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Performance assessment of semiempirical molecular orbital methods in the structural prediction of Sb(III) and Bi(III) complexes

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Abstract In this paper we carried out a systematic study in order to assess the quality of some semiempirical methods (AM1, PM3 and PM6), comparing predicted structural properties of many Sb(III) and Bi(III) complexes with the corresponding experimental data, indicating which one is more appropriate to describe the structure of such compounds. Root-mean squared deviation (RMSD) and unsigned mean error (UME) were used to evaluate the accuracy of the semiempirical methods to predict the ground state geometries of complexes with many ligand types. Our results have shown that, in general, PM3 predicts more accurately the geometry of Sb(III) complexes, being considered by us as the method of choice to study Sb(III) complexes with a great variety of ligands. PM6 is indicated as the method of choice to study Bi(III) complexes with many types of ligands and also to study Sb(III) thiocompounds, even though PM6 showed an inability to reproduce Sb-N bonds for complexes with flexible ligands, presenting an average deviation of 71.5 % compared the X-ray data.

Keywords Antimony · Bismuth · Coordination compounds · Semiempirical methods

Introduction

The interest in the chemistry of antimony and bismuth compounds is due to the great variety of applications in: catalysis, organic synthesis and human health [1, 2]. Antimony (Sb) and bismuth (Bi) atoms belong to group 15 of the periodic table

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and, although they are not life essential elements, they play an important therapeutic role in human health by means of interactions with biomolecules [3].

Compounds containing antimony and bismuth can interact with DNA basis, proteins and enzymes, which are closely related to their absorption, accumulation, reduction and excretion in the human body. Pharmacologically, these compounds are used as antimicrobial, anticancer, antibacterial and antiviral agents [3, 4]. Given their widespread use in healthcare applications, the study of the interactions of such substances with biomolecules is very important to understand the mechanisms of drugs containing their corresponding ions in biological systems.

Antimony compounds, such as meglumine antimoniate (Glucantime®) and sodium stibogluconate (Pentostam®), are used in parasitic disease treatment, such as Leishmaniasis and Schistosomiasis [5–7]. Furthermore, antimony compounds have been largely used: in pharmacology, in the syphilis treatment, as spermicide and in cancer treatment [5, 8, 9].

The bismuth complexes used in medicine have been known since the Middle Ages [10]. Nowadays, their applications to human healthcare are directed to cancer treatment and as antimicrobial agents, as well as being largely used in gastrointestinal disturbances and peptic ulcer therapy [11–13]. In particular, the compounds: bismuth subsalicylate (BSS, Pepto-Bismol®), colloidal bismuth subcitrate (CBS, De-Nol®) and ranitidine bismuth citrate (RBC, Tritec®), are largely used in infections treatment caused by *Helicobacter pylori* [11, 14, 15].

Recent investigations have just shown the promising potential of ^{212}Bi and ^{213}Bi radionuclides in small tumor treatment, acting as radioactive markers when combined with monoclonal antibodies, polypeptides, proteins and other vectors that can be combined with an appropriate chelate ligands, such as diethylene triamine pentaacetic acid (DTPA), 1,4,7,10-tetra-azacyclo-dodecane 1,4,7,10-tetra-acetic acid (DOTA) and porphyrins [3, 10, 11, 16].

All these substances can be modified by molecular rational design in order to satisfy in vivo stability requirements for the

metal-ligand bond, without any dissociation. In this context, theoretical methodologies are important tools to carry out the rational design of new drugs, as well as, to perform studies on the interaction of metal ions with proteins, ion selectivity by ligands and specific catalytic processes [17]. However, few theoretical studies involving antimony and bismuth compounds can be found in literature, in comparison to other elements used in medicine. As few as they may be, though, some of them are remarked in the following paragraphs.

B3LYP hybrid functional was used to study the adduct formation SbF_5 with carbonyl halides (COCl, COClF and COF) [18], as well as, Cl/F exchange reaction mechanism and kinetics of the interaction of SbF_5 with $COCl_2$ [19].

A theoretical investigation of chemical bond to the formation of many antimony adducts by means of NBO method, using B3LYP functional, was carried out by Poleshchuk and collaborators [20]. The authors used the 3-21G*/ECP (taking relativistic effects into account) basis set for the Sb atom and the 6-311G(2d,p) for the other elements. Optimized geometry, nuclear quadrupole resonance frequency ^{35}Cl-NQR and adduct formation bond energies presented a good agreement with experimental data [20].

Virko and collaborators have shown that the mPW1PW functional predicts geometries and vibrational normal modes of antimony and bismuth triiodide more accurately when compared to DFT/B3LYP, Hartree-Fock and MP2 methods [21].

Yurchenko and collaborators used high-level *ab initio* calculations, CCSD(T), to compute the potential energy surface (PES) of BiH_3 [22]. Bismuth atom was described by scalar-relativistic pseudopotential in conjunction with (12s12p10d5f3g2h)/ [8s8p7d5f3g2h] set of contracted Gaussian-type orbitals. A fit of the PES to experimental data allowed a good reproduction of the observed values for the vibrational band centers and provided predictions for several overtone and combination bands that have not been observed yet [22].

The structural and electronic aspects of the polyhedral fullerenes composed of group 15 elements (phosphorus, arsenic, antimony, and bismuth) with up to P_{888}, As_{540}, Sb_{620}, and Bi_{620} were studied by Karttunen and collaborators at the DFT and MP2 levels [23]. The authors found out that their structures and stabilities converge smoothly toward their experimental bulk counterparts. In addition, they were able to observe that the group-15 polyhedral fullerenes are thermodynamically stable with respect to the experimentally known tetra-atomic allotropes [23].

