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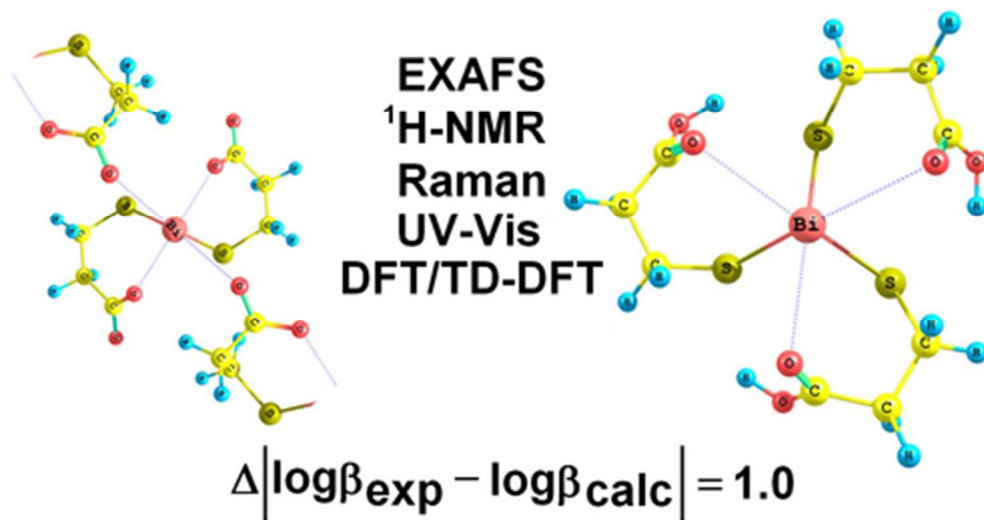


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The coordination mode for interactions between Bi(III) and H₂MPA has been found. Complexation thermodynamics has been investigated experimentally and theoretically by DFT modeling using various density functionals
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ARTICLE

Complexation of Bi(III) with 3-mercaptopropionic acid in aqueous solutions: a combined experimental and theoretical study

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This paper deals with complex formation of Bi(III) with 3-mercaptopropionic acid (H₂MPA, H₂L) in aqueous perchloric solutions. An extensive investigation on stoichiometry, stability and geometry of complex species in aqueous solutions and of solid H[Bi(MPA)₂]⁺H₂O complex have been carried out by UV-Vis, ¹H-NMR, Raman, ICP-AES and EXAFS spectroscopic methods combined with an ab initio research. All complex species have cyclic S,O-chelate structures. An ab initio simulation on thermodynamics of complexation of Bi(III) by H₂MPA have been carried out aiming to choose an appropriate quantum chemical methodology. The most accurate results have been achieved with M06 density functional, SMD solvation model and Def2-TZVPP basis set with discrepancies of stability constants within ± 1.0 logarithmic unit.

Introduction

As well as other mercapto acids, 3-mercaptopropionic acid, HSCH₂CH₂COOH (H₂MPA) is a biologically active reagent [1-4]. It serves as a traceless linker for chemical and enzymatic synthesis of oligosaccharides [5] and as an inhibitor of neurulation movements in amphibian larvae [6]. Also 3-mercaptopropionic acid is a potent inhibitor of fatty acids oxidation in rat heart mitochondria [7].

There are multiple reports focused on complexation of H₂MPA with Zn(II), Ni(II), In(III), Cd(II), Hg(II), Co(III) Lanthanides(III), Pd(II) and Pt(II) [8 - 21]. The reason for the choice of bismuth(III) ion is essentially due to the fact that bismuth compounds have attracted attention recently because of their multiple applications in diverse areas including medicine materials and material sciences. The medicinal application of bismuth compounds is focused in two fields: antimicrobial and anticancer [22, 23].

Previous works have shown that interaction of bismuth(III) with H₂MPA in neutral pH media leads to formation of cluster compounds [24, 25]. Current research is dedicated to study of complexation of H₂MPA with Bi(III) in strong perchloric solutions. This condition is able to provide simpler model with contribution from the poly-nuclear species being rather negligible and consequently more detailed description.

The complexation of H₂MPA with Bi(III) ions in aqueous perchloric solutions has been investigated by using a combination of experimental (UV-Vis, ¹H-NMR, Raman, ICP-

AES and EXAFS spectroscopic methods) and computational (density functional theory) tools in order to attain structural and electronic properties of the resulting complex species.

