (ii) to achieve the theoretical analysis of the complex by quantum-chemical calculations. The purpose of our investigation will be to provide a basis for the further research on the elimination of toxic heavy metals in the body.

2. Methods

2.1. Experimental method

2.1.1. Reagents

Luteolin was purchased from Ark Pharm Inc. (USA). $(CH_3COO)_2Pb{\cdot}3H_2O$ was purchased from Macklin Biochemical Co. Ltd. (Shanghai, China). All solvents and reagents were of analytical grade.

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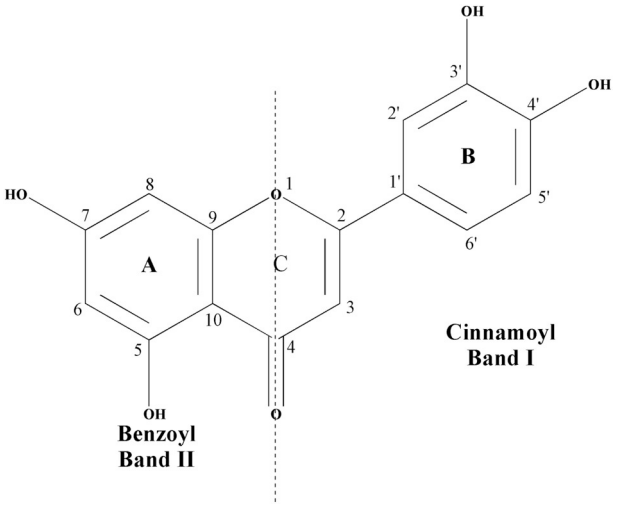

Scheme 1. The structure of luteolin.

2.1.2. Synthesis of the complex

To prepare the complex, 0.572 g (2 mmol) of luteolin was dissolved in 30 mL ethanol-water solution, and then 20 mL of $(CH_3COO)_2Pb{\cdot}3H_2O$ (in the molar ratio of Pb(II):ligand as 1:2) solution was added drop wisely with continuous stirring. According to the optimal reaction conditions [27], the solution was adjusted to pH = 6 by NaOH (1 M) and the mixture solution were heated (70 °C) in the water-bath for 15 min. The orange precipitate was washed three times with ethanol, and several times with distilled water, then dried under vacuum for 20 h. Finally, the complex was weighed and calculated the yield.

2.1.3. Physical measurements

UV–visible spectroscopic studies of luteolin-lead (II) complex and luteolin were performed in dimethylsulfoxide solution using UV–visible spectrophotometer (T60, PG Instruments Ltd., Leicestershire, UK), respectively. The complex (0.1 mg) and luteolin (0.1 mg) were mixed with 10 mg of dry KBr, ground, and loaded on the FT-IR instrument (Nicolet-200SXV, Nicolet, USA), respectively. And each sample was scanned from 500 to 4000 cm^{-1}. The spectra data were analyzed by using ORIGIN 8.0 software. The 6210 Time-of-Flight LC/MS system (G1969A, Agilent Technologies, Santa Clara, CA) was used for obtaining Mass spectra. The column was replaced by zero dead volume cell. The mobile phase was a 50:50 mixture of acetonitrile (A) and 0.2% aqueous solution of formic acid (D). The flow-rate was maintained at 0.2 $mL{\cdot}min^{-1}$. The 1 μL sample (1 mg/1 mL DMSO, dimethylsulfoxide) was injected in a 1200 Series HPLC system (Agilent Technologies, Waldbronn, Germany) and DAD (Diode Array Detector) detector. The mass spectrometer was run in positive ESI mode with molecular ions and scanning range (m/z) was 100–3200. Air at 350 °C and 12 $L{\cdot}min^{-1}$ was used for desiccation and nitrogen at 45 psi was used for dispersion. The capillary voltage was set at 4000 V and the fragmentor voltage was 140 V. The SEM (Scanning Electron Microscope) equipped with an EDS (Energy Dispersive Spectroscopy, Oxford Instruments) was used to perform the elemental analysis of the luteolin-Pb(II) complex. Spot scanning analysis of the sample was conducted, and the weight percentages and atomic number percentages of the elements in different regions of the sample were quantitatively analyzed. The three different positions in the sample were taken for analysis and the average value was calculated. The samples dissolved in d^6-DMSO (deuterated dimethyl sulfoxide) solutions were detected at 298.7 K using Superconducting Nuclear Magnetic Resonance Spectrometer operating at 400 MHz.