In another study, ground state geometries, vibrational normal modes and energetic aspects of a set of aquabismuth(III) complexes and bismuth-oxo clusters of stoichiometry $Bi_6O_{8-n}(OH)_n^{(2+n)+}$ (n=0-4) were calculated at Hartree-Fock and MP2 level, with the use of different basis set and ECPs [24]. The optimized geometries of aqua complexes, $Bi(H_2O)_n^{3+}$ (n=1–6), presented a certain degree of distortion, validating the inert pair effect of Bi^{3+} ion. The authors also

have considered it consistent with the experimental Bi-O bond lengths in bismuth-oxo clusters as well as the geometries of Bi(III) nonahydrate and hexahydrate aqua-complexes [24].

In addition, thermodynamic parameters of hydration for Bi(I), Bi(II) and Bi(III) ions as well as their redox potentials were calculated at DFT/B3LYP level [25]. Kuznetsov and collaborators used Hay-Wadt ECP [26] to describe the core electrons for bismuth and double zeta basis set (DZ) with, respectively, 3d and 2p polarization functions for oxygen and hydrogen orbitals. The solvent effects were obtained by polarizable continuum model PCM. The authors pointed out that the obtained results were compatible with the experimental data.

Semiempirical methods also have been used to study antimony and bismuth compounds due to its theoretical simplicity. The study of gas-phase electronic structure of $SbCl_5 \cdot L$ complexes (where L=Lewis base), performed by Poleshchuk and collaborators, indicated that the semiempirical method PM3 satisfactorily reproduces their ground state geometries, energetic parameters and NQR frequencies [27].

The thermodynamic parameters (ΔH_f, ΔS_f, and ΔG_f) of a series of inorganic and organometallic antimony and bismuth compounds have been calculated at PM3 level [28]. The results indicated that PM3 correctly reproduces the tendencies in the thermodynamic properties of these compounds, showing a linear dependence between experimental and calculated values [29, 30].

However, there is no study in literature which has evaluated in a systematic way the performance of semiempirical methods in relation to predicting the structural parameters of Sb(III) and Bi(III) complexes with different ligand types. Therefore, in our article we carried out a systematic study in order to assess the quality of some semiempirical methods (AM1, PM3 and PM6), comparing predicted structural properties of many Sb(III) and Bi(III) complexes with the respective experimental data, indicating which one is more appropriate to describe the structure of such compounds.

Methodologies

In order to assess the performance of semiempirical methods AM1, PM3 and PM6 concerning to the accuracy in predicting geometric features (conformation, coordination polyhedron and bond lengths) of Sb(III) and Bi(III) complexes with a variety of ligands types: macrocyclic, heterocyclic, thiocompounds, carboxylate ligands and organometallic compound, we have calculated their gas-phase ground state geometries using the aforementioned semiempirical methods.

All the calculations were carried out using software package MOPAC 2009 [31], without symmetry imposition, and in Cartesian coordinates. The geometry optimization termination criteria were set equal to 0.1 kcal·mol^{-1}·Å^{-1} and for SCF convergence criteria we have used 1.10^{-10} kcal mol^{-1}.

Furthermore, we have carried out vibrational frequency calculations in order to guarantee that the optimized geometries were, indeed, minimum energy geometries. When the optimized structure presented imaginary frequencies, it was re-optimized until it did not.

The starting geometries used in all geometry optimizations were obtained from X-ray crystallography in the Cambridge Structural Database (CSD) [32]. All-atoms superposition between predicted geometries and experimental ones, as well as, comparisons of bond distances between all atoms of the coordination polyhedron and metal-ligand atom bond lengths were performed using the X-ray structure of the complexes, also, obtained from the Cambridge Structural Database (CSD) [32]. For our initial search, we have selected all coordination complexes deposited in the CSD containing the elements antimony and bismuth limited to those that had their 3D coordinates determined, were not-disordered, were neither powder structures nor polymeric and which presented an R factor≤0.1. There were 2943 coordination complexes containing antimony and 1188 coordination complexes with bismuth which matched our criteria.

From these quantities, we have not taken into account the structures presenting atoms in which at least one of the three considered semiempirical methods did not have parameters. We have also ignored many repeated structures of the same molecule, which were obtained from different crystallographies, as well as, those structures in which the antimony and bismuth atoms simply appear as counter ions.

After a detailed analysis, 54 antimony and 75 bismuth structures were selected, representing the whole set after such filters have been applied.

The compounds were categorized into five groups based on the ligand type: (a) macrocyclic, (b) heterocyclic, (c) presenting coordinated sulfur atoms, (d) with coordinated carboxylate groups and (e) organometallic compounds. Figure 1 presents representative complexes for each considered group. This was carried out aiming at knowing the predictive power of the semiempirical methods, both in relation to all complexes and by groups.

We have considered three quantities that allowed assessing the performance of the semiempirical methods in predicting the ground state geometry of the antimony and bismuth coordination compounds. The first one was the root-mean squared deviation of all-atoms superposition ($RMSD_{sup}$) between X-ray geometry and the one calculated with each of the considered semiempirical methods. Second and third quantities were the unsigned mean errors, respectively, of the bond distances considering all atoms in the coordination polyhedron (UME_{poly}) and only the bond lengths metal-ligand atom (UME_{M-L}). The expressions to calculate those quantities can be seen in Eqs. (1) and (2), respectively.

$$RMSD_{sup} = \sqrt{\frac{\sum_{i=1}^{N}\left(\vec{r}_{i,exp} - \vec{r}_{i,calc}\right)^2}{N}} \tag{1}$$

$$UME = \frac{1}{n}\sum_{i=1}^{n}\left|d_{exp} - d_{calc}\right| \tag{2}$$

In Eq. (1), $\vec{r}_{i,exp}$, represents the 3D vector of Cartesian coordinates for the atom i in the X-ray structure, and $\vec{r}_{i,calc}$,

