Theoretical Studies of Xanthates in Heavy Metal Complexation: Understanding the Structural, Thermochemical, and Electronic Aspects

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Heavy metals have been widely discussed as a significant cause of environmental disasters in recent decades. One of the main focuses has been exploring agents and mechanisms capable of removing these metals from nature. Under this perspective, xanthates have been studied as sequestering agents of these metals in aqueous environments. In this theoretical study, complexes of cadmium(II) and mercury(II), with different coordination modes and geometric isomers of the xanthate ligands (n-propyl, n-butyl, and n-pentyl xanthates), were evaluated using density functional theory. To verify the versatility of coordination modes of the xanthates, monodentate and bidentate structures were optimized. For these compounds, structural, thermochemical, and electronic parameters were studied. The thermochemical results showed that all complexes are formed through exothermic and spontaneous processes. Electronic analysis showed that the mercury(II) complexes have a higher covalent character of the Hg–S bond, in contrast with the cadmium(II) complexes, which exhibited a higher ionic character of the Cd–S bond. Through the analysis of the natural bond orbitals, the Lewis acid-base nature of these complexes was confirmed and corroborated by the softness calculations, with the participation of the p orbitals of the sulfur and s orbitals of the metal centers.

Keywords: xanthates, Cd$^{2+}$, Hg$^{2+}$, EDA, NBO, thermochemical parameters

Introduction

Coordination chemistry is an area of science that compounds can be formed through a Lewis acid-base interaction. In these reactions, the acidic species are metal centers, and the basic species are ligands with a pair of electrons available for donation. The complexes present structures composed of an organic/inorganic fraction coordinated to metal centers. These compounds have been extensively explored in several areas, such as biological and technological fields. In the environmental area, the study of complexes with heavy metals has been of great interest because these metals pose risks to nature and human life as they are bioaccumulators and non-biodegradable. Consequently, they can cause diseases such as cancer, kidney dysfunction, and even death. Cadmium and mercury are present in the list of chemicals whose excess in nature is considered a public health problem, according to the World Health Organization (WHO). Disinformation and irregular disposal of these materials have caused contamination by heavy metals, in different aqueous environments. Therefore, several compounds have been studied and used to remove these metals. A class of organic compounds that have been used are xanthates. The good performance of xanthates is due to their versatility in coordinating with metal centers, resulting from the presence of characteristic group –OCS$_2$ with hard (O) and soft (S) donor atoms.

In the last ten years, several studies have investigated the efficiency of cellulose xanthates in removing heavy metals to minimize the cost of production and the environmental impact. To become more environmentally friendly, cellulose sources such as apple pomace and rice husk were used. In addition to application in the environmental area, xanthates also have properties such as antibacterial and anticancer in the medicinal area. Finally, xanthates have also been applied in the technological area for the...
manufacturing of thin films and the optimization of epoxy resin curing processes.  

In this work, theoretical studies of thermochemical and electronic analysis of cadmium(II) and mercury(II) complexes with xanthate ligands (n-propyl, n-butyl, and n-pentyl xanthates) were carried out through Density Functional Theory (DFT). Several studies have shown the DFT’s efficiency in determining geometries, and spectroscopic and electronic properties of complexes with group 12 metal ions.  

From an X-ray structural perspective, studies show the formation of cadmium(II) and mercury(II) complexes with polymeric structures. Furthermore, the cadmium(II) and mercury(II) compounds preferentially assume tetrahedral and linear geometries. However, these complexes are found in the literature, containing other geometries. For mercury(II) complexes coordinated with 3 to 8 substituents, assuming T-shaped, tetrahedral, trigonal bipyramidal, square pyramid, octahedral, pentagonal bipyramidal, and hexagonal bipyramidal distorted geometries were found. In the case of cadmium(II) complexes, in addition to tetrahedral structures, structures with octahedral, pentagonal bipyramidal, and trigonal bipyramid distorted geometries have been observed.

**Methodology**

The structure of cadmium(II) and mercury(II) hexaaqua complexes and their alkyl xanthate ligands were optimized using the DFT method with Gaussian 09 software. The starting structures for the optimization were the hexaaqua complexes, followed by the complex substituted structures with xanthate ligands in different positions and geometries, where in all cases, the ChemCraft software was used. These calculations and thermochemical analyses (including enthalpy, entropy, and Gibbs free energy at 298 K) employed the M06L and wB97XD functionals, using the 6-311++G** basis set for carbon, oxygen, hydrogen, and sulfur atoms. The LANL2TZ basis set utilized for Cd²⁺ and Hg²⁺ metal ions. The local meta-generalized gradient approximation density functional M06L was selected for its superior performance in thermochemical analyses and non-covalent interactions compared to other functionals like B3LYP, M05, and BP86. M06L was parameterized to offer optimal performance for thermochemical calculations involving main group elements and transition metals. This functional also demonstrated promising results for geometry optimization and vibrational frequency calculations. To corroborate the obtained results, the wB97XD functional was used since it is also a functional parametrized for high-quality results in thermochemical analysis, focusing on covalent and non-covalent interactions with long-range correction for inclusion of dispersion effect. The coordination of heavy metals with lignin matrix has been successfully explored in a recent study for this functional.  

For this work, the results with wB97XD are also available in the Supplementary Information (SI) section. The electronic analysis utilized Gamess software and M06L functional, including Energy Decomposition Analysis (EDA) and Natural Bond Orbitals (NBO), to scrutinize the interaction between the metal ion and the xanthate ligand. The statistical analysis was performed to investigate the results further, considering the average between the complexes with n-propyl, n-butyl, and n-pentyl xanthates.

The substitution reactions of aqua ligands in the aqua mercury(II) and cadmium(II) complexes by xanthate ligands were performed to better understand the use of xanthates for sequestering heavy metals from aqueous environments, as outlined by our research group in a previous study. Owing to the coordination modes versatility of xanthates, reactions with ligands acting as monodentate and bidentate coordination modes at cis and trans positions were analyzed (Figure 1). For monodentate complexes, two different structures were evaluated, one featuring a hydrogen bond between the xanthate’s oxygen and the aqua ligand’s hydrogens, referred as monodentate with hydrogen bond (MDbh) and the other are the monodentate complexes without this interaction, labeled as MD (monodentate). Bidentate complexes are designated as B, while those with a mixed coordination mode are labeled as B/MD. The choice of structures with octahedral geometry was supported by literature, with several studies indicating the prevalence of this geometry alongside linear and tetrahedral ones for Hg²⁺ and Cd²⁺ ions.

The substitution reactions were analyzed in two steps to better understand the electronic properties of the involved species. Figure 2a shows the two steps for forming complexes with monodentate coordination, and Figure 2b presents the steps for forming bidentate complexes. In this way, structures of the cationic and neutral complexes (first and the second substitution reactions, respectively) were optimized, as illustrated in the following sections. The sum of the thermal correction and the vibrational zero point energy with the interaction energy was considered in our study. Therefore, it was possible to determine the parameters of enthalpy variation (ΔH) and Gibbs free energy (ΔG) through the energy difference of the products by the reagents. The entropy variation (ΔS) was calculated using the Gibbs-Helmholtz equation (ΔG = ΔH – TΔS), where T is the temperature. The parameters calculated for the first substitution reaction were named ΔH,F, ΔG,F, ΔH,S, ΔG,S.
and $\Delta S_{FS}$, while the data for the second substitution were named $\Delta H_{SS}$, $\Delta G_{SS}^{298}$, and $\Delta S_{SS}$. In addition, all parameters were corrected by basis set superposition errors (BSSE) calculations.

The energy decomposition analysis (EDA) was also performed to understand how the ligand and aqua complex interact. This analysis allows an assessment of the bond character between two fragments through electrostatic energy ($\Delta E_{elec}$), Pauli energy ($\Delta E_{Pauli}$), and orbital energy ($\Delta E_{Orb}$), whose sum corresponds to the total interaction energy (equation 1). The orbital energy corresponds to the sum of the exchange energy ($\Delta E_{EX}$), polarization energy ($\Delta E_{Pol}$), and dispersion energy ($\Delta E_{Disp}$) (equation 2).

\[
\Delta E = \Delta E_{elec} + \Delta E_{Pauli} + \Delta E_{Orb} \tag{1}
\]
\[
\Delta E_{Orb} = \Delta E_{EX} + \Delta E_{Pol} + \Delta E_{Disp} \tag{2}
\]

Results and Discussion

Optimization structures and thermochemical studies

The thermochemical analysis of the cadmium(II) and mercury(II) complexes was performed through the substitution reactions of aqua ligands in the hexaaqua complex by alkyl xanthate ligands: $n$-propyl xanthate (L1), $n$-butyl xanthate (L2) and $n$-pentyl xanthate (L3). Therefore, the structures of alkyl xanthates and the hexaaquacadmium(II) and hexaaquamercury(II) complexes were first optimized (Figure 3).
results indicate that the formation of these complexes occurs through exothermic and spontaneous processes. In addition, the values of $\Delta H_{rs}$ and $\Delta G_{rs}^{298}$ were higher when compared to the $\Delta H_{fs}$ and $\Delta G_{fs}^{298}$ parameters in both metal complexes (Tables 1 and 2). The nature of the reacting species can explain this. In the first substitution reaction, a strong electrostatic interaction is expected since the interaction occurs between species of charge $+2$ ([M(OH)$_3$]$^{2+}$) and $-1$ (L$^-$. The second substitution reaction occurs between species of charge $+1$ ([ML(OH)$_2$]$^+$) and $-1$ (L$^-$. This interaction still has a considerable electrostatic character but is less energetic than expected for the first substitution reaction, according to the results presented in “Energy decomposition analysis” sub-section.