Systematic research on thermodynamics of complex formation of Bi(III) with S-donor organic polyfunctional ligands in aqueous solutions and on structure of such complex species is important not just in terms of coordination chemistry. A detailed information on bismuth(III) speciation in aqueous solutions is necessary in many application fields. For instance, these thermodynamic and structural data might seem useful for optimization of nanoparticles availability from various sulfur containing bismuth(III) precursor complex species in aqueous solutions [26-29].

One of the most powerful ways to characterize interactions between metal ions and bio-relevant ligands is the integration of experimental methods with quantum chemical methodologies, which provides accurate calculations of the spectroscopic and physicochemical properties of bioinorganic systems by wave-function (ab initio) and DFT methods [30].

The aim of the current research was to find an appropriate quantum chemical methodology, which could provide high agreement between results of experimental and theoretical investigations of complexation of Bi(III) with 3-mercaptopropionic acid in perchloric aqueous solutions.

Experimental

The chemicals

All chemicals were of analytical grade: Bi₂O₃, HClO₄, Na₂CO₃ and disodium EDTA. H₂MPA was available from Sigma-Aldrich.

The stock solution of bismuth(III) triperchlorate was prepared by dissolution of accurate weight of Bi₂O₃ in concentrated HClO₄ had been standardized before with 0.1 N Na₂CO₃ solution. The acid was taken in excess to provide C_{H+} = 1.5 M in the Bi(III) stock solution. The accurate concentration of Bi(III) was determined by complexometric titration with 0.05 M disodium EDTA solution (pyridylazoresorcin served as indicator). The excess acidity of stock bismuth triperchlorate solution was determined by Gran titration [31].

The NaClO₄ solution was obtained by neutralization of Na₂CO₃ with perchloric acid. The concentration of sodium perchlorate was determined gravimetrically as Na₂SO₄. 1 ml of NaClO₄ solution was dissolved in 1 ml of concentrated sulphuric acid and evaporated then. The dry salt was subsequently calcined at 650 °C to constant mass.

The stock solution of 3-mercaptopropionic acid was obtained by dilution of accurate aliquot of pure reagent in adjusted volume. The H₂MPA stock solutions also contained 0.5 M HClO₄.

Equipment

The UV-Vis electronic absorption spectra (EAS) were measured with an Evolution 300 scanning spectrophotometer (ThermoScientific, England) using 1 cm quartz cells. Cell thermostating (± 0.1 K) was performed with a Haake K15 thermostat connected to Haake DC10 controller. The absorbance was measured within 220 - 450 nm.

The ICP-AES has been performed with an iCAP 6500 spectrometer (ThermoScientific, UK). TGA had been carried out on the simultaneous SDT-Q600 TA Instruments thermal analyzer in the argon atmosphere within 20-200 °C at the scan rate of 10 °C/min.

The Raman spectra were recorded with a Nicolet Almega XR Raman spectrometer at 785 nm excitation wavelength and 4 cm⁻¹ resolution.

The Hi-Res ¹H-NMR spectra of aqueous solutions of Bi(III)-H₂MPA compounds were measured with a Bruker Avance III spectrometer (600 MHz ¹H-resonance gradient coil). The D₂O/H₂O mixture served as external standard with deuterium signal being the reference one. The spectra were obtained with 17-millisecond pulses, water suppression was performed by selective saturation with gradients based on a conventional Bruker pulse sequence (zgesgp). The Fourier spectrum was obtained by transformation of 32K points and consequent convolution with exponential function with 0.8 Hz broadening.

The EXAFS spectra in transmission mode both of a solid compound and of aqueous Bi(III)-H₂MPA solution were

collected at the synchrotron radiation channel of the VEPP-3 storage ring (The Budker Institute of Nuclear Physics of SB RAS). The electrons energy and current of the storage ring were set to 2 GeV and 70-140 mA respectively. The measurements were conducted beyond Bi(III) L_{III}-edge at 800 eV using the Si(111) double-crystal monochromator. The ionization chambers were filled with Ar/He gas mixture and with xenon gas as monitoring and final detectors respectively. The solid complex was grinded with cellulose powder filler and pelletized. The aqueous solution was placed into a 10-mm Teflon cell with Mylar windows. Four scans were taken for each sample at 298 K and averaged to improve the statistics.

Sample preparation

The stoichiometry of Bi-H₂MPA species was determined by isomolar ratio method (Table 1). Perchloric acid was taken in excess to prevent bismuth(III) hydrolysis.

Stability constant for M(HL) species has been determined under the condition of metal excess. Each set of process solutions included a solution of ligand (C_{H2L}), a series of solutions containing bismuth(III) (C_M) and a series of solutions containing both bismuth(III) and ligand (C_M + C_{H2L}).