Fig. 1 Representative examples of complexes investigated, where M=Sb(III) or Bi(III)

Macrocyclic　　　Heterocyclic　　　Sulfur

Organometallic

Carboxylate
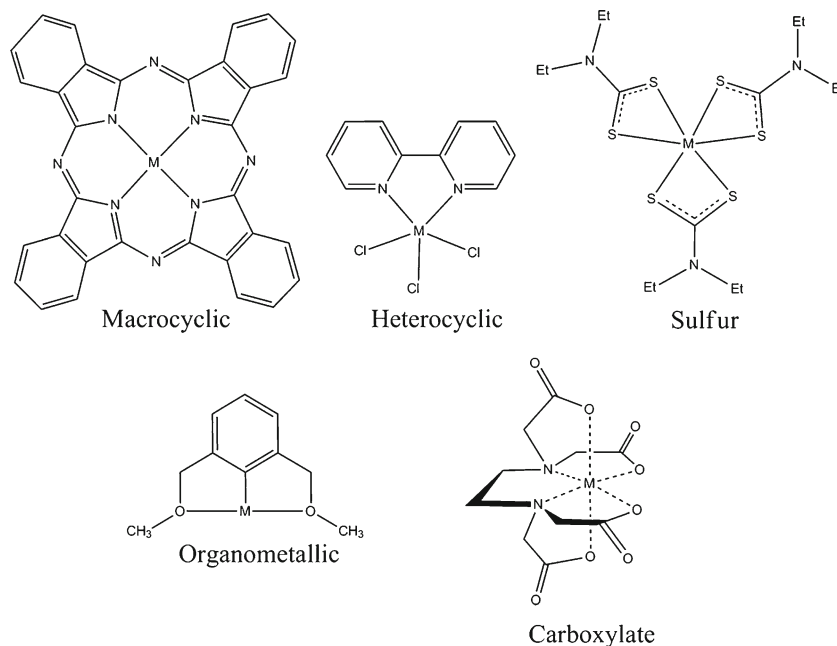
the same quantity for the same atom i in the calculated one. N is the number of atoms in each structure.

In Eq. (2), d_{exp} and d_{calc} are, respectively, bond distances in the X-ray structure and in the calculated one. Equation 2 was used to calculate both UME_{poly} and UME_{M-L}. So it can be either the number of metal-ligand atom bond lengths or the number of bond distances between all atoms in the coordination polyhedron.

All histograms for UME_{poly} and UME_{M-L} were built considering optimal bin size, according the reference [33].

Results and discussion

Antimony (III) complexes

In Fig. 2(a) we can see the results of average values for $RMSD_{sup}$, categorized by Sb(III) complex group (see Fig. 1), for AM1, PM3 and PM6 semiempirical methods. Similarly, in Fig. 2(b) the average values for UME_{poly} and UME_{Sb-L} are depicted.

A close examination in Fig. 2 suggests that the AM1 and PM3 methods reproduce with good accuracy the ground state geometries of most of the Sb(III) complexes, presenting $RMSD_{sup}$ values of less than 1.06 Å for all the Sb(III) complexes groups. In addition, we can see that PM3 is more accurate than AM1 in bond distances prediction between all coordination polyhedron atoms, UME_{poly}, and Sb-L antimony-ligand atom bond lengths, with average values of UME_{Sb-L} less than 0.315 Å.

In contrast, PM6 method presented large average values for $RMSD_{sup}$ and UMEs for all Sb(III) compound groups, except for Sb(III) complexes containing sulfur ligands. For this
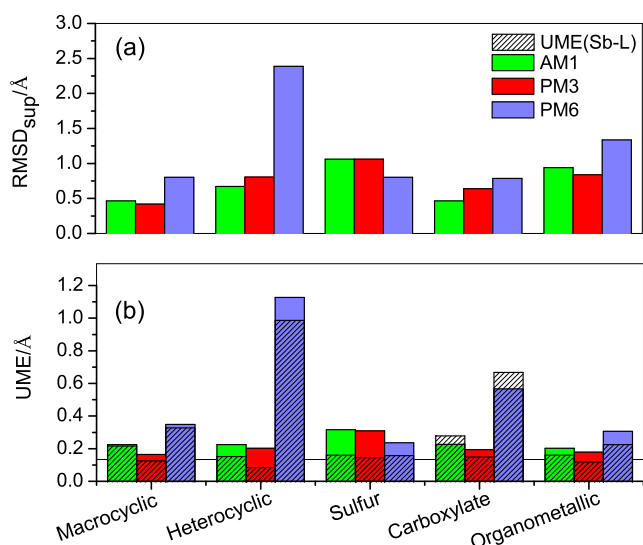
group, PM6 method showed a better predictive capacity than the other methods, being 24 % more accurate than both PM3 and AM1 in terms of $RMSD_{sup}$, Fig. 2(a). An explanation for this may be related to the insertion of the 3d orbital in the basis set to the sulfur atom in method PM6 [34], which probably results in a better description of the chemical bond (Sb-S) and consequently for the geometries of such compounds. This was also pointed out in a study of Thiel and Voityuk, who presented a parameterization of MNDO/d method with the explicit inclusion of 3d orbitals in the basis set for sulfur and other hypervalent atoms [35–37]. These authors reported they have managed to obtain an increased accuracy in some molecular property predictions when the 3d orbitals are included to sulfur, mainly in hypervalent compounds.

The results in both Fig. 2(a) and (b) point out that PM3 predicts more accurately the geometries of Sb(III) complexes with macrocyclic ligands than PM6 and AM1, presenting average values for $RMSD_{sup}$ of 0.421 Å, for UME_{poly} of 0.165 Å and for UME_{Sb-L} of 0.131 Å. However, PM6 presented large $RMSD_{sup}$ of 2.6 Å for JUWHIS complex, (Fig. S1 in Supplementary material), which has been assigned mainly to the rupture of the Sb–N bond after geometry optimization. Another fact that may have contributed to large deviation in this structure is the high flexibility of macrocyclic ring.