**Analysis of cadmium(II) complexes**

Figure 4 illustrates the optimized structures of cationic cadmium(II) complexes with the M06L functional. Structures in Figures 4a-4c correspond to monodentate complexes with hydrogen bonds (MD$_{hs}$), and structures in Figures 4d-4f consist of complexes without hydrogen bonds (MD). Finally, the structures in Figures 4i-4g correspond to bidentate cationic complexes, resulting from the substitution of two aqua ligands by one xanthate ligand. A comparison between the monodentate cationic cadmium(II) complexes MD$_{hs}$ and MD indicates that the second exhibited higher spontaneity of formation than the first one, with a $\Delta G^{298}$ difference of 12.59 $\pm$ 0.97 kcal mol$^{-1}$ (Table 1). This suggests that those complexes exhibit better coordination sphere organization due to a higher M–L electrostatic interaction shown in the monodentate MD cationic complexes, as seen in “Energy decomposition analysis” sub-section.

The bidentate cationic complexes (Figures 4g-4i) showed $\Delta G^{298}$ values higher (1.65 $\pm$ 1.38 kcal mol$^{-1}$) than the monodentate MD complexes. This was expected, as there is an increase in entropy caused by higher aqua ligands number exchange due to the formation of the bidentate

<table>
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<tr>
<th>Complex$^a$</th>
<th>$\Delta H_{hs}$ / (kcal mol$^{-1}$)</th>
<th>$\Delta G_{hs}^{298}$ / (kcal mol$^{-1}$)</th>
<th>$-T\Delta S_{hs}$ / (kcal mol$^{-1}$)</th>
<th>$\Delta H_{fs}$ / (kcal mol$^{-1}$)</th>
<th>$\Delta G_{fs}^{298}$ / (kcal mol$^{-1}$)</th>
<th>$-T\Delta S_{fs}$ / (kcal mol$^{-1}$)</th>
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<td>$-172.86$</td>
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<td>$-T\Delta S_{fs}$ / (kcal mol$^{-1}$)</td>
<td>$\Delta H_{fs}$ / (kcal mol$^{-1}$)</td>
<td>$\Delta G_{fs}^{298}$ / (kcal mol$^{-1}$)</td>
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<td>$-T\Delta S_{fs}$ / (kcal mol$^{-1}$)</td>
<td>$\Delta H_{fs}$ / (kcal mol$^{-1}$)</td>
<td>$\Delta G_{fs}^{298}$ / (kcal mol$^{-1}$)</td>
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$^a$L1: n-propyl xanthate; L2: n-butyl xanthate; L3: n-pentyl xanthate; MD$_{hs}$: monodentate with hydrogen bond; MD: monodentate without hydrogen bond; FS: first substitution; B: bidentate; SS: second substitution; T: temperature at 298 K; $\Delta H$: enthalpy variation; $\Delta G$: Gibbs free energy variation; $\Delta S$: entropy variation.
Table 2. Thermochemical parameters for the mercury(II) complexes, calculated with M06L functional

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<th>Complex       </th>
<th>ΔH₂⁹⁸ / (kcal mol⁻¹)</th>
<th>ΔG₂⁹⁸ / (kcal mol⁻¹)</th>
<th>-TΔS₂⁹⁸ / (kcal mol⁻¹)</th>
<th>Complex       </th>
<th>ΔH₂⁹⁸ / (kcal mol⁻¹)</th>
<th>ΔG₂⁹⁸ / (kcal mol⁻¹)</th>
<th>-TΔS₂⁹⁸ / (kcal mol⁻¹)</th>
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<td>[HgL₁(OH₃)₃]⁺·B⁺</td>
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<tr>
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<td>ΔG₂⁹⁸ / (kcal mol⁻¹)</td>
<td>-TΔS₂⁹⁸ / (kcal mol⁻¹)</td>
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<td>ΔH₂⁹⁸ / (kcal mol⁻¹)</td>
<td>ΔG₂⁹⁸ / (kcal mol⁻¹)</td>
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<td>ΔG₂⁹⁸ / (kcal mol⁻¹)</td>
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*1L: n-propyl xanthate; L2: n-butyl xanthate; L3: n-pentyl xanthate; 'MD': monodentate without hydrogen bond; 'MDm': monodentate with hydrogen bond; 'B': bidentate; 'B/MD': bidentate and monodentate; 'FS': first substitution; 'SS': second substitution; T: temperature at 298 K; ΔH: enthalpy variation; ΔG: Gibbs free energy variation; ΔS: entropy variation.

coordination of the xanthate ligand. Consequently, the increase in entropy generates more negative ΔG²⁹⁸ values (Table 1). Moreover, it is possible to observe that the Gibbs free energy values at 298 K for the monodentate MD and bidentate complexes present a discrete difference due to the bidentate coordination, leading to a four-membered ring with high tension, where S–M–S angle is less than 90°.

An opposite trend was observed in the case of monodentate neutral complexes (Figure 5). The monodentate MDₘₙ complexes had ΔH and ΔG²⁹⁸ values around 5.55 ± 2.02 and 3.72 ± 3.02 kcal mol⁻¹ higher than the monodentate MD complexes (Table 1) due to the formation of a hydrogen bond. This indicates a lower stabilization trend of the monodentate MD complexes because of the higher repulsion energies favoring MDₘₙ complexes, as described in “Energy decomposition analysis” sub-section. In addition, these complexes showed larger Cd–S distances (“Geometrical parameters” sub-section), which results in smaller ΔG²⁹⁸ values of these complexes compared to the MDₘₙ monodentate complexes.

The cis/trans isomers analysis of the monodentate neutral complexes was also performed with the diverse structures containing hydrogen bonds. Table 1 shows that the cis-MDₘₙ complexes presented higher values of ΔH and ΔG²⁹⁸ than the trans-MDₘₙ complexes. However, the monodentate MD and bidentate complexes did not show a significant difference between cis and trans isomers. The difference of ΔH and ΔG²⁹⁸ between cis-MD and trans-MD...
complexes was $1.29 \pm 0.71$ and $0.53 \pm 1.37$ kcal mol$^{-1}$, respectively. In monodentate MD$_{\text{HB}}$ complexes, the difference in $\Delta H$ and $\Delta G^\circ$ for cis and trans was $3.54 \pm 0.88$ and $4.64 \pm 2.09$ kcal mol$^{-1}$, respectively. These results indicate that in monodentate MD$_{\text{HB}}$ complexes, there is a preference for the formation of cis isomers. In contrast, this preference is not obvious in monodentate MD complexes.

The structures of the bidentate neutral cadmium(II) complexes were optimized with M06L functional (Figure 6). A comparison with the monodentate complexes...
shows that the bidentate complexes have lower interaction enthalpies (8.45 ± 3.35 kcal mol⁻¹) and higher ΔG₂⁹⁸ values (4.88 ± 3.83 kcal mol⁻¹). As well as in bidentate cationic complexes, these results are associated with the entropic contribution in these systems due to the higher number of aqua ligands that exchange in the substitution reaction, further disordering the system.