2.2. Calculation methods

All computations were carried out by manipulating the GAUSSIAN 03 program package [28]. The vibrational frequencies and the fully optimized geometries have been determined by using the spin-unrestricted three-parameter hybrid [29] B3LYP density method [30]. The introduction of diffuse orbitals in the basis set does not improve the description of this molecular system, thus the 6-31G (d, p) basis set was used for the C, H, and O atoms [31,32] and the SDD basis set was used for Pb [33]. All possible combination patterns between luteolin and Pb (II) were optimized. In the meanwhile, zero point energies, thermal enthalpies and thermal free energies were compared for all optimized configurations to find the most stable molecular structure that was verified by harmonic vibrational frequencies (the number of imaginary frequencies NIMAG = 0). In addition, the solvation effect of the complex and luteolin were calculated using the PCM (polarizable continuum model) [34,35]. The dielectric constant of ethanol has been fixed at 24.85.

The CDA for the complex molecule was calculated by using Multiwfn software [36], which can describe the electronic interactions between the fragments [37]. The interactions between the main orbitals in the complex were analyzed with VMD 1.9.3 visualization software [38].

3. Results and discussions

To explore chelating site of the reaction between luteolin and Pb(II), the luteolin-Pb(II) complex was synthesized with yield of 87.87%. The synthetic product was analyzed by spectroscopy and theoretical researches to study the main complex and its chelation site in product.

3.1. UV–vis spectroscopic analysis

In the absorption spectrum of luteolin, the absorption band in the 268 nm is related to A-ring absorption (benzoyl system, Band II), while the absorption 355 nm corresponds to $\pi \rightarrow \pi^*$ transition B-ring absorption (cinnamoyl system, Band I) (Fig. 1) [39]. The significant change is that the absorption peak at 355 nm decreases and a band at 424 nm appears when luteolin is chelated with Pb(II). The bathochromic shift of about 69 nm takes place in cinnamoyl system that confirms formation of the complex between luteolin and Pb(II). The band at 424 nm should be attributed to ligand-to-metal charge transitions. Judging from the molecular structure of luteolin, it can also be inferred that luteolin may chelate the metal ion via two sites, 5-

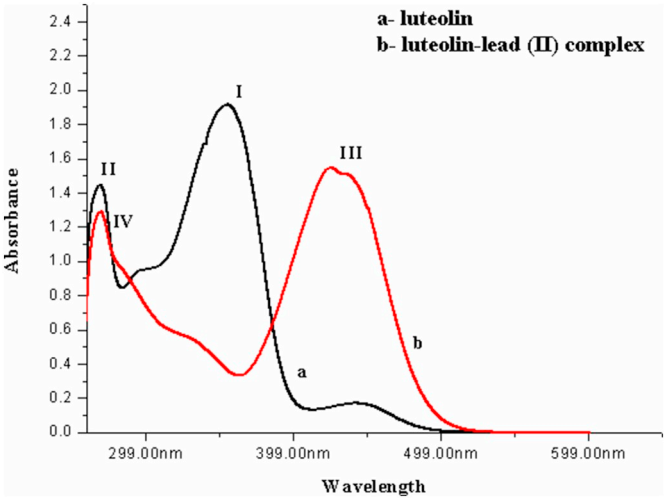

Fig. 1. The UV–vis spectra of free luteolin and luteolin-lead (II) complex in DMSO.