For Sb(III) complexes with heterocyclic aromatic amines, PM6 method presented very large $RMSD_{sup}$ and UMEs average values (see Fig. 2), indicating a possible inability of such method to accurately perform a geometrical prediction for this compound group. Our results indicate a tendency of the Sb-N bonds to rupture in such Sb(III) complexes, which may be related to a Sb-N bond low representativeness in the PM6 parameterization set, leading to the poor quality of diatomic parameters involving these atoms.

Further considerations on the results obtained with the method PM6 show that the lowest values of UME_{poly} and UME_{Sb-L} were observed to CIDWIV01 and MEDGAD complexes (Figs. S5 and S6 respectively). For CIDWIV01 complex, the UME_{poly} and UME_{Sb-L} values were, respectively, equal to 0.096 Å and 0.017 Å, while for MEDGAD the values were equal to 0.218 Å (UME_{poly}) and 0.270 Å (UME_{Sb-L}). CIDWIV01 complex presents three nitrogen and three sulfur atoms bonded to Sb(III) ion. Therefore, low values for UMEs may be related to the good description of Sb-S bond by method PM6, as has been previously discussed (Figs. S5, S6). In the case of MEDGAD complex, low UMEs values can be related to the rigidity of its structure mainly due to steric effects arising from the existence of the substituents– $Si(CH_3)_3$ and 2-methyl-pyridyl in each of the three bidentate ligand.

For the group of complexes with coordinated carboxylate ligands, the PM3 is the most accurate method to reproduce geometrical features of both coordination polyhedra and Sb-ligand atom bond lengths, see Fig. 2(b).

Fig. 2 Average values of: (a) root-mean squared deviation ($RMSD_{sup}$) and (b) unsigned mean errors (UMEs) for Sb(III) complexes. The dashed regions in (b) are assigned to the UME_{Sb-L} and the filled regions to UME_{poly}

Our findings for the organometallic compounds point out that both methods AM1 and PM3 predict the ground state geometries of such complexes in a similar way, with $RMSD_{sup}$ average values of 0.939 Å for AM1, 0.838 Å for PM3. For the UME_{poly}, the average values were 0.203 Å for AM1 and 0.178 Å for PM3 (see Figs. S13–15).

Figure 3 and Fig. S16 (see Supporting information) show, respectively, the histograms for UME_{poly} and UME_{Sb-L} considering all 54 studied Sb(III) complexes and the three semi-empirical methods.

About 53 % of the Sb(III) complexes were predicted with UME_{poly} around 0.11 Å when their geometries were optimized with the PM3 semiempirical method.

The same analysis can be carried out to AM1 and PM6 methods. For AM1 23 complexes (40.7 %) showed UME_{poly} around 0.13 Å and for PM6 17 complexes presented UME_{poly} around 0.40 Å. Therefore, our results indicate that PM3 predicts both the coordination polyhedra and Sb-L bond distances better than AM1 and PM6 methods. For PM3, the average value of UME_{Sb-L} is around 0.14 Å, see Fig. S16 in the Supplementary material.

Summarizing for Sb(III) complexes, we can conclude that PM3 reproduces more accurately both the bond distances between all atoms of the coordination polyhedra and bond lengths Sb-L for most of the investigated complexes. This assertion indicates that PM3 is the method of choice to predict ground state geometries for Sb(III) complexes with several ligand types.

PM6 is the best method to reproduce the geometries of Sb(III) complexes with ligands whose electron-donor atom is sulfur, mainly due to the good description of Sb-S bond as a consequence of explicit inclusion of sulfur 3d orbitals. On the other hand, PM6 does not reproduce the geometry of Sb(III) complexes with heterocyclic aromatic amines due to the bad description of Sb-N bond.

Performance assessment regarding the bonds (Sb-N)

With the purpose of specifically assessing semiempirical calculation methods in relation to Sb-N bond description, we have analyzed the bond lengths for 40 Sb(III) complexes (of which, 26 complexes were present in the initial set and the remaining 14, are new Sb(III) complexes) with different types of ligands presenting at least one electron-donor nitrogen atom coordinated to antimony trivalent ion. Table S2 (see Supporting information) shows all details of the selected complexes for this analysis.

In Table 1 we present the predicted and experimental average values of such bond lengths, as well as, the corresponding average deviations in relation to X-ray structures of