**Analysis of mercury(II) complexes**

The mercury(II) complexes showed variations in the first coordination sphere due to the loss of one or more aqua ligands. As discussed in the previous section, the cadmium(II) complexes did not present this trend. Optimized structures of cationic mercury(II) complexes, using the M06L functional are presented in Figure 7. Only in the cationic complexes with n-butyl and n-pentyl xanthate ([HgL2(OH)₂]⁺·2H₂O-MD and [HgL3(OH)₂]⁺·MD in) (Figures 7b, 7c), the hydrogen bond was formed between the oxygen of the xanthate and the hydrogen of the aqua ligand. Table 2 shows that the complex [HgL1(OH)₂]⁺·H₂O-MD presented higher ΔG₂⁹⁸ (−215.33 kcal mol⁻¹) when compared to the [HgL2(OH)₂]⁺·MD in and [HgL3(OH)₂]⁺·MD in complexes, which have values of −192.18 and −193.96 kcal mol⁻¹, respectively. This difference in ΔG₂⁹⁸ values is associated with the higher entropy observed for the [HgL1(OH)₂]⁺·H₂O-MD complex due to the loss of the aqua ligand from the first coordination sphere, which caused the increased disorder of the system. Moreover, the optimized structures of the cationic complexes [HgL1(OH)₂]⁺·B, [HgL2(OH)₂]⁺·B, and [HgL3(OH)₂]⁺·B (Figures 7d-7f) showed the formation of the bidentate coordination, differently the analogous cadmium(II) complexes (Figures 4d-4f), which were monodentate MD-type. The structural differences will be better discussed in “Geometrical parameters” sub-section.
Table 2 also shows that the cationic complexes of the [HgL(OH$_2$)$_2$]$^+$-B type (Figures 7d-7f) exhibited ΔH and ΔG$^{298}$ values about 9.89 ± 0.59 and 11.87 ± 3.47 kcal mol$^{-1}$ higher than the monodentate complexes (Figures 7a-7c). Furthermore, a comparison between the [HgL(OH$_2$)$_2$]$^+$-B and [CdL(OH$_2$)$_2$]$^+$-MD type shows that the mercury(II) complexes with seven-coordination have higher ΔG$^{298}$ values, with an average of −212.36 ± 11.20 kcal mol$^{-1}$ (Table 2) when compared to cadmium(II) complexes (−188.77 ± 3.85 kcal mol$^{-1}$, Table 1). For monodentate complexes, only [HgL$_n$(OH$_2$)$_n$]$^+$·H$_2$O-MD did not exhibit a hydrogen bond between the xanthate’s oxygen atom and the aqua ligand’s hydrogen, as described in “Geometrical parameters” sub-section.

The monodentate neutral mercury(II) complexes structures were optimized using the M06L functional (Figure 8). The structures also showed differences from the analogous cadmium(II) complexes due to the trend of breaking one or two Hg–OH$_2$ bonds. Only the cis-[HgL(OH$_2$)$_2$]$^+$-MD$_{im}$ and [HgL(OH$_2$)$_2$]$^+$-H$_2$O-MD$_{im}$ complexes showed hydrogen bond formation, following the same trend as the cationic complexes. A detailed analysis of the geometric parameters is described in “Geometrical parameters” sub-section.

The thermochemical parameters for the monodentate mercury(II) neutral complexes show that the cis-[HgL(OH$_2$)$_2$]$^+$-MD$_{im}$ and [HgL(OH$_2$)$_2$]$^+$-H$_2$O-MD$_{im}$ complexes presented higher spontaneity of formation, with ΔG$^{298}$ values of −114.28 and −110.84 kcal mol$^{-1}$, respectively (Table 2), when compared to the analogous MD complexes (cis-[HgL(OH$_2$)$_2$]$^+$-MD and [HgL(OH$_2$)$_2$]$^+$-H$_2$O-MD).

For the monodentate neutral complexes with the ligands n-propyl (L1) and n-pentyl (L3) xanthates (Figures 8a, 8c, 8d, and 8f), it was observed higher ΔG$^{298}$ values (−139.17 ± 0.01 kcal mol$^{-1}$, for L1 complexes and −113.46 ± 1.12 kcal mol$^{-1}$, for L3 complexes), compared with the monodentate complexes (−130.79 ± 0.85 kcal mol$^{-1}$, for L1 complexes and −97.26 ± 2.07 kcal mol$^{-1}$, for L3 complexes) in the Figures 8g and 8i.

Finally, the optimized structures for the bidentate neutral mercury(II) complexes with the M06L functional (Figure 9) were analyzed. Mercury(II) complexes tended to break the M–OH$_2$ bond, as observed in monodentate mercury(II) complexes, but in contrast to the analogous cadmium(II) complexes. Therefore, higher entropies were observed in mercury(II) complexes (23.13 ± 8.64 kcal mol$^{-1}$) than in cadmium(II) complexes (12.66 ± 3.82 kcal mol$^{-1}$). The higher entropy resulted in more negative ΔG$^{298}$ values in the bidentate mercury(II) complexes (ΔG$^{298}$ = −124.70 ± 9.77 kcal mol$^{-1}$) than in the analogous cadmium(II) complexes (ΔG$^{298}$ = −109.52 ± 3.83 kcal mol$^{-1}$). Furthermore, trans-[HgL$_2$(OH$_2$)$_2$]-B/MD complex shows ring formation with just one xanthate ligand (Figure 9d). However, the thermochemical parameters did not demonstrate significant

**Figure 8.** Optimized structures of monodentate neutral complexes: (a) [HgL$_n$(OH$_2$)$_n$]$^+$·H$_2$O-MD; (b) cis-[HgL(OH$_2$)$_2$]$^+$-MD$_{im}$; (c) [HgL$_2$(OH$_2$)$_2$]$^+$·H$_2$O-MD; (d) [HgL$_2$(OH$_2$)$_2$]$^+$·2H$_2$O-MD; (e) [HgL(OH$_2$)$_2$]$^+$-H$_2$O-MD$_{im}$; (f) [HgL(OH$_2$)$_2$]$^+$-2H$_2$O-MD; (g) [HgL(OH$_2$)$_2$]$^+$·H$_2$O-B/MD; (h) cis-[HgL$_2$(OH$_2$)$_2$]$^+$-MD; (i) cis-[HgL(OH$_2$)$_2$]$^+$-MD; (j) trans-[HgL(_1)$_2$(OH$_2$)$_2$]$^+$-MD; (k) [HgL$_2$(OH$_2$)$_2$]$^+$·H$_2$O-MD; (l) [HgL(OH$_2$)$_2$]$^+$·H$_2$O-MD.
differences in the obtained results (Table 2). The distances of the Hg–L bonds are better discussed in “Geometrical parameters” sub-section.

A comparison between the complexes of cadmium(II) and mercury(II) shows a higher formation trend of the xanthate complexes with the ion Hg$^{2+}$. This is observed through the $\Delta H$ and $\Delta G_{298}$ values of mercury(II) monodentate complexes, which show energies 3.48 and 11.88 kcal mol$^{-1}$ higher than analogs cadmium(II) complexes. The same trend was observed for the bidentate complexes, in which mercury(II) complexes showed energies of 4.72 and 15.18 kcal mol$^{-1}$ higher than bidentate cadmium(II) complexes. In the case of ligands, considerable differences were not observed in mercury(II) and cadmium(II) complexes since the difference between the carbonic chains is only the addition of the methyl group.

Geometrical parameters

The Cd–S and Hg–S distances were evaluated for the complexes studied using the M06L functional. Moreover, the distances between the atoms involved in the hydrogen bonds and S–OH$^2$ interactions are described in the next sections.

Hydrogen bond analysis

The distances between the xanthate’s oxygen and the hydrogen from aqua ligands were analyzed to confirm the presence or absence of hydrogen bonds in the monodentate complexes. For this purpose, the distances between the oxygen and hydrogen atoms obtained in the calculations were compared with the van der Waals radius sum. Hydrogen bonds were considered when the distances had a value smaller than the sum of this radius. The sum of the van der Waals radius between oxygen (1.42 Å) and hydrogen (1.06 Å), reported in the literature, was 2.48 Å.\cite{57} Tables S3 and S4 (SI section) show the O–H distances for the monodentate neutral and cationic cadmium(II) complexes. The distances in the range (1.992-2.010 Å) were observed between the oxygen of the xanthate and hydrogen atom of aqua ligands in the cationic MD$_{HB}$ complexes (Figures 4a-4c, Table S3). These interactions are hydrogen bonds because the observed value was below the van der Waals radius sum. The O–H distances (Table S3) in the case of the monodentate cationic cadmium(II) complexes, Table S4 shows that the O–H distances in the MD complexes, the values were 3.904-4.671 Å. This confirms the occurrence of hydrogen bonds only in the MD$_{HB}$ complexes, which can be verified in Figures 4 and 5. Furthermore, S–H interactions (Table S4) were observed in the monodentate neutral complexes MD since the distance between the sulfur and hydrogen is in the range 2.274-2.624 Å, which is below the sum of the van der Waals radius of sulfur (1.80 Å) and hydrogen (1.06 Å), of 2.86 Å.\cite{57} The S–H interaction was also observed in the monodentate neutral complexes MD$_{HB}$, between the sulfur of the second xanthate (that is not making the O–H interaction) and the hydrogens of the aqua ligand.