Samples for Raman, ¹H-NMR and EXAFS spectroscopy have been prepared according to Table 1.

Table 1. Sample preparations

Method	Conditions (298 K)
Raman	C _M = 0.1 M, C _{H2L} = 0.3 M, C _{HClO4} = 0.8 M
¹ H-NMR	C _M = 0.1 M, C _{H2L} = 0.3 M, C _{HClO4} = 0.8 M
EXAFS	C _M = 0.1 M, C _{H2L} = 0.6 M, C _{HClO4} = 1.0 M
Uv-Vis:	
Stoichiometry and stability constants for M(HL) ₂₋₃ species	C _M = 2.5·10 ⁻⁴ M, C _{H2L} = 1.5·10 ⁻⁴ M - 4.5·10 ⁻³ M, C _{HClO4} = 0.5-2.0 M
Stability constants for M(HL) species	C _M = 1.5·10 ⁻³ M - 2.0·10 ⁻² M, C _{H2L} = 1.5·10 ⁻⁴ , C _{HClO4} = 0.5 - 2.0 M, I = 0.5 - 2.0 (NaClO ₄)

The solid complex was obtained from mixing 4.5 ml of 0.25 M Bi(ClO₄)₃ stock solution containing excess acidity of 1.1 M (HClO₄) and 0.1 ml of pure H₂MPA. The yellow precipitate appeared instantly after mixing the reagents. The precipitate was collected; a dry weight of 20 mg was dissolved in 100 ml of 10% nitric acid solution. The ICP-AES analysis found 49.5 % of Bi and 15.0 % of S (calculated for H[Bi(MPA)₂]₂·H₂O: Bi = 47.9 %, S = 14.7 %). TGA-measurements of H[Bi(MPA)₂]₂·H₂O compound showed up to 200 °C the weight loss of 4.8% (Calc. - 4.3%). Thus, analysis of the complex salt has indicated that the compound contains one molecule of crystallization water.

Uv-Vis study

Process of complex formation causes change of electronic absorption spectra: ΔA = A_{complex} - A_M - A_{H2L} (A - absorbance, L² = MPA²). Mathematical processing of UV-Vis EAS has been carried out with Scilab 5.5 software [32]. The number of

absorbing species N contributing to the absorbance matrix has been estimated with the factor indication function (IND) [33]. Calculation of stability constants has been performed by the non-linear LSR analysis. The A values served as raw data for calculation of cumulative conditional stability constants β' (temperature, ionic strength and medium were fixed) [34] and have been enclosed in the ESI† (Tables S1 and S2). The values $\varepsilon_{\text{H2L}}^{267} = 4$ and $\varepsilon_{\text{Bi}}^{267} = 2$ have been used during computation of A_{calc} . The optimal values for β'_n and ε_n^{λ} were found from the condition of minimum net discrepancy [34, 35]:

$$\sum (A_{\text{exp}} - A_{\text{calc}})^2 \rightarrow \min. \quad (1)$$

The common $A - \lambda$ and $\Delta A - \lambda$ plots for Bi(III)-H₂MPA perchloric aqueous solutions are shown in Figures 1A, C and S1). Examples calculations on Eq.(1) are shown in Figures 1B and 1D.