Fig. 3 Histograms for unsigned mean error (UME_{poly}) for all Sb(III) complexes
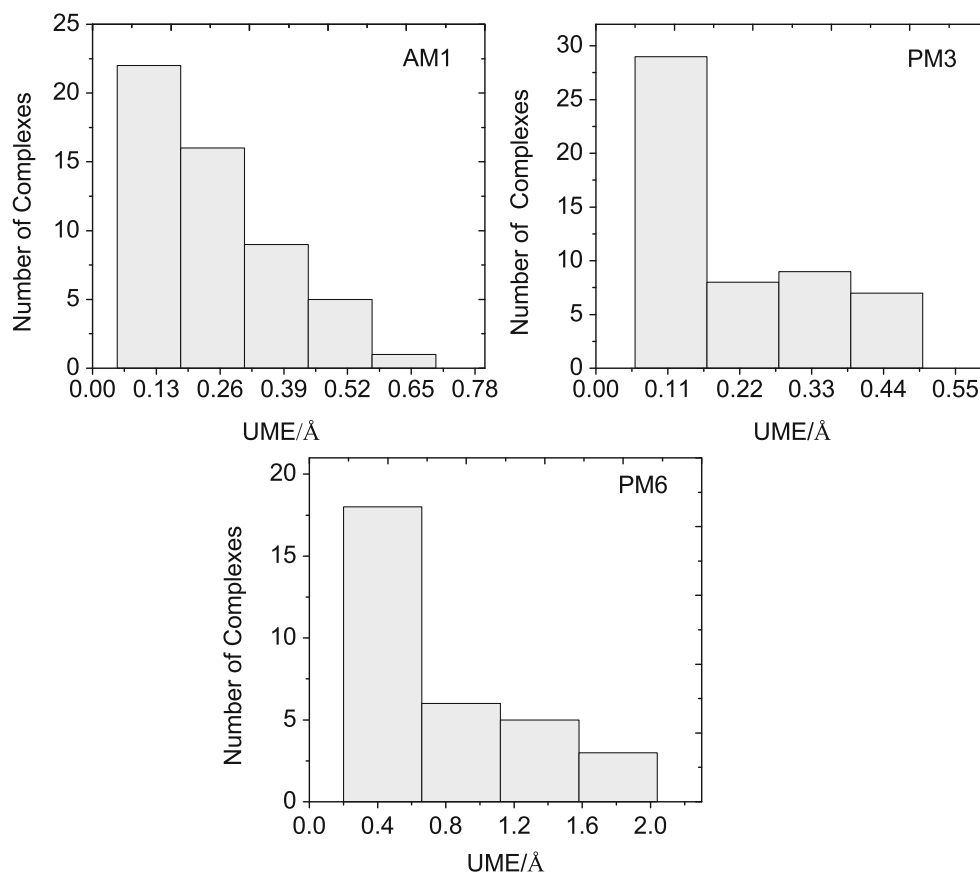
Table 1 Calculated and experimental Sb-N average bond length and statistical data for bond length deviation in relation to X-ray structure

	$\overline{d}$ (Å)	$\overline{UME} = \frac{\sum_{i=1}^{n} UME_{Sb-N}}{q}$	$\overline{X} = \frac{\sum_{i=1}^{n} X}{q}$	σ_X	$\sigma_{UME_{Sb-N}}$
X-ray	2.386				
AM1	2.551	0.271	0.115	0.088	0.205
PM3	2.365	0.099	0.040	0.032	0.082
PM6	3.937	1.748	0.715	0.499	1.191

$X = \{[|(\sum d_{exp}) - (\sum d_{cal})|]/\sum d_{exp}\}$ $UME_{Sb-N} = \{[|(\sum d_{exp}) - (\sum d_{cal})|]\}/n$; n=number of bonds; q=number of structures; σ = standard deviation

studied complexes. Our analysis was based on the strategy carried out by Seitz and Alzakhem to assess the performance of the semiempirical (AM1, PM3, or PM6) /Sparkle models to predict average bond lengths for the Ln-OH$_2$ (Ln=Eu or Tb) bonds [38].

Our results indicated that PM3 method predicts more accurately Sb-N bond lengths with a significant absolute deviation of 0.099 Å, being 63 % more accurate than AM1. On the other hand, PM6 did not present a good performance to predict Sb-N bond lengths, showing very large values, around 3.937 Å, and mean relative deviation (in percentage) of 75.1 % compared to bond lengths of X-ray structure, see Table 1.

This new analysis reinforces what we have previously observed about PM6: this method presents an inability to properly describe Sb-N bonds, which may be related to the low number of molecules containing such bond in its parameterization data set.

From the average bond length analysis calculated by method PM6, we have observed that around 70 % of the molecules showed Sb-N bond rupture after the geometry optimization. A common characteristic observed in these molecules is the presence of flexible ligands with single bonds adjacent to Sb-N bonds. In such cases, the complexes assumed a conformation so that the distances between antimony and nitrogen atoms became very large to represent a coordinated bond.

In a more detailed view of such PM6 inability, we present in Fig. 4 the optimized geometries for the complexes: BPYSBC10, KEDFII and RITPEQ. We can see for the BPYSBC10 complex such rupture of the Sb-N bond, resulting in SbCl$_3$ with pyramidal geometry and the ligand 2,2'-bipyridine (Bpy) at trans conformation. These geometries are quite similar to the same experimentally observed for SbCl$_3$ and Bpy molecules separately. This observation suggests that geometries for both SbCl$_3$ and Bpy are well represented in the database used in PM6 parameterization, while the distorted square-based pyramidal geometry of BPYSBC10 complex is not.

Not all investigated complexes with Sb-N bonds presented rupture of such bond after geometry optimization with PM6 method. Among those in which the Sb-N bond rupture was not observed there are macrocyclic ligands with rigid structures, such as porphyrins, phthalocyanines and ligands with

some rigidity due to double bonds (C=C) adjacent to Sb-N bond.

Bismuth (III) complexes

In this section, we will assess the semiempirical methods AM1, PM3 and PM6 performance to predict the ground state geometries of Bi(III) complexes, using the same approaches employed in the previous section for the Sb(III) complexes. In Fig. 5, we can see the RMSD$_{sup}$, UME$_{poly}$ and UME$_{Bi-L}$ average values for all Bi(III) complexes.

In an overview, we can see that both PM3 and PM6 methods predict with good accuracy the ground state geometries of complexes with Bi(III), with similar average values for RMSD$_{sup}$. Exceptions were observed for complexes containing sulfur ligands, for which PM6 method outperformed PM3, see Fig. 5(a).