The monodentate mercury(II) complexes showed optimization structures with different trends than the monodentate cadmium(II) complexes, as mentioned in “Analysis of mercury (II) complexes” sub-sections. In the case of the monodentate cationic mercury(II) complexes (Figure 7), [HgL(OH)$^2$)$_3]^+$ complexes were obtained only with the $n$-butyl (L2) and $n$-pentyl (L3) xanthate ligands, where the average of the distances between the oxygen atoms of the xanthate and hydrogen of the aqua ligands was 2.033-2.062 Å, in the [HgL2(OH)$^2$)$_3]^+$ and [HgL3(OH)$^2$)$_3]^+$ complexes (Table S5, SI section). In the case of the [HgL1(OH)$^2$)$_4]^+\cdot$H$_2$O-MD complex, distances with an average of 3.540 ± 0.197 Å were observed. The absence of a hydrogen bond between

Figure 9. Optimized structures: (a) [HgL1$_2$(OH)$_2$].H$_2$O-B; (b) [HgL2$_2$(OH)$_2$].H$_2$O-B; (c) [HgL3$_2$(OH)$_2$].H$_2$O-B; (d) trans-[HgL1$_2$(OH)$_2$].B/MD; (e) trans-[HgL2$_2$(OH)$_2$].B; (f) trans-[HgL3$_2$(OH)$_2$].B. Hydrogen bond in blue dashed lines.
the oxygen of the xanthate and the H of the aqua ligand in this complex is due to the rupture of the Hg–O (OH₂) bond, which remained in the system through hydrogen bonds with the other aqua ligand. In the case of the monodentate neutral mercury(II) complexes, hydrogen bonds between the oxygen of the xanthate and the hydrogen of the aqua ligand were only observed in the complexes with the n-butyl xanthate ligand (L2) (Figures 8b and 8e). Table S6 (SI section) shows that the distances between these atoms were 1.959 and 1.998 Å for the cis-[Hg(L2)₂(OH₂)₂]-MD₄⁰ and [Hg(L2)₂(OH₂)₃]H₂O-MD₄⁰ complexes, respectively. [Hg(L1)₂(OH₂)₃]H₂O-MD, [Hg(L3)₂(OH₂)₃]H₂O-MD, [Hg(L1)₂(OH₂)₃]H₂O-MD, and [Hg(L3)₂(OH₂)₃]2H₂O-MD complexes (Figures 8a, 8c, 8d, and 8f) did not show hydrogen bonds between the xanthate and aqua ligands since the H–O distances of 1.959 Å). In these neutral complexes, ruptures of the Hg–O bond were observed (Figures 9a–9d), which resulted in a hydrogen bond between the uncoordinated water molecule and the aqua ligand without interaction with the xanthate ligand. As for the cadmium(II) complexes, H–S interactions were observed in all the monodentate complexes analyzed, with a range of 2.432–2.623 Å (Table S6).

**Metal-ligand bonds analysis**

M–L distances obtained in the optimized structures are analyzed and compared with those observed in crystalline structures reported in the literature. The monodentate cadmium(II) complexes showed that the Cd–S bond is slightly shorter in the cationic complexes than in neutral complexes (Table S7). This is due to the higher electrostatic attraction of the M–L bond in cationic complexes compared to the neutral complexes, as shown in “Energy decomposition analysis (EDA)” sub-section. This higher Cd–S bond approximation in the monodentate cationic complexes corroborates with the thermochemical data observed in “Optimization structures and thermochemical studies” sub-section. These complexes showed higher enthalpy and Gibbs free energy values than neutral complexes. Furthermore, Table S7 shows that the Cd–S distances ranged from 2.502–2.513 Å for MD₄⁰ monodentate cationic complexes, calculated through the M06L functional. In the case of MD monodentate cationic complexes, the Cd–S distance range was 2.577–2.587 Å. A comparison of the Cd–S distances observed in crystal structures (2.64–2.73 Å) and the calculated distances in this work shows values close to those observed experimentally. In the case of the Cd–O bonds (Table S8, SI section), distances of 2.386–2.773 Å were observed for the monodentate cationic complexes. Crystal structures described in the literature point to a range of 2.33–2.46 Å for these bonds, and the results with this functional indicated minor accuracy.

An overall analysis of the monodentate neutral cadmium(II) complexes shows that the Cd–S distances (Table S7) agree with the range 2.64–2.73 Å of the experimental works. This is because the monodentate neutral complexes showed a range of 2.594–2.701 Å for the Cd–S bond in calculations. A comparative analysis between the MD₄⁰ and MD monodentate cationic and neutral complexes shows that the Cd–S bond is slightly higher for the MD-type complexes. This is due to a higher repulsion observed in the MD monodentate complexes compared to the MD₄⁰ complexes, as discussed in “Energy decomposition analysis (EDA)” sub-section. This repulsion causes the M–L bond distance to be longer for these complexes and the stabilization trend to be lower than that of MD₄⁰ complexes, as indicated by the thermochemical parameters in “Optimization structures and thermochemical studies” sub-section. Moreover, no significant difference was observed between the Cd–S distances of the cis and trans complexes. In the case of the monodentate MD₄⁰ complexes, a difference of 0.021 Å was observed between the cis and trans complexes. For the monodentate MD complexes, a smaller difference of 0.005 Å was observed between the cis and trans complexes. This indicates that the difference in geometric isomerism does not considerably influence the description of monodentate MD complexes. This observation was noticed in the thermochemical analysis of “Optimization structures and thermochemical studies” sub-section.

The complexes calculated with the M06L presented a Cd–O distance range of 2.379–2.518 Å, as observed in Table S8. The bond distance values agree with what was observed experimentally in the literature (2.33–2.46 Å). A general comparison between the cationic and neutral complexes indicates that the Cd–O distances were slightly longer in the neutral complexes than in the cationic complexes. This is because there is the presence of more aqua ligands and less xanthate in the cationic complexes than in the neutral complexes.

The bidentate cationic and neutral cadmium(II) complexes were also evaluated. Table S9 (SI section) illustrates the values of the Cd–S and Cd–O distances. All the Cd–S distances are within the experimentally observed range of 2.64–2.73 Å. Our research group has obtained Cd–S distances of 2.546 Å in previous work. The bidentate complexes showed higher Cd–S distance values than the monodentate complexes, with ranges of 2.683–2.699 Å (Table S9). This longer Cd–S distance tendency occurs...
due to the approximation of two sulfur atoms in each xanthate ligand to the metal center. Since sulfur is a larger atom than oxygen, the approximation of two sulfur atoms to the metal center is less effective when compared to the monodentate system. Table S9 shows a Cd–O distance range of 2.448–2.504 Å for the bidentate neutral complexes. However, it showed values close to the range of 2.33–2.46 Å found for the Cd–O bond in the crystal structures. Those longer Cd–O distances in the bidentate complexes occur because the aqua ligand finds a higher stereochemical hindrance when approximating the metal center due to the higher number of Cd–S bonds in the bidentate complexes when compared to the monodentate complexes.

The M–L bond was also analyzed for the cationic and neutral mercury(II) complexes with the M06L functional (Tables S10-S12, SI section). The optimization structures of the cationic mercury(II) complexes (Figure 7) showed that there was the formation of the bidentate complexes [HgL(OH)₂]⁺-B and [HgL(OH)₂]⁺-B type, differently from the cationic cadmium(II) complexes, which only converged to the last type. A comparison between the monodentate and bidentate cationic complexes of the [HgL(OH)₂]⁺-B type shows that the Hg–S distances were longer in the bidentate complexes, with an average of 2.693 ± 0.000 Å. In contrast, the monodentate complexes showed values of 2.503 ± 0.013 Å. The higher Hg–S distance is due to the high coordination number, especially with the presence of two sulfur atoms, which causes a higher repulsion. On the other hand, the Hg–S distances were similar between the two types of bidentate complexes, [HgL(OH)₂]⁺-B (2.693-2.694 Å) and [HgL(OH)₂]⁺-B (2.655-2.664 Å) (Tables S10 and S12). All the Hg–S bonds of the cationic complexes showed values that are comparable with the crystal structures data, whose Hg–S distance range is 2.41-2.84 Å. ⁶¹

The monodentate neutral complexes showed Hg–S distances within the range observed experimentally, ⁶¹ even with the change of coordination sphere. Table S10 shows that the [HgL(L₂)₂(H₂O)-MD complex has a smaller Hg–S distance than the cis-[HgL(L₃)₂(OH₂)]-MD complex. The same trend is observed for the cis complexes with L₁, where the complex has fewer aqua ligands bound to the metal center and smaller Hg–S distances. This indicates a better superposition between the orbitals involved in the Hg–S bond due to the better proximity of the sulfur atoms to the metal center. Thus, better organization of the coordination sphere corroborates the thermochemical results through the ΔG values obtained by the loss of aqua ligands (“Analysis of mercury(II) complexes” sub-section).