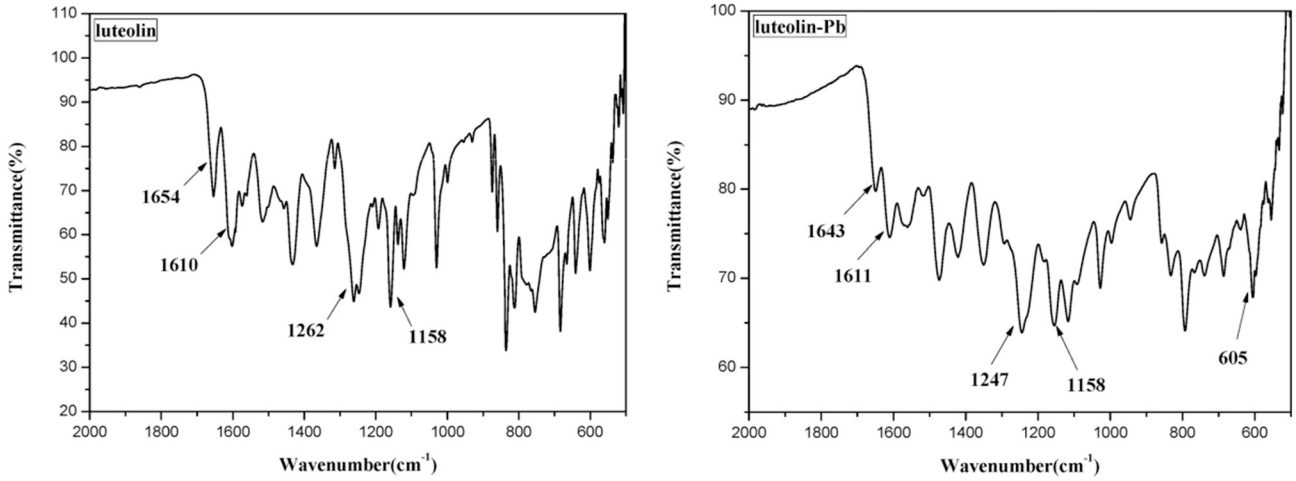

Fig. 2. The IR spectra of the luteolin of luteolin and the luteolin-lead (II) complex.

hydroxy-4-oxo system and 3′,4′-hydroxy system. The molecule structure of luteolin has an acidic 5-OH group and a 4-CO group that is more suitable for complexation [40]. Therefore, the complex of 5-hydroxy-4-oxo site chelating can provide more stable molecule with lower energy. It shows that the spectral shift and the molecular structure of ligand are highly informative for the coordination. From what has been discussed above, 5-hydroxy-4-oxo system may be a proper site to be involved in complex formation.

3.2. Infrared spectral study of the complex

To achieve a better insight into the luteolin-Pb(II) complex, both free luteolin and the complex are investigated by IR spectroscopy. Fig. 2 depicts FT-IR spectroscopy of luteolin and the complex, and the spectral data are listed in Table 1. Because of the complexity of flavonoids' structure, the spectrum of luteolin is relatively complicated.

By comparing the absorption data of free luteolin with the complex, the presence of ν (Pb—O) (605 cm^{-1}) in the spectrum of the complex indicates formation of Pb—O bond via the complexation [41]. As regards the ν(C═O) stretching vibration peak, it declines by 11 cm^{-1} from 1654 cm^{-1} of luteolin to 1642 cm^{-1} of the complex. The phenomenon indicates that the O-atom of carbonyl group is involved in chelation. It makes the electron cloud of carbonyl group go further away from center of the bond and move to oxygen atom, and then the density of electron cloud of carbonyl bond is decreased, leading to the reduction of the double bond strength of carbonyl group. The vacant orbitals of Pb (II) could make the electrons transferring to near the location of Pb(II), thus reduction of C-OH bond strength leads to declining the absorption peak of ν(C—OH). As a result, the stretching mode of ν(C—OH) has been shifted from 1262 cm^{-1} (in luteolin) to 1247 cm^{-1} (in the complex). On the contrary, the ν(C—O—C) vibration frequency is no changed at 1158 cm^{-1}, indicating that the ring oxygen atom is excluded from involvement in the complexation reaction [42]. The IR spectral results discussed above illustrate the formation of the complex and confirm that the Pb (II) has bonded to 4-carbonyl group.