BPYSBC10

KEDFII

RITPEQ
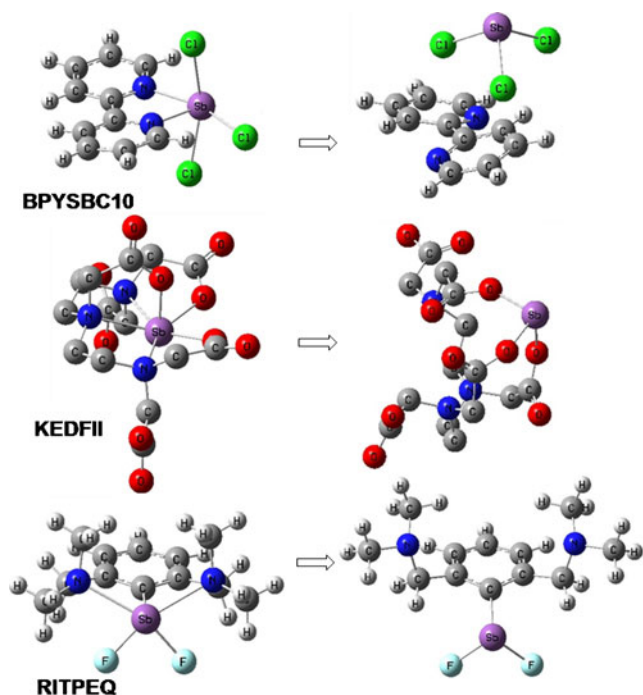
Fig. 4 Representative example of some complexes with Sb-N bonding. On the left, the X-ray geometries are shown labeled with CSD name. On the right, the corresponding geometries calculated by PM6 method
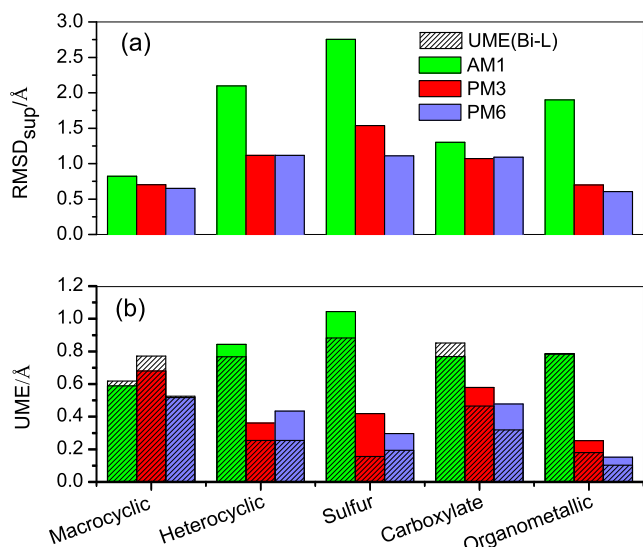
Fig. 5 Average values of: (**a**) root-mean squared deviation (RMSD$_{sup}$) and (**b**) unsigned mean error for Bi(III) complexes. The dashed regions in (**b**) are assigned to the UME$_{Bi-L}$ and the filled regions to UME$_{poly}$

Bond distances in the coordination polyhedron and the Bi-L bond lengths were more accurately predicted by PM6 for all classes of studied complexes, except in the case of complexes containing heterocyclic ligands, Fig. 5(b), for which the best method was the PM3.

In opposition, method AM1 presented the largest RMSD$_{sup}$ and UMEs values for most groups of studied complexes. We believe this detail may be related to the fact that in this set of structures there are many molecules with Bi-hyp bonds (hyp meaning hypervalent atom as S, Cl, Br and I). Since the AM1 method was parameterized without taking into account molecules with hypervalent atoms, it might be that it is actually inappropriate to be used in the prediction of some molecular properties of compounds containing such atoms [39], which is why we have obtained such high error rates for AM1 geometry optimizations of Bi-hyp bonds.

Calculations carried out with AM1 method for the bismuth trihalides BiX$_3$ (X=Cl, Br and I) reveal a tendency to make their geometries flat (D$_{3h}$ point group), which disagrees with experimental C$_{3v}$ geometries. This evidence is shown in Fig. 6. For these calculations, the starting geometries were extracted from the MOPAC website [31].

For molecules with Bi-S bonds, AM1 suggests that S-S bonds stabilize the molecular system more than Bi-S bond, which disagrees with X-ray experimental data. Once again, this behavior is shown in Fig. 6.

For the Bismuth complexes with macrocyclic ligands, PM3 presented larger average values for UME$_{poly}$ and UME$_{Bi-L}$, see Fig. 5(b).

When investigating the complexes with the largest absolute deviations, we have observed that all of them had crown ether ligands with four or five oxygen atoms in the macrocyclic ring
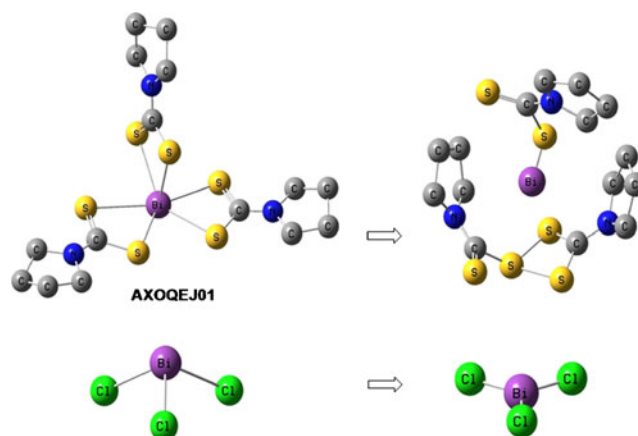

Fig. 6 X-ray geometries for AXOQEJ01 complex and BiCl$_3$ on the left, and, on the right, their corresponding geometries calculated by AM1

(Figs. S20–21). In these cases, the average Bi-O bond lengths predicted by PM3 are very large, around 5.178 Å, while the experimental value is 2.828 Å, a finding that was not observed in calculations with AM1 and PM6 methods. This behavior indicates that PM3 cannot correctly reproduce the coordination mode of bismuth halides with crown ether ligands.