Table S11 (SI section) for monodentate cationic and neutral complex presents Hg–O distances range of 2.549-2.742 Å for the M06L functional. These values are above those observed in experimental work (2.26-2.54 Å). ⁶² In a recent study developed by our research group, ⁶³ Hg–OH₂ distances were obtained with a range of 2.200-2.300 Å. The longer distances obtained in the complexes analyzed in this work are also associated with a higher amount of aqua ligands around the metal center when compared to the previous study.

The conclusion of the coordination sphere analysis of the mercury complexes was carried out for the bidentate systems. The trans-[HgL(L₁)₂(OH₂)]-B/MD (Figures 9d) complex was the only one that did not present the two ligands in bidentate coordination mode. The monodentate ligand showed a distance between one sulfur atom and the metal center of 3.106 Å, above the range observed in the literature of 2.41-2.84 Å. ⁶¹ The other Hg–S bonds observed in the bidentate neutral complexes showed distances within the expected range, in agreement with the experimental data ⁶⁴ (Table S12). In the case of the bidentate cationic complexes, the Hg–S distances were shorter, with ranges of 2.655-2.664 Å. Furthermore, when cis precursor complexes were used, the bidentate complexes also tended to break one Hg–OH₂ bond. However, the trans complexes showed Hg–O distance ranges higher than expected in the literature (2.26-2.54 Å), ⁶² with values of 2.606-2.639 Å.

**Charge analysis**

Mulliken (MPA) and Natural (NPA) Population Analyses were also performed through the M06L functional to better understand the M–L bonds in the complexes studied. The results of Mulliken (Table S13, SI section) and NPA (Table S14, SI section) for the cadmium(II) complexes show that the Cd²⁺ ion has positive values in all complexes. In NPA atomic charge values, it is observed that the cationic complexes exhibited higher charges when compared to the neutral complexes. Average charges on the Cd²⁺ ion of 1.510 ± 0.013, 1.527 ± 0.030, and 1.536 ± 0.033 e⁻ were observed for the monodentate neutral complexes and 1.564 ± 0.007, 1.561 ± 0.018, and 1.572 ± 0.006 e⁻ for the monodentate cationic complexes with L₁, L₂, and L₃, respectively. For the bidentate complexes, the same trends were observed in the NPA, where the neutral complexes exhibited an average positive charge on Cd²⁺ of 1.442 ± 0.002 e⁻, while the cationic complexes exhibited charges of 1.553 ± 0.003 e⁻. Also, through NPA, it was possible to verify that all the cadmium(II) complexes studied showed negative charges on the SCS fragment, with a charge range between −0.399 and −0.628 e⁻. In addition, no significant differences in the SCS fragment charges were observed among the ligands analyzed, which
indicates that the calculation was not sensitive to the compounds analyzed. Despite this, the results obtained from the NPA for cadmium(II) complexes agreed with the expected trends.

Mulliken and Natural Population Analyses were also evaluated for the mercury(II) complexes (Tables S15 and S16, SI section). Similar to the cadmium(II) complexes, NPA for mercury(II) complexes showed the same trend of higher positive charges on Hg$^{2+}$ ion in the cationic complexes compared to the neutral ones. For monodentate neutral complexes, averages of $1.254 \pm 0.024$, $1.275 \pm 0.065$, and $1.256 \pm 0.050$ $e^-$ were observed for the complexes with L1, L2, and L3, respectively. On the other hand, the monodentate cationic complexes exhibited higher values of $1.324 \pm 0.042$, $1.328 \pm 0.035$, and $1.312 \pm 0.060$ $e^-$.

In the case of the bidentate complexes, charges on the Hg$^{2+}$ ion of $1.226 \pm 0.004$ and $1.330 \pm 0.001$ $e^-$ were observed for the neutral and cationic complexes, respectively. These trends agree with what was observed in the thermochemical parameters (“Optimization studies and thermochemical studies” sub-section), in which the cationic complexes showed higher ΔH and ΔG$^{298}$ values than the neutral complexes. This is due to the higher electrostatic attraction between the metal center and the xanthate ligands in the cationic complexes, as shown in the energy decomposition analysis (“Energy decomposition analysis (EDA)” sub-section). Besides, the MPA (Tables S13 and S15) did not correspond to the results observed in the NPA because it overestimated the covalent character of the bond and also presented large charge variations with small changes in the basis sets applied. Tables S13 and S16 show that although the charges for the Cd$^{2+}$ and Hg$^{2+}$ ions are positive, there is no propensity for the charges to be higher in the cationic complexes, which does not agree with the thermochemical trends obtained. As with the cadmium(II) complexes, the SCS fragment also showed negative values in the mercury(II) complexes (Tables S15 and S16). These results indicate that the SCS fragment has electrons to be donated to the metal center, acting as Lewis bases. Figure 10 illustrates the highest occupied molecular orbital (HOMO) orbitals (p-type orbital) of the n-propyl (L1), n-butyl (L2), and n-pentyl (L3) xanthate ligands.

Energy decomposition analysis (EDA)

The complexes studied were analyzed according to the decomposition of energies, as described in equations 1 and 2. The interaction energies between the reagents (aqua complex and xanthate ligand) of the first substitution reaction were evaluated in the cationic cadmium(II) complexes (Table 3). The higher values for the electrostatic component corroborate with the thermochemical analysis of these compounds, in which high values of ΔH and ΔG$^{298}$ were observed, indicating a strong electrostatic interaction between the species. The electrostatic component average in the monodentate cationic complexes was $-172.17 \pm 0.53$ kcal mol$^{-1}$ for the MD$_{begin{array}{c}3 \end{array}}$ complexes and $-192.83 \pm 0.69$ kcal mol$^{-1}$ for the MD complexes. The monodentate complexes’ average covalent ($E_{ax}$ + $E_{bx}$ + $E_{h}$) component was $-121.86 \pm 1.23$ and $-120.57 \pm 0.39$ kcal mol$^{-1}$ for the MD$_{begin{array}{c}3 \end{array}}$ and MD complexes, respectively. In the case of bidentate complexes, higher values of the electrostatic component were also observed, with a difference of ca. $66.78 \pm 1.04$ kcal mol$^{-1}$ in the covalent component. This high electrostatic energy confers a total interaction energy elevated (Table 3).

A comparison between the MD$_{begin{array}{c}3 \end{array}}$ and MD monodentate cationic complexes also confirms the trend observed in the thermochemical analysis, in which the MD cationic complexes presented higher values of ΔH and ΔG$^{298}$. MD complexes have larger electrostatic interaction energies ($20.66 \pm 1.10$ kcal mol$^{-1}$) than MD$_{begin{array}{c}3 \end{array}}$ complexes. This larger attractive electrostatic force results in a higher enthalpy of CD–S interaction in these complexes, making the formation of these systems more spontaneous than in the MD$_{begin{array}{c}3 \end{array}}$ complexes.

Table 4 presents the values of the energies obtained through the EDA for the neutral cadmium(II) complexes. A comparison between Tables 3 and 4 shows that the electrostatic energies of the neutral complexes are smaller than the electrostatic energies of the cationic complexes. This is reflected in the decrease in ionic contribution between the complexes of the first and second substitution reactions since the values obtained were $65.40 \pm 0.73$, $77.96 \pm 5.48$ and $78.71 \pm 1.51$ kcal mol$^{-1}$ for the monodentate

![Figure 10. HOMO canonic orbitals of the ligands: (a) n-propyl xanthate (L1); (b) n-butyl xanthate (L2); (c) n-pentyl xanthate (L3).](image-url)
MD$_{inh}$, MD, and bidentate complexes, respectively. The thermochemical and NPA analyses agree with this result, in which the neutral complexes showed lower enthalpy and Gibbs free energies values than the cationic complexes. Moreover, the cationic complexes exhibited higher positive charges on the metal ion compared with the neutral complexes. A higher repulsion is observed in the MD complexes (65.037 ± 7.090 kcal mol$^{-1}$) in comparison to the MD$_{inh}$ complexes (61.781 ± 8.205 kcal mol$^{-1}$) (Table 4). This result also supports the thermochemical parameters discussed. Finally, a comparison between the bidentate and monodentate complexes shows that the bidentate complexes had higher total interaction energy, with an average of $-158.633 ± 1.020$ kcal mol$^{-1}$, while the monodentate complexes had an average total energy of $-147.209 ± 4.420$ kcal mol$^{-1}$. This agrees with