Table 1
Assignment of the IR spectra of the luteolin and the complex (band position cm^{-1}).

Compound	ν(C═O)	ν(C═C)	ν(C—OH)	ν(C—O—C)	ν(Pb—O)
Luteolin	1654	1610	1262	1158	–
Luteolin-Pb (II)	1642	1611	1247	1158	605

3.3. Mass spectroscopy analysis

Fig. 3 depicts the ESI-mass spectrum of the luteolin-lead(II) complex dimethylsulfoxide solution. The base signal at m/z = 287.97 is designated as protonated luteolin, [luteolin + H]$^+$, whereas the peak at m/z = 779.06 could be assigned to a 2:1 luteolin-Pb(II) complex, [(luteolin)$_2$-Pb(II)]. The peak at m/z = 493.01 and m/z = 330.99 represent the 1:1 luteolin-lead complex, [luteolin + Pb(II)], and [luteolin + 3H_2O], respectively.

It can be observed that fragments of two luteolin-Pb(II) complexes appear in mass spectra. From intensity analysis of the mass spectra, the intensity of 2:1 luteolin-Pb(II) complex was only slightly higher 1:1 luteolin-Pb(II) complex. There are two possible reasons for the presence of 1:1 complex: (a) one of the products of reaction between luteolin and Pb(II), and (b) the fragment formed from 2:1 complex during ionization. In order to define the main product of luteolin reacted with Pb(II), the elemental analysis was used for further analysis.

3.4. Elemental analysis of the complex

The elemental analysis of luteolin-Pb(II) complex was conducted with SEM-EDS to determine the main product of reaction between luteolin and Pb(II) in this work. The experimental and theoretical values of elemental analysis of the complexes are listed in Table 2. The results are shown that the weight percentages of C, O and Pb in complex were 47.54 ± 0.32%, 25.09 ± 0.18% and 27.37 ± 0.21%, respectively. In addition, the atomic number percentages were 70.05 ± 0.45%, 27.48 ± 0.20% and 2.47 ± 0.28% for C, O and Pb, respectively. It is obvious that the experimental values of product are closer to the theoretical values of 2:1 complex than 1:1 complex. In addition, the experimental values of product are slightly higher than the theoretical values of the 2:1 complex for oxygen and carbon. One reason for this result could be related to carbon conductive adhesive which is struck with X-rays to cause an increase in carbon content. The other reason could be that the residue of reaction solvent gives rise to elevate carbon and oxygen content. In summary, the conclusion could be drawn from the results described above that the 2:1 complex is the main product of reaction between luteolin and Pb(II).

3.5. ^1H NMR analysis

In light of the above spectral analysis, luteolin is reacted with Pb(II) through 5-hydroxy-4-oxo system. The 5-hydroxyl group could lose hydrogen due to acidic nature of 5-OH proton under certain conditions, thus the situation of hydrogen of 5-OH was analyzed by ^1H NMR spectroscopy under this synthetic condition.