In Fig. 7, we present superpositions of geometries calculated with PM3 and corresponding crystallographic ones (in blue) for three complexes with crown ether ligands. We can observe that the macrocyclic rings were correctly described by PM3, in contrast to the BiCl$_3$ coordination mode to crown ether ligands containing four and five oxygen atoms. On the other hand, such method reproduces more accurately the coordination mode only in the case of ligands with six oxygen atoms. UME$_{Bi-L}$ deviations for the three mentioned complexes were: 1.550 Å (KOZKUF01), 1.440 Å (KAMWIE) and 0.421 Å (KAMWOK).

The results shown in Fig. 5(b) indicate that PM3 better reproduces the coordination polyhedron of bismuth complexes with heterocyclic ligands, being 57 % more accurate than AM1 and 17 % than PM6. In relation to Bi-L bond lengths, both methods PM3 and PM6 are more accurate than AM1, presenting lower deviations compared to experimental bond lengths.
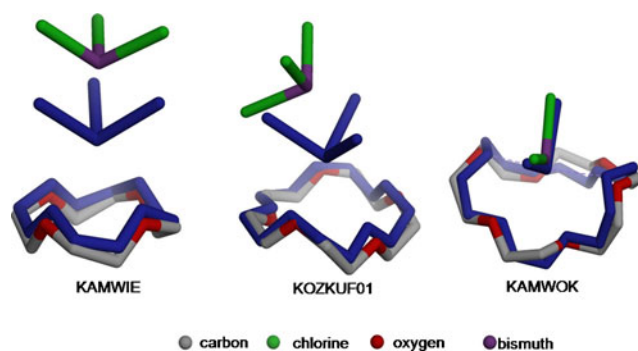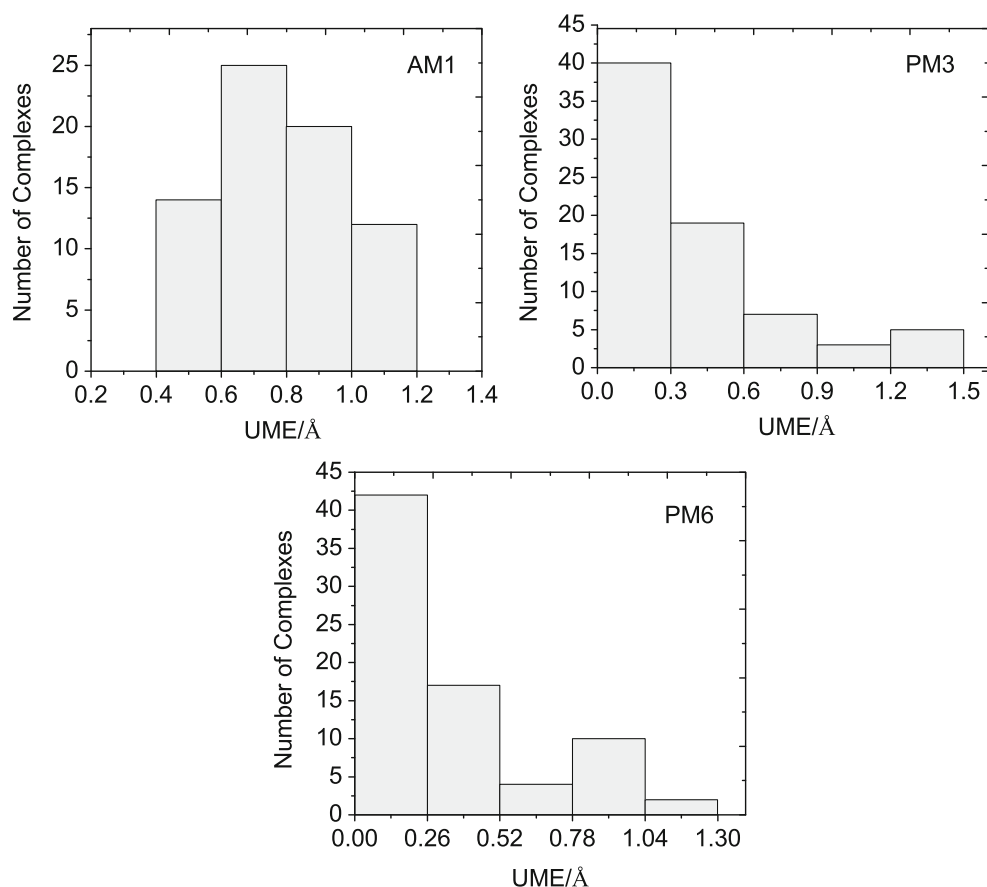

Fig. 7 Superpositions of structures calculated by method PM3 and X-ray structures (blue) for three Bi(III) complexes with crown ether ligands
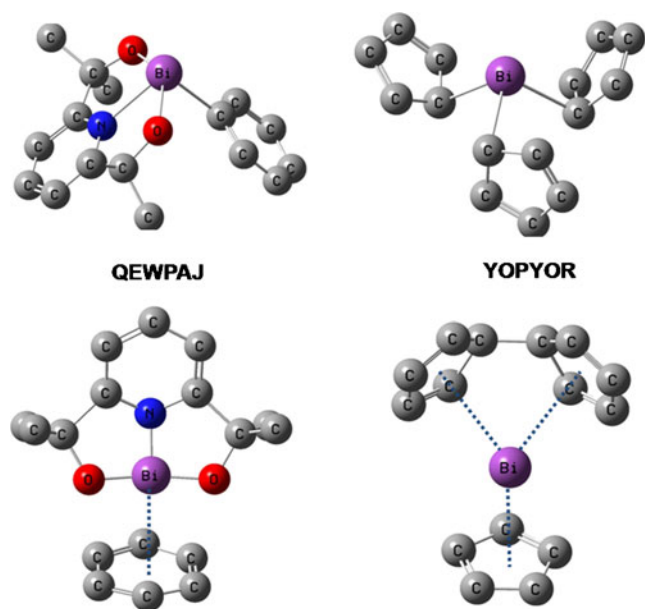
Fig. 8 X-ray structures labeled with CSD code, on the top, and their corresponding calculated by AM1, on the bottom. The broken lines represent possible cation-π interactions