### Table 3. Energies obtained by calculating EDA for monodentate, and bidentate cationic cadmium(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>MD$^a$</th>
<th>ES$^b$ / (kcal mol$^{-1}$)</th>
<th>EX$^b$ / (kcal mol$^{-1}$)</th>
<th>REP$^b$ / (kcal mol$^{-1}$)</th>
<th>POL$^b$ / (kcal mol$^{-1}$)</th>
<th>DIS$^b$ / (kcal mol$^{-1}$)</th>
<th>Et$^b$ / (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>[CdL1(OH)$_3$]$^+$</td>
<td>–172.57</td>
<td>–0.56</td>
<td>55.70</td>
<td>–74.86</td>
<td>–46.01</td>
<td>–238.29</td>
<td></td>
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<tr>
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<td>–172.37</td>
<td>–0.53</td>
<td>54.86</td>
<td>–76.68</td>
<td>–46.04</td>
<td>–240.76</td>
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<td>[CdL3(OH)$_3$]$^+$</td>
<td>–171.57</td>
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<td>54.39</td>
<td>–74.92</td>
<td>–46.26</td>
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<td>MD$^a$</td>
<td>ES$^b$ / (kcal mol$^{-1}$)</td>
<td>EX$^b$ / (kcal mol$^{-1}$)</td>
<td>REP$^b$ / (kcal mol$^{-1}$)</td>
<td>POL$^b$ / (kcal mol$^{-1}$)</td>
<td>DIS$^b$ / (kcal mol$^{-1}$)</td>
<td>Et$^b$ / (kcal mol$^{-1}$)</td>
</tr>
<tr>
<td>[CdL1(OH)$_3$]$^+$</td>
<td>–192.04</td>
<td>–1.78</td>
<td>56.32</td>
<td>–76.15</td>
<td>–42.28</td>
<td>–255.93</td>
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<tr>
<td>[CdL2(OH)$_3$]$^+$</td>
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<td>57.68</td>
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<td>–76.71</td>
<td>–42.93</td>
<td>–255.91</td>
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</tbody>
</table>

$^a$L1: n-propyl xanthate; L2: n-butyl xanthate; L3: n-pentyl xanthate; $^b$MD$_{inh}$: monodentate with hydrogen bond; MD: monodentate without hydrogen bond; B: bidentate; ES: electrostatic; EX: exchange; REP: Pauli repulsion; POL: polarization; DIS: dispersion; Et: total interaction energy.

### Table 4. Energies obtained by calculating EDA for monodentate, and bidentate neutral cadmium(II) complexes

<table>
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<tr>
<th>Complex</th>
<th>MD$^a$</th>
<th>ES$^b$ / (kcal mol$^{-1}$)</th>
<th>EX$^b$ / (kcal mol$^{-1}$)</th>
<th>REP$^b$ / (kcal mol$^{-1}$)</th>
<th>POL$^b$ / (kcal mol$^{-1}$)</th>
<th>DIS$^b$ / (kcal mol$^{-1}$)</th>
<th>Et$^b$ / (kcal mol$^{-1}$)</th>
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<tr>
<td>cis-[CdL1$_2$(OH)$_3$]</td>
<td>–117.66</td>
<td>–10.6</td>
<td>76.49</td>
<td>–63.38</td>
<td>–34.07</td>
<td>–149.22</td>
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<tr>
<td>trans-[CdL1$_2$(OH)$_3$]</td>
<td>–98.28</td>
<td>0.26</td>
<td>51.55</td>
<td>–53.96</td>
<td>–41.84</td>
<td>–142.28</td>
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<tr>
<td>cis-[CdL2$_2$(OH)$_3$]</td>
<td>–100.36</td>
<td>2.72</td>
<td>60.12</td>
<td>–55.34</td>
<td>–51.19</td>
<td>–144.04</td>
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<td>trans-[CdL3$_2$(OH)$_3$]</td>
<td>–112.84</td>
<td>6.67</td>
<td>61.97</td>
<td>–51.70</td>
<td>–52.02</td>
<td>–147.92</td>
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<tr>
<td>Complex</td>
<td>MD$^a$</td>
<td>ES$^b$ / (kcal mol$^{-1}$)</td>
<td>EX$^b$ / (kcal mol$^{-1}$)</td>
<td>REP$^b$ / (kcal mol$^{-1}$)</td>
<td>POL$^b$ / (kcal mol$^{-1}$)</td>
<td>DIS$^b$ / (kcal mol$^{-1}$)</td>
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<td>–54.97</td>
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<tr>
<td>cis-[CdL2$_2$(OH)$_3$]</td>
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<td>–56.04</td>
<td>–35.79</td>
<td>–145.20</td>
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<tr>
<td>trans-[CdL2$_2$(OH)$_3$]</td>
<td>–119.71</td>
<td>–3.83</td>
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<td>–44.03</td>
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<td>–6.56</td>
<td>71.27</td>
<td>–55.90</td>
<td>–35.76</td>
<td>–144.91</td>
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<td>trans-[CdL3$_2$(OH)$_3$]</td>
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<td>63.13</td>
<td>–53.24</td>
<td>–37.48</td>
<td>–147.53</td>
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<tr>
<td>Complex</td>
<td>MD$^a$</td>
<td>ES$^b$ / (kcal mol$^{-1}$)</td>
<td>EX$^b$ / (kcal mol$^{-1}$)</td>
<td>REP$^b$ / (kcal mol$^{-1}$)</td>
<td>POL$^b$ / (kcal mol$^{-1}$)</td>
<td>DIS$^b$ / (kcal mol$^{-1}$)</td>
<td>Et$^b$ / (kcal mol$^{-1}$)</td>
</tr>
<tr>
<td>cis-[CdL3$_2$(OH)$_3$]</td>
<td>–105.69</td>
<td>–7.60</td>
<td>56.28</td>
<td>–64.42</td>
<td>–35.39</td>
<td>–156.82</td>
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<tr>
<td>cis-[CdL3$_2$(OH)$_3$]</td>
<td>–110.21</td>
<td>–5.89</td>
<td>57.29</td>
<td>–62.20</td>
<td>–37.18</td>
<td>–158.19</td>
<td></td>
</tr>
</tbody>
</table>

$^a$L1: n-propyl xanthate; L2: n-butyl xanthate; L3: n-pentyl xanthate; $^b$MD$_{inh}$: monodentate with hydrogen bond; MD: monodentate without hydrogen bond; B: bidentate; ES: electrostatic; EX: exchange; REP: Pauli repulsion; POL: polarization; DIS: dispersion; Et: total interaction energy.
the thermochemical analysis (“Optimization structures and thermochemical studies” sub-section), in which the bidentate complexes showed higher $\Delta G^{298}$ values.

As mentioned, the second substitution reaction also has a considerable electrostatic character since the reaction occurs between positive and negative-charged species. However, the energy values obtained through the EDA show that this interaction has no predominantly electrostatic character. The average electrostatic contribution to the formation of neutral cadmium(II) complexes was $-106.76 \pm 8.75$ kcal mol$^{-1}$ for the MD$_{\text{bidentate}}$ complexes, $-114.87 \pm 5.93$ kcal mol$^{-1}$ for the monodentate MD complexes, and $-109.08 \pm 2.14$ kcal mol$^{-1}$ for the bidentate complexes. The average for the covalent contribution in MD$_{\text{monodentate}}$, MD, and bidentate species is $-99.34 \pm 4.81$, and $-106.97 \pm 3.38$ kcal mol$^{-1}$, respectively. The difference between the electrostatic and covalent contributions in the neutral complexes is small, with approximately the same contribution of covalent and ionic Cd–S interaction, in contrast with cationic complexes (Figure 11).

After that, the EDA calculations for the mercury(II) complexes were performed as presented in Tables 5 and 6. The analysis of cationic complexes was performed between the fragments [Hg(OH$_2$)$_5$]$^{2+}$ or [Hg(OH$_2$)$_4$]$^{2+}$ .H$_2$O with the xanthate ligand. The analyzed fragments for the monodentate neutral complexes were [HgL(OH$_2$)$_4$]$^+$ or its various hydrated species with the xanthate ligand. For bidentate neutral complexes, the analyzed fragments were [HgL(OH$_2$)$_2$]$^+$ or [HgL(OH$_2$)$_3$]$.\text{H}_2\text{O}$ with the xanthate ligand.