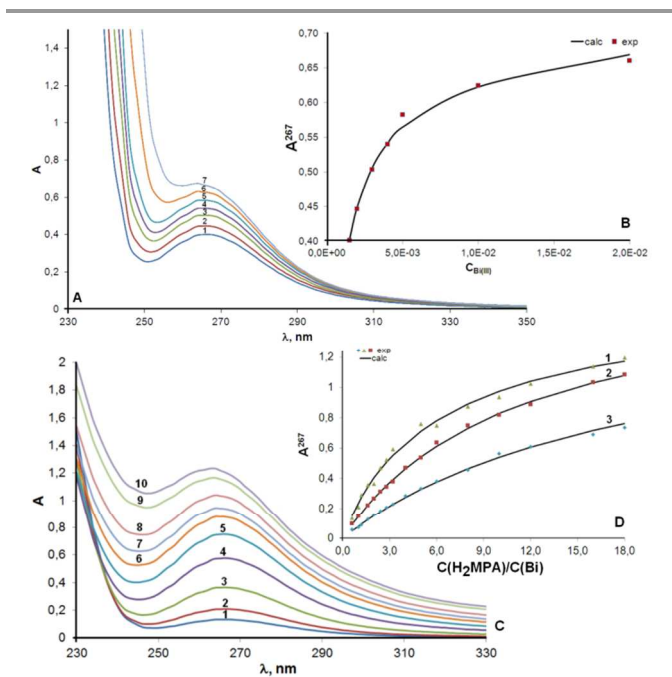


Fig. 1 The A versus λ (A) and $(A_{\text{exp}} - A_{\text{calc}})$ versus C_{Bi} (B) plots for Bi(III)-H₂MPA system. $C_{\text{Bi}} \cdot 10^{-3}$ M: 1.5(1); 2.0 (2); 3.0 (3); 4.0 (4); 5.0 (5); 10.0 (6); 20.0 (7). $C_{\text{H2MPA}} = 1.5 \cdot 10^{-4}$ M. 0.5 M HClO₄, $I = 0.5$ (HClO₄). The A versus λ (C) and $(A_{\text{exp}} - A_{\text{calc}})$ versus $C_{\text{H2MPA}}/C_{\text{Bi}}$ plots at different acidities (D): 1 – 0.5 M HClO₄, 2 – 1.0 M HClO₄, 3 – 2.0 M HClO₄. $C_{\text{Bi}} = 2.5 \cdot 10^{-4}$ M. $C_{\text{H2L}} \cdot 10^{-4}$ M: 1.5(1); 2.5 (2); 5.0 (3); 10.0 (4); 15.0 (5); 20.0 (6); 25.0 (7); 30.0 (8); 40.0 (9); 45.0 (10) 298 K. $l = 1$ cm

Ab initio study

Calculations were carried out using the GAMESS US 2013 R1 program package [36] with the Super-computer of Institute of Space and Information Technologies (SFU) [37]. Geometry optimization was performed by density functional theory (DFT) with the hybrid functional PBE0 [38] under Grimme's empirical correction [39, 40] and M06 [41], M06-L [42], M11 [43], M11-L [44] density functionals. The Def2-SVP or Def2-TZVPP [45] basis set including ECP pseudopotential for Bi was applied to every atom in the complex during every computational procedure. The solvent effects were evaluated

using the SMD solvation model [46] (water built-in parameters were used). The UV-Vis EAS of complex species were reproduced from the vertical excitation energies for the first 11 singlet excited states (TD-DFT/PBE0/SMD). The optimized geometries and molecular orbitals were visualized with the ChemCraft software [47]. The MO's percentage composition was found with the QmForge software [48].

EXAFS spectra analysis

The XAS Bi-L_{III} spectra were processed in several stages including extrapolation of pre-edge absorption region into the EXAFS region, separation of smooth and oscillating components, construction of the normalized oscillating component of the absorption coefficient on the scale of photoelectron wavevectors and consequent Fourier transformation to construct the atomic radial distribution function (Figure 2).

All of these spectrum processing procedures were performed using VIPER software [49]. The local environment of the Bi(III) atom was modeled with EXCURV 98 software [50] for Fourier-filtered ($\Delta R = 1.2 - 2.5$ Å) k -weighted data within 3 - 10 Å⁻¹ range of wavevectors for solid compound and k^2 -weighted data within 3 - 11 Å⁻¹ range of wavevectors for liquid solution.

During the data processing the phase and amplitude properties were calculated using von-Bart and Hedin approximation. The amplitude damping factor S_0^2 , caused by multi-electron effects, was taken to be 0.8 and fixed during the spectrum modelling of solutions allowing R (bond distance), σ^2 (Debye-Waller parameter) and sometimes N (coordination number) to float. Coordination numbers have been fixed during final modelling.

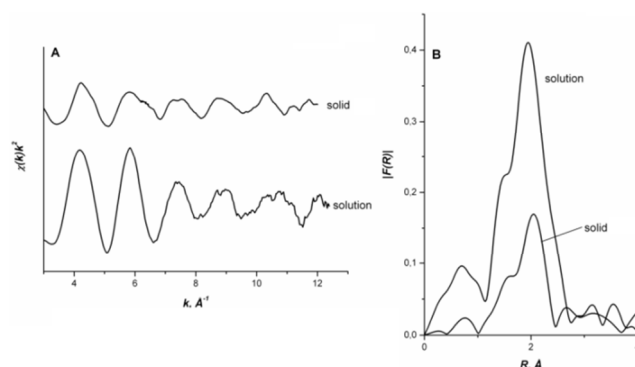


Fig. 2 Bi_{LIII} EXAFS-spectra $k^2\chi(k)/A$ and their Fourier transformation modules (B) for the solid complex and its aqueous solution

Results and discussion

A spectroscopic and an ab initio investigation of complex formation in aqueous solutions

UV-VIS STUDY

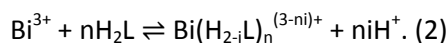
The study under the condition of monocomplex species dominance ($C_{\text{M}} \gg C_{\text{H2L}}$) has revealed absorbance maximum at 267 nm being invariant at different bismuth concentrations,

thus one may conclude monocomplex BiH_mL is the only product and the contribution from the poly-nuclear species $\text{Bi}_n\text{H}_m\text{L}$ is rather negligible.