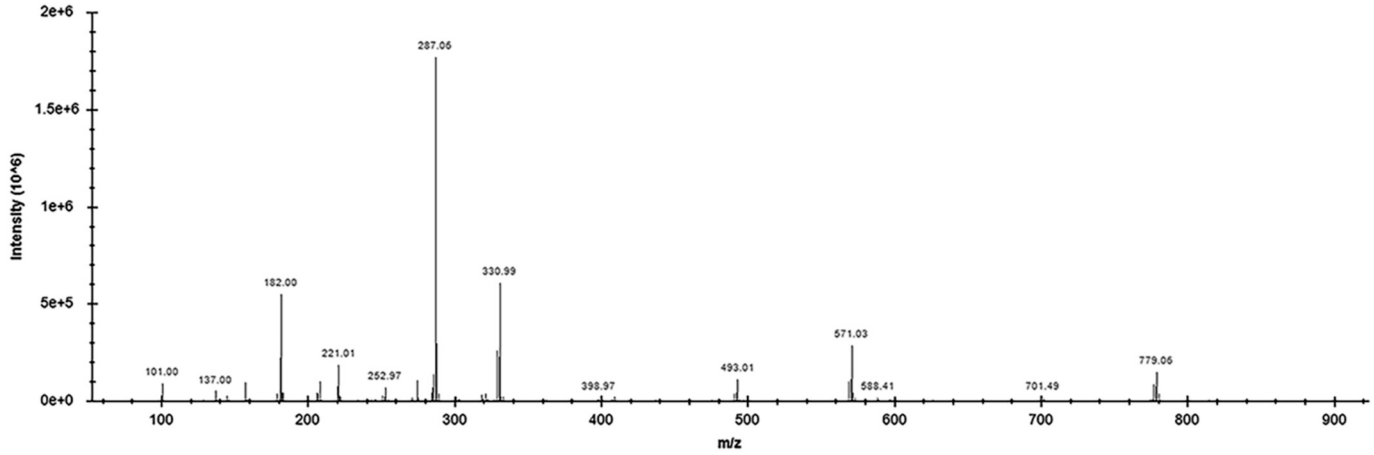

Fig. 3. Mass spectroscopy of the luteolin-Pb(II) complex.

Table 2
SEM-EDS elemental analysis of the luteolin-Pb(II) complex.

Elements	Wt (%)			At (%)		
	Experiment	Theory		Experiment	Theory	
		2:1	1:1		2:1	1:1
C	47.54 ± 0.32	47.44	37.27	70.05 ± 0.45	69.77	68.18
O	25.09 ± 0.18	25.28	19.88	27.48 ± 0.20	27.90	27.27
Pb	27.37 ± 0.21	27.28	42.86	2.47 ± 0.28	2.33	4.55

Wt: the weight percentage; At: the atomic number percentage.

Luteolin: δ 12.94 (1H, 5-OH); δ 10.74 (1H, 7-OH); δ 9.46 (1H, 4′-OH); δ 9.42 (1H, 3′-OH); δ 7.39 (1H, 6′-H); δ 7.37 (1H, 2′-H); δ 6.86 (1H, 5′-H); δ 6.64 (1H, 3-H); δ 6.42 (1H, 8-H); δ 6.16 (1H, 6-H).

Luteolin-Pb(II) complex: δ13.36 (1H, 5-OH); δ 10.67 (1H, 7-OH); δ 9.39 (1H, 4′-OH); δ 9.36 (1H, 3′-OH); δ 7.16 (1H, 6′-H); δ 7.14 (1H, 2′-H); δ 6.79 (1H, 5′-H); δ 6.47 (1H, 3-H); δ 6.37 (1H, 8-H); δ 6.13 (1H, 6-H).

In ^{1}H NMR spectra of free luteolin, the intramolecular hydrogen bond which is interaction between C5-OH and the acceptor C4═O results in the absorption peak of 5-hydroxyl proton locating at 12.94 ppm. Compared with the spectra of complex, we can see chemical shift of 5-OH group proton transferred to 13.36 ppm. The possible reason for this phenomenon is that the vacant orbitals of Pb(II) could make the electrons of 5-hydroxyl transferring to near the location of Pb(II), leading to the density of electron cloud of hydrogen is decrease. Therefore, the chemical shift of 5-OH group proton is moved toward the lower field (high frequency). It can be implied that the 5-hydroxyl group has not deprotonated when luteolin is reacted with Pb(II) through 5-hydroxy-4-oxo system.