Table 5 presents the values of the energies obtained for cationic mercury(II) complexes. As seen in the optimized structures of these complexes in Figure 7, the monodentate MD$_{\text{bidentate}}$ complex formed only with the L$_2$ ligand (Figure 7b), differently from the cationic cadmium(II) complexes. However, Hg$^{2+}$ exhibited two types of bidentate cationic complexes: [HgL(OH$_2$)$_5$]$^{-}$-B and [HgL(OH$_2$)$_4$]$^{-}$-B. The monodentate cationic complexes showed lower electrostatic energy than the bidentate cationic complexes, with values of $-166.817 \pm 3.292$, $-187.167 \pm 0.185$ and $-188.873 \pm 3.245$ kcal mol$^{-1}$ for the monodentates, [HgL(OH$_2$)$_5$]$^{-}$-B and [HgL(OH$_2$)$_4$]$^{-}$-B complexes, respectively. The total interaction energy for these complexes exhibited a trend proportional to that observed in the electrostatic energy, with values of $-261.023 \pm 2.041$, $-268.273 \pm 0.130$ and $279.980 \pm 3.484$ kcal mol$^{-1}$ for the monodentates, [HgL(OH$_2$)$_5$]$^{-}$-B and [HgL(OH$_2$)$_4$]$^{-}$-B complexes, respectively. As for the cadmium(II) cationic complexes, the mercury(II) complexes showed a higher electrostatic than covalent character, which indicates a strong electrostatic contribution to the M–L bond. However, the difference between the ionic and covalent character in the mercury(II) complexes was smaller than the difference in the cadmium(II) complexes. In the case of the monodentate cationic cadmium(II) complexes, a difference of 50.30, 72.26, and 66.78 kcal mol$^{-1}$ was observed for the MD$_{\text{bidentate}}$, MD, and bidentate complexes. In the cationic mercury(II) complexes, the difference between the ionic and covalent character was 21.20, 14.16, 44.97, and 22.80 kcal mol$^{-1}$ for the MD$_{\text{bidentate}}$, MD, [HgL(OH$_2$)$_5$]$^{-}$-B and [HgL(OH$_2$)$_4$]$^{-}$-B complexes, respectively. This indicates that the Hg–S bond has a larger covalent contribution than the Cd–S bond.

As with the monodentate cationic complexes, the monodentate neutral mercury(II) complexes showed hydrogen bond formation between the xanthate and...
Theoretical Studies of Xanthates in Heavy Metal Complexation

Table 5. Energies obtained by calculating EDA for monodentate, and bidentate cationic mercury(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>ES' / (kcal mol⁻¹)</th>
<th>EX' / (kcal mol⁻¹)</th>
<th>REP / (kcal mol⁻¹)</th>
<th>POL / (kcal mol⁻¹)</th>
<th>DIS / (kcal mol⁻¹)</th>
<th>Et / (kcal mol⁻¹)</th>
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<tr>
<td>[HgL1(OH)₂]⁺·H₂O-MD</td>
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<td>[HgL2(OH)₂]⁺·MD</td>
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<tr>
<td>[HgL3(OH)₂]⁺·MD</td>
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<td>−105.06</td>
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<td>−261.40</td>
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<tr>
<td>Complex</td>
<td>ES' / (kcal mol⁻¹)</td>
<td>EX' / (kcal mol⁻¹)</td>
<td>REP / (kcal mol⁻¹)</td>
<td>POL / (kcal mol⁻¹)</td>
<td>DIS / (kcal mol⁻¹)</td>
<td>Et / (kcal mol⁻¹)</td>
</tr>
<tr>
<td>[HgL1(OH)₂]-B</td>
<td>−187.38</td>
<td>−5.87</td>
<td>61.06</td>
<td>−96.82</td>
<td>−39.16</td>
<td>−268.17</td>
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<td>[HgL2(OH)₂]-B</td>
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<td>61.29</td>
<td>−97.89</td>
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<td>−268.23</td>
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Table 6. Energies obtained by calculating EDA for monodentate, and bidentate neutral mercury(II) complexes

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<tr>
<th>Complex</th>
<th>ES' / (kcal mol⁻¹)</th>
<th>EX' / (kcal mol⁻¹)</th>
<th>REP / (kcal mol⁻¹)</th>
<th>POL / (kcal mol⁻¹)</th>
<th>DIS / (kcal mol⁻¹)</th>
<th>Et / (kcal mol⁻¹)</th>
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<td>[HgL1(OH)₃]⁻·H₂O-MD</td>
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<td>64.09</td>
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<td>[HgL1(OH)₃]⁻·2H₂O-MD</td>
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<td>84.26</td>
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<td>−54.91</td>
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<td>−71.41</td>
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<td>0.22</td>
<td>70.12</td>
<td>−74.79</td>
<td>−56.61</td>
<td>−157.75</td>
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<tr>
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<td>−6.84</td>
<td>71.01</td>
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<th>EX' / (kcal mol⁻¹)</th>
<th>REP / (kcal mol⁻¹)</th>
<th>POL / (kcal mol⁻¹)</th>
<th>DIS / (kcal mol⁻¹)</th>
<th>Et / (kcal mol⁻¹)</th>
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<td>−37.68</td>
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<td>69.85</td>
<td>−70.31</td>
<td>−36.33</td>
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<tr>
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<td>−10.06</td>
<td>75.16</td>
<td>−60.94</td>
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<td>68.5</td>
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<td>−38.38</td>
<td>−156.72</td>
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<tr>
<td>cis-[HgL3(OH)₃]⁻·MD</td>
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<td>−9.93</td>
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<td>−60.91</td>
<td>−34.62</td>
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<td>[HgL3(OH)₃]⁻·H₂O-MD</td>
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<td>−11.74</td>
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<th>EX' / (kcal mol⁻¹)</th>
<th>REP / (kcal mol⁻¹)</th>
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<td>−66.82</td>
<td>−37.80</td>
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<td>66.80</td>
<td>−65.84</td>
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<td>−155.64</td>
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<tr>
<td>[HgL3(OH)₃]⁻·H₂O-B</td>
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<td>−6.82</td>
<td>69.29</td>
<td>−70.51</td>
<td>−42.13</td>
<td>−161.97</td>
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</tbody>
</table>

---

1: L: n-propyl xanthate; L2: n-butyl xanthate; L3: n-pentyl xanthate; MD: monodentate without hydrogen bond; MDₘ: monodentate with hydrogen bond; B: bidentate; ES: electrostatic; EX: exchange; REP: Pauli repulsion; POL: polarization; DIS: dispersion; Et: total interaction energy.
Finally, the differences between the covalent and ionic contributions of the Hg–S bonds for the cationic and neutral complexes can be observed through the plots in Figure 12. The ionic character of the Hg–S bond is smaller than that of the Cd–S bond (Figure 11). In addition, the mercury(II) complexes exhibited a covalent character of the Hg–S bond higher than or equal to the ionic character (Figure 12). The cationic complexes still exhibited higher ionic character due to the higher positive charge at the metal center. However, the covalent character in these complexes is also higher than in the analogous cadmium(II) complexes.

In a recent paper, our research group also presented the results of EDA calculations for zinc(II) complexes containing n-propyl, n-butyl, and n-pentyl xanthates ligands under the same calculation method. Thus, it was possible to compare the polarization energies of the complexes analyzed with the metals of group 12. The monodentate neutral mercury(II) complexes showed more negative values of polarization energy among the three metal centers evaluated (Figure 13). The averages observed were −67.94 ± 4.65, −58.30 ± 4.78 and −60.10 ± 3.27 kcal mol$^{-1}$, for mercury(II), cadmium(II) and zinc(II) complexes, respectively. This result corroborates the higher affinity of Hg$^{2+}$ ions for xanthate ligands, as observed in the thermochemical analysis, where the mercury(II) complexes showed higher Δ$G^{298}$ values (“Optimization structures and thermochemical studies” sub-section). On the other hand, there was no trend of increasing polarization energy when comparing the zinc(II), cadmium(II), and mercury(II) complexes because the zinc(II) complexes showed more negative polarization energies than the cadmium(II) complexes (Figure 13). However, this result also corroborates the thermochemical analysis, where the zinc(II) complexes showed higher Δ$G^{298}$ values than the cadmium(II) complexes (“Optimization structures and thermochemical studies” sub-section). This is because the zinc(II) complexes had a shorter M–L distance due to the smaller radius of the metal center than the others in group 12. The average observed for the Zn–S distance was 2.287 ± 0.107 Å, while in the cadmium(II) and mercury(II) complexes, the M–S distance was 2.654 ± 0.040 and 2.676 ± 0.072 Å, respectively. Furthermore, the zinc(II) complexes exhibited an ionic character of the M–S bond of −115.162 ± 6.390 kcal mol$^{-1}$, while the cadmium(II) complexes exhibited values of −110.236 ± 6.628 kcal mol$^{-1}$. This indicates that the Zn–S bond has a better coordination sphere organization due to a greater electrostatic attraction between the species. However, compared to the mercury(II) complexes, the Gibbs free energies and polarization values for the zinc(II) complexes were lower. This is because the mercury(II) complexes have a strong covalent contribution in addition to the ionic character (Figure 13), something expected given the nature of the sulfur and Hg$^{2+}$ species, as noted in “Softness analysis” sub-section.

Natural bond orbitals

Natural Bond Orbital (NBO) analysis confirmed the Lewis acid-base nature of the cadmium(II) and mercury(II) complexes. Thus, donor/acceptor interaction energies were obtained from the second-order perturbation energies. Average interaction energies of 147.42 ± 30.24 and 104.72 ± 22.88 kcal mol$^{-1}$ were observed for the cadmium(II) and mercury(II) complexes, respectively (Tables S17-S20, SI section). The interaction energy calculated in the NBO presents the M–L bond with a covalent character, so the general result did not follow the expected results. A detailed analysis of the interaction energies of the cationic complexes confirm the Lewis acid-base nature of the cadmium(II) and mercury(II) complexes.