The largest $RMSD_{sup}$ and UMEs average values obtained with AM1 were related to the large distortions in geometries after the geometry optimization. We have observed that 60 %

of the Bi(III) complexes presented Bi-S bond and, in such cases, AM1 does not reproduce this bond in a good agreement with the experimental data. Besides, we have detected a tendency of AM1 to favor cation-π interaction between bismuth and aromatic rings in the ligand structure.

For the class of bismuth complex with sulfur ligand, PM6 once more is the best method to predict the geometries and the bond lengths in the coordination polyhedra, presenting small deviations compared to X-ray structures. In Fig. 5(a) and (b) these results can be verified. This ability of PM6 may be once more related to the insertion of 3d orbitals for the sulfur atom in PM6 parameterization.

The coordination polyhedra and the Bi-L bond lengths for the complexes with coordinated carboxylate ligands were more accurately reproduced by PM6 than PM3. The percentage deviation of average values for UME_{poly} comparing the two methods revealed that PM6 is 18 % more accurate than PM3. The same comparison can be carried out using UME_{Bi-L} where, PM6 outperformed PM3 by 31 %.

The results shown in Fig. 5(a) and (b) indicate that PM6 reproduces more accurately the geometries of organometallic compounds, as well as their coordination polyhedra and Bi-L bond lengths. Consistent with these results, PM3 average values for UME_{poly} and UME_{Bi-L} were, respectively, 40.7 % and 42.2 % larger than corresponding values obtained with PM6.

Fig. 9 Histograms for unsigned mean error (UME_{poly}) for all Bi(III) complexes

AM1 presented the largest RMSD$_{sup}$ and UMEs deviations compared to the other two methods, which has been assigned to the incorrect description of Bi-C bond and the tendency of AM1 to prefer stacking type interactions between bismuth and aromatic ring, as seen in Fig. 9. In addition, we have detected that in nearly 71 % of the calculated Bi(III) molecules, AM1 suggests that the interaction between the aromatic ring and the bismuth atom results in a more stable structure, in contradiction to the X-ray experimental results, as seen in Fig. 8.

In Fig. 9, and Fig. S34 (see Supporting information), we show, respectively, the histograms for UME$_{poly}$ and UME$_{Sb-L}$ considering all Bi(III) complexes and the three semiempirical methods.

Our results indicate that PM6 reproduces more accurately the bond lengths in the coordination polyhedron and the Bi-L bond lengths, with most of the complexes presenting UME$_{poly}$ around 0.13 Å and UME$_{Bi-L}$ of 0.12 Å (see Fig. S34 Supporting information).

Summarizing, we have observed that both methods PM3 and PM6 similarly predict the Bi(III) complex geometries, such that PM6 is more accurate than PM3 in the prediction of bond distances in coordination polyhedron and Bi-L bond lengths. An exception for that is in the cases of complexes with heterocyclic ligands. However, PM3 does not correctly reproduce the coordination mode of bismuth trihalides BiX$_3$ (X=Cl, Br and I) with crown ether ligands containing four or five oxygen atoms in the macrocyclic ring.

Similarly to the Sb(III) complexes with sulfur ligands, PM6 reproduces more accurately the ground state geometries of Bi(III) complexes with such ligands, showing the important role of the inclusion of 3d sulfur orbital for a good description of Bi-S bond and consequently for the description of their geometries. We can thus conclude that PM6 is the semiempirical method of choice to study ground state geometries of Bi(III) complexes with macrocyclic, coordinated carboxylate ligands, ligands with donor sulfur atoms, and organometallic ligands.

AM1 presents severe inabilities to correctly predict Bi(III) complexes geometries containing the ligands considered in the study. In the case of complexes with aromatic ring ligands in their structure, there is a tendency of AM1 to consider which cation-π interactions stabilize more the molecular system in comparison with Bi-C bonds, which completely disagrees with X-ray structures.

Conclusions

In this paper we have carried out a systematic study in order to assess the quality of some semiempirical methods (AM1, PM3 and PM6), comparing predicted structural properties of many Sb(III) and Bi(III) complexes with the corresponding experimental data, indicating which one is more appropriate to describe the ground state structure of such compounds.

As a result of the work presented here, the following recommendation are made: (a) For work involving antimony complexes in general, AM1 and PM3 should be used; (b) compounds involving Sb-S bond should be calculated using PM6, while AM1 and PM3 give qualitatively correct results, PM6 method is the most accurate for this type of system; (c) PM6 should not be used for Sb(III) compounds with flexible ligands containing Sb-N bond because it breaks this bond, presenting a deviation of 71.5 % compared to the experimental average bond length.

For Bi(III) complexes our recommendation are: (a) PM6 is the most accurate semiempirical method for this type of system, in general; (b) AM1 should not be used because it does not correctly reproduce the geometries of Bi(III) complexes presenting significant deviations compared to the X-ray geometries; (c) PM3 method should not be used to study BiX$_3$ (X=Cl, Br and I) adducts with crown ether ligand (containing four and five oxygen atoms in the macrocyclic ring) because PM3 fails in reproducing their coordination mode.

We expect that the results presented here can be used to motivate that new theoretical and experimental studies on the biochemistry of Sb and Bi can be accomplished.

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