In addition with this, the spectra data shows the chemical shifts of complex which are shifted to higher field as compared with those of free luteolin. The phenomenon of chemical shifts is attributed to conjugation effect which is caused by coordination effect when the complex is formed. Accordingly, it can be presumed that 5-hydroxyl group still retains proton when luteolin is reacted with Pb(II).

3.6. The theoretical analyses of the luteolin-lead (II) complex

3.6.1. Structural analysis

Base on the obtained experimental results, the ligand and the 2:1 complex were calculated by the DFT (density function theory) calculations at the B3LYP/6-31G (d, p) level. The theoretical calculations illustrate that the luteolin molecule is a nonplanar structure in both vacuum and ethanol. Considering the different possibilities of orientation of the B ring, the molecule structure with a dihedral D (O1-C2C1′-C6) = 164.04° is found to be the most stable structure by Single-point Energy Calculation. The lowest energy structure of luteolin (Fig. 4) exhibits that it possesses two possible chelating sites in complexation: the 5-hydroxy-carbonyl and the 3′,4′-dihydroxyl system. Calculations clarify that the complex (catechol site chelate) lies 91.62 kcal·mol^{-1} above the lowest energy complex (5-hydroxy-carbonyl site chelate). It is conducive to the formation of complex at 5-hydroxy-carbonyl site according to the minimum energy principle [43]. Therefore, the complex in 2:1 stoichiometry formed via 5-hydroxy-4-carbonyl site is used for further investigation.

The main geometrical parameters of luteolin and the complex are presented in Table S1. It clearly states that the molecular structure of luteolin is affected by complexation. In comparison to the free luteolin molecule, the most obvious changes is destruction of the hydrogen bond

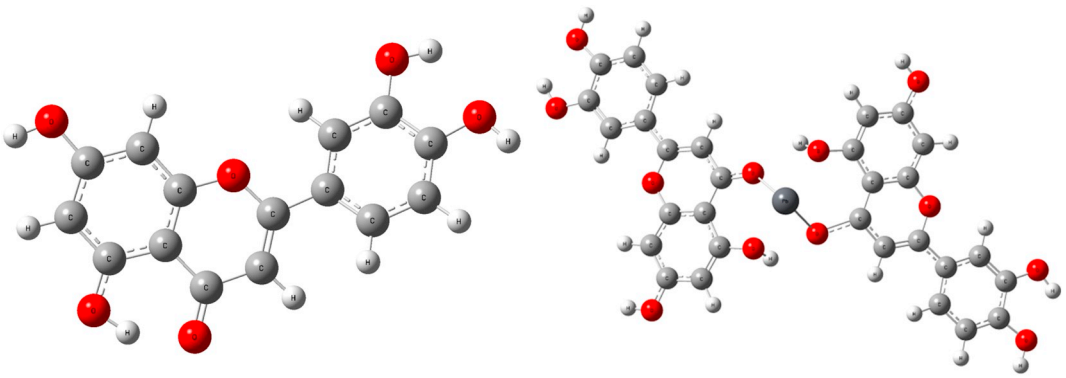

Fig. 4. The optimized geometries of luteolin and the complex.