Figure 12. Comparison of the covalent/ionic nature of the Hg–S bond in mercury(II) complexes, with ligands: (a) n-propyl xanthate; (b) n-butyl xanthate; (c) n-pentyl xanthate.
cadmium(II) complexes shows that there was a trend of higher NBO energies for the bidentate complexes compared to the monodentate complexes (Table S17).

The bidentate cadmium(II) complexes exhibit a higher covalent character of the Cd–S bond than the monodentate complexes. This trend was more prominent in the neutral complexes, in which a difference of 61.71 kcal mol\(^{-1}\) was observed between bidentate and monodentate complexes. Furthermore, the NBO results for neutral complexes indicate a higher covalent character in the Cd–S bond than the cationic complexes (Table S17). This agrees with the studies described in this work, where the cationic complexes showed a strong electrostatic contribution of the M–S bond.

The opposite was observed for mercury(II) complexes, in which monodentate cationic complexes showed higher energies (176.29 ± 26.57 kcal mol\(^{-1}\)) compared to bidentate complexes of the \([\text{HgL(OH}_2]^+\cdot\text{B}\] (122.74 ± 0.97 kcal mol\(^{-1}\)) and bidentate complexes of the \([\text{HgL(OH}_2]_2^-\cdot\text{B}\] (130.03 ± 0.78 kcal mol\(^{-1}\)) type. The same was observed for the neutral complexes, in which the monodentate complexes showed higher energies (108.27 ± 24.21 kcal mol\(^{-1}\)) than the bidentate ones (97.62 ± 20.01 kcal mol\(^{-1}\)). This divergence in NBO data for the mercury(II) complexes suggests that the size of the mercury ion influences the effectiveness of the superposition of the orbitals involved in the Hg–S bond. However, comparing the mercury(II) complexes that lost aqua ligands from the first coordination sphere and those that maintained the octahedral geometry showed that the donor/acceptor energy was higher in the complexes where one or two Hg–OH\(_2\) bonds were disrupted. This indicates that the covalent character of the Hg–S bond is higher in the complexes that exhibited tetra and penta coordinate geometries. Another point to be highlighted is that although the magnitude of the energies and the correlations with the other analyzers were not observed, it is worth mentioning that the values were proportionally high when compared to other studies in the literature. This may explain the relevance of the covalent character in Hg–S bonds.

In addition to the donor/acceptor interaction energies, the NBO provided the contributions of the orbitals in the metal center and the sulfur atoms participating in the M–L bond formation. Thus, major contributions were observed from the s orbital of the metal center and the p orbital of the sulfur atom in both cadmium(II) and mercury(II) complexes. In the Cd\(^{2+}\) ion, the contribution of the s orbital was 99.23 ± 0.25%, and in the sulfur atom, it was 94.62 ± 1.20% for the p orbital. In the cadmium(II) complexes, contributions of 99.55 ± 0.27% of the s orbital in the Cd\(^{2+}\) ion and 93.56 ± 2.20% of the p orbital in the sulfur were observed. Figure 14 illustrates the s and p orbitals in the monodentate cadmium(II) and bidentate mercury(II) complexes with L1 and L2 ligands. Through NBO analysis, it was possible to confirm the Lewis acid-base nature of the complexes, with electron density donation from the p orbital of sulfur to the s orbital of the metal center.

Softness analysis

As the metal ions studied in this work belong to the same group in the periodic table, a softness analysis was performed to verify the expected trend in Pearson’s theory of acidity and basicity. The Cd\(^{2+}\) and Hg\(^{2+}\) ions belong to group 12 of the periodic table, as the Zn\(^{2+}\) ion. According to this theory, Hg\(^{2+}\) is the softest Lewis acid, followed by Cd\(^{2+}\) and Zn\(^{2+}\). Therefore, the energies of the HOMO and lowest unoccupied molecular (LUMO) orbitals, obtained through the optimization structures calculation, were analyzed to...
confirm this expected trend. Equations 3 and 4 were used to calculate the softness. In the equations, $\eta$ and $S$ correspond to the hardness and softness indices, respectively.\(^{65}\)

$$\eta = \frac{1}{2} (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})$$

(3)

$$S = \frac{1}{\eta}$$

(4)

Figure 15 illustrates the softness plots for cadmium (green) and mercury (red) complexes. The results showed that the mercury(II) complexes presented higher softness values, with an average of $0.72 \pm 0.09$, compared to an average of $0.63 \pm 0.08$ for the cadmium(II) complexes. Thus, these compounds followed the expected trend by Pearson’s theory, corroborating the higher covalent M–L bond character observed in the electronic analysis of the mercury(II) complexes.

Conclusions

The results of the thermochemical and electronic analyses showed that the cadmium(II) and mercury(II) complexes tend to form xanthate complexes with different geometries and coordination modes. Furthermore, the presence of stable complexes in the conformation of monodentate ligands may indicate the predominance of polymeric complexes known by literature through interaction with neighboring units in a crystalline arrangement. The cationic cadmium(II) complexes showed monodentate $\text{MD}_{\text{HB}}$, $\text{MD}$, and bidentate $[\text{CdL(OH}_2]_2\text{]}^{2-}\text{B}$

Figure 14. Structures of the cadmium(II) and mercury(II) complexes with the natural orbitals involved in the M–L interaction: (a-b) $s$ and $p$ in the monodentate complex; (c-d) $s$ and $p$ in the bidentate complex.

Figure 15. The softness of cadmium(II) (green) and mercury(II) (red) complexes, with ligands: (a) $n$-propyl xanthate; (b) $n$-butyl xanthate; (c) $n$-pentyl xanthate.
type coordination modes. All the converged structures exhibited Cd–S distances within the range observed in the literature, 2.64–2.73 Å. However, the cationic mercury(II) complexes exhibited different structures, in which bidentate complexes of the [HgL(OH)₂]⁺-B type were formed in addition to bidentate complexes of the [HgL(OH)₄]⁻-B type. On the other hand, the structural analysis showed that the Hg–O distances in complexes were longer than the range observed in the literature. In addition, the cadmium(II) and mercury(II) complexes were also analyzed for the presence of hydrogen bonds. In neutral cadmium(II) complexes, hydrogen bonds were observed between the oxygen of the xanthate ligand and the hydrogen of the aqua ligand. Furthermore, H–S interactions were observed in the ligands where there was an absence of the H–O interaction. In the case of neutral mercury(II) complexes, only complexes with n-butyl xanthate ligand exhibited hydrogen bonds. In addition, Hg–OH₂ bond breaks and longer distances between the metal center and the other aqua ligands were observed, resulting in coordination numbers of four and five.

Thermochemical analysis showed that both cationic and neutral complexes are formed through exothermic and spontaneous processes. This was observed through the negative values of ΔH and ΔG²⁹⁸ calculated in the substitution reactions. In addition, the products of the first substitution reactions had higher energies when compared to the neutral complexes. These high energies for forming cationic complexes are associated with a strong electrostatic attraction between charged species. In addition, thermochemical analysis confirmed a higher affinity for forming xanthate complexes with mercury(II) than with cadmium(II). This was verified through the values of ΔG²⁹⁸, in which the monodentate and bidentate mercury complexes showed higher energies than the cadmium complexes. These observations were confirmed by calculating the softness of the species, in which the mercury complexes showed a higher softness than the cadmium complexes.

The energy decomposition analysis showed that the M–S interactions have no purely ionic or covalent character. In the case of cationic complexes, ionic interaction was the majority when compared to the neutral complexes, corroborating with the thermochemical analysis. In the cadmium(II) complexes, the ionic contribution of the Cd–S bond was larger than the covalent component. In contrast, the mercury(II) complexes showed a larger covalent character of the Hg–S bond than the ionic contribution. This result agrees with what was expected since the interaction between soft species occurs through mostly covalent interactions. The NBO energies revealed that the cadmium(II) complexes present better orbital superposition for the bidentate complexes than the monodentate complexes. Furthermore, it was also found that the neutral cadmium(II) complexes exhibited higher covalent contributions than the cationic complexes, which corroborates the thermochemical and EDA data. However, the mercury(II) complexes showed an opposite trend. Also, NBO analysis confirmed the nature of the sulfur atom as a Lewis base through the p orbital, which donates electron density to the s orbital of the metal center.

**Supplementary Information**

Supplementary information (thermochemical analysis (wB97XD); M–L, O–H and S–H bond distances (M06L and wB97XD); Mulliken population analysis (MPA); natural population analysis (NPA); hybridization and interaction energy of natural bond orbitals, and optimization structures of cadmium(II) and mercury(II) complexes (wB97XD)) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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