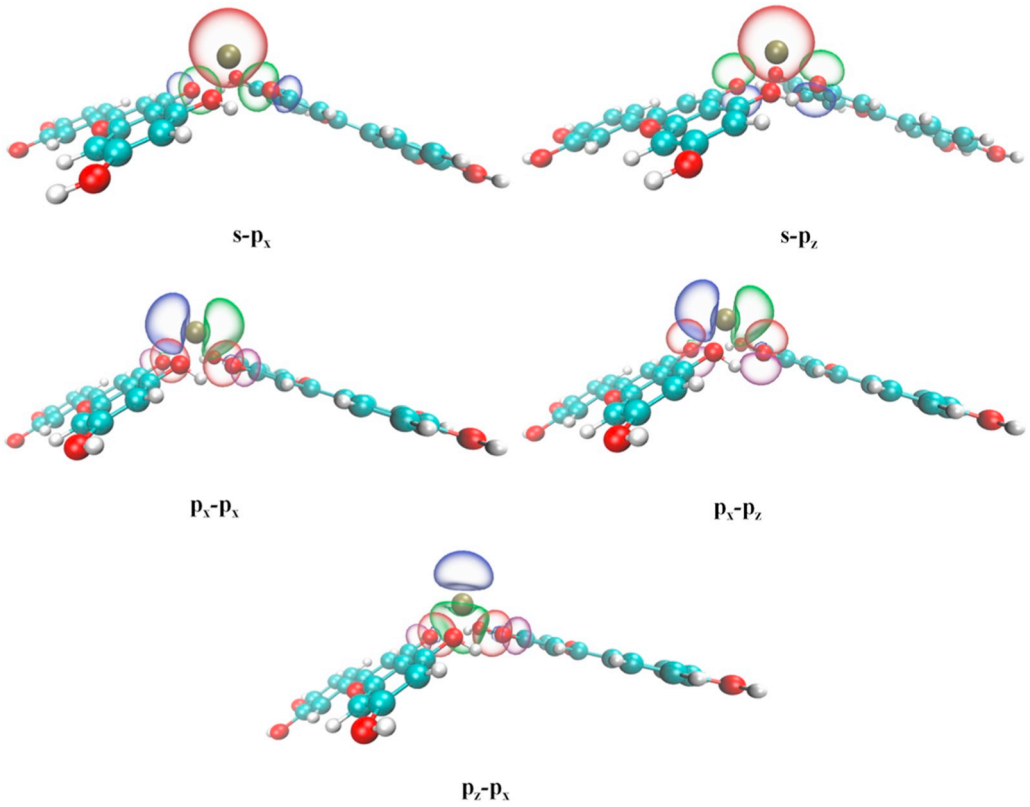

Fig. 5. The interaction of the atomic orbitals in complex.

(O4···H5) and bond lengths of C4—O4 and C5—O5 is increased by 0.047 and 0.048 Å in the rings A and C, respectively. The complexation on the 5-hydroxy-carbonyl site not affects the bond angles of the B ring as same as the bond lengths in the B ring; nevertheless, the bond angles of the rings A and C are slightly modified. In addition, the individual luteolin in the complex tends to be planar, where the dihedral D (O1C2-C1′C6′) is changed from 161.80° of the free ligand to 178.55° of the complex.

3.6.2. Orbital analysis

The nature of the bond Pb—O4 is visually traced by the relevant molecular orbitals of the complex (Fig. 5). For the complex, the occupied molecular orbitals represent the σ bonding of Pb—O4 which is mainly originated from the interaction of s-p_z, s-p_x, p_x-p_x, p_z-p_x, p_x-p_z orbitals of the two atoms. The CDA calculation illustrates that 0.257 electron is transferred from one luteolin to the bonding region, while no electron is back donated from Pb (II). The same results are also found in another luteolin of the complex.

The frontier orbitals of luteolin and the complex are described in Fig. 6. The HOMO (highest occupied molecular orbital) of the luteolin mainly presents the charge density distributions on the A ring, whereas the LUMO (lowest unoccupied molecular orbital) locals a charge density distributed on the whole molecule. The HOMO → LUMO transition shows a low charge transfers from the A ring to the B ring in luteolin. The corresponding molecular orbitals of the complex have the different charge distributions that the HOMO → LUMO + 1 transition exhibits charge transition toward the carbonyl group of ring C. As the second-order nonlinear optical properties of molecules relate with the molecular orbital composition, electron transition and charge transfer of the ground state and excited state [44], a ligand-to-metal charge transfer would be the origin of the bathochromic effect observed in the spectrum.

4. Conclusion

The complex was synthesized through the reaction between luteolin and Pb(II), and characterized by spectroscopic techniques and quantum-chemical calculation. Research data suggest that luteolin reacts with Pb(II) through the chelation sites of 4-carbonyl and 5-hydroxy in two luteolin molecules. In the process of synthesis, it has been found that the complex is not only difficult to dissolve in both water and organic solvent, but also not easy to decompose at relatively high temperature. In addition, luteolin is reacted with Pb(II) to give the yield of 87.87%. It is speculated that the material rich in luteolin has great potential to be used as the health care product for the human body to eliminate lead, so as to reduce the harm caused by lead poisoning, especially children. In the later work, the effects of the complexation of luteolin on the organism will be carried out.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jinorgbio.2019.01.007.

Abbreviations

DAD	Diode Array Detector
NIMAG	the number of imaginary frequencies
CDA	charge decomposition analysis
SEM	Scanning Electron Microscope
EDS	Energy Dispersive Spectroscopy
B3LYP	Becke3–Lee–Yang–Parr
PCM	polarizable continuum model
DFT	density function theory
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital

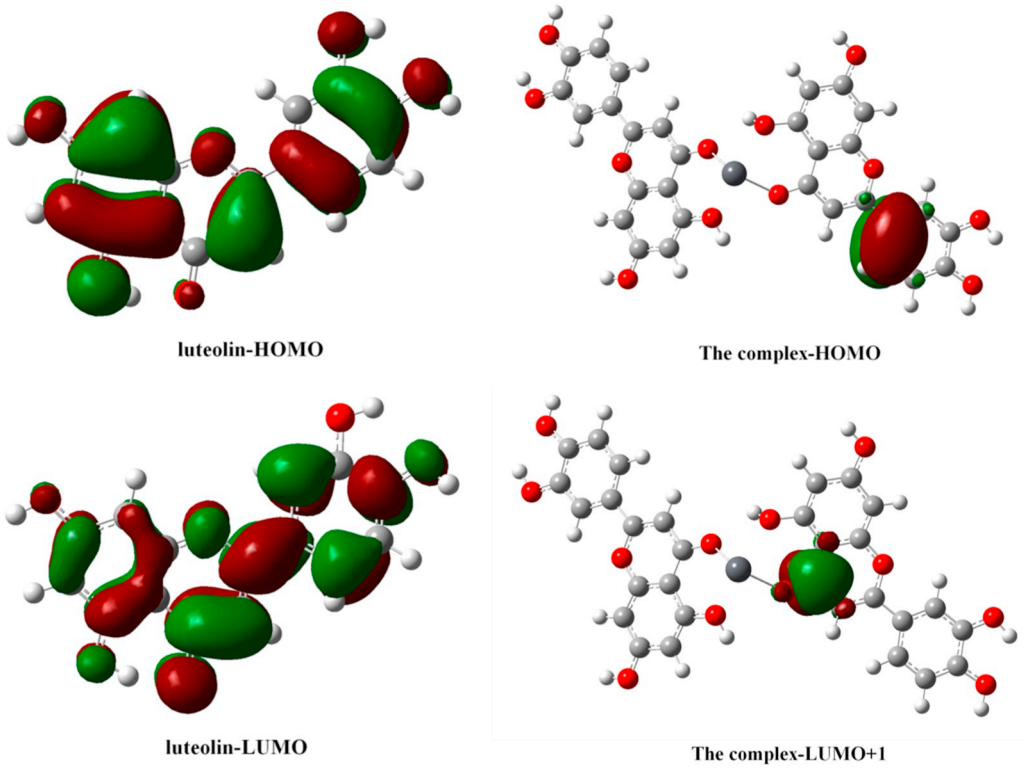

Fig. 6. The plots of the frontier orbitals involved in the electronic transitions calculated of luteolin and its complex.

Acknowledgements

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