The number of absorbing species of 2 under the condition of $C_M > C_{\text{H}_2\text{L}}$ within 245 – 320 nm is equivalent of metal ion and mono complex species being the only absorbing species and consistent with Figure S1 since the ligands contribution in the absorbance matrix is of negligible quantity.

Though, according to the method of isomolar series (Figure 1D) at $\text{H}_2\text{L}:\text{M}$ mole ratio ≥ 3.0 , the dominating species under such conditions has $\text{M}:\text{H}_2\text{L}$ stoichiometry = 1:3. There are five absorbing species contributing to the UV-Vis EAS of solution under the condition of $C_{\text{H}_2\text{L}} > C_M$ within 230 – 330 nm and such species are metal ion, free ligand, mono, bis and tris complex species. The EAS of bis and tris species have the same absorption maximum at 267 nm – likewise the EAS of mono complex species.

In general, process of interaction of Bi(III) with H_2MPA in strongly acidic ($C_{\text{H}^+} = 0.5 \text{ M}$) solutions is described with Equation 2:



The $\beta^n - [\text{H}^+]$ relationship (n is equal to 1 in the case of monocomplex species) has shown displacement of one proton being substituted by bismuth(III) upon complexation ($i = 1$). The stepwise stability constants ($\log K_n$) for complex species of H_2MPA with Ni^{2+} [8], Zn^{2+} [8, 10], Cd^{2+} [14], In^{3+} [11, 12], Ln^{3+} [13] and protonation constants (K^{H}) [51] of 3-mercaptopropionic acid in water solutions are given in Table 2.

Table 2. The $\log K_n$ and K^{H} values at 298 K

Species	Ni^{2+}	Zn^{2+}	Cd^{2+}	In^{3+}	Ln^{3+}	H^+ [1]
ML	5.2	6.8	8.8	11.87	1.40 – 1.74	10.03, I_1 9.96, I_2
ML_2	4.4	6.5	4.8	7.66	-	4.26, I_1 4.09, I_2
ML_3	-	-	-	6.25	-	-
Coordination	S, O	S, O	S, O	S	O	$L = \text{S}^-$; $L_2 = \text{COO}^-$
Background, I	0.2	0.2	0.1	0.1	2.0	$I_1 = 2.0$; $I_2 = 0.5$

Confidence limits for $\log K_n$ and K^{H} do not exceed ± 0.1 and ± 0.005 , respectively

Calculation of β values (“true” stability constant) was carried out using $\text{p}K_{\text{H}_2\text{MPA}}$ values from Table 1 by the following expression:

$$\beta = \beta' \cdot (1 + K^{\text{H}}[\text{H}^+]). \quad (3)$$

The averaged $\log \beta'$ and $\log \beta$ values are given in Table 3. The “ \pm ” values represent confidence limits ($P = 0.95$) throughout the article.

Table 3. Conditional (β') and “true” (β) cumulative stability constants of $\text{Bi}(\text{HMPA})_n^{(3-n)+}$ complex species and $\epsilon_{\text{complex}}^{267}$ in aqueous perchloric solutions (298 K)

Ionic strength, I	Background, M	N	$\log \beta'_n$	ϵ^{267}	$\log \beta_n$
0.5	0.5 HClO_4	1	3.04 ± 0.02	4388 ± 150	13.1 ± 0.1
		2	5.21 ± 0.14	3600 ± 250	15.2 ± 0.1
		3	8.28 ± 0.08	5500 ± 200	17.8 ± 0.1
1.0	0.5 HClO_4 + 0.5 NaClO_4	1	2.99 ± 0.02	4491 ± 150	13.1 ± 0.1
		1.0 HClO_4	1	2.66 ± 0.05	4327 ± 150
	2.0 HClO_4	2	4.81 ± 0.1	4200 ± 250	15.2 ± 0.1
		3	7.42 ± 0.08	5550 ± 200	17.8 ± 0.1
		2	2.51 ± 0.02	4128 ± 150	13.2 ± 0.1
		2	4.34 ± 0.1	4000 ± 250	15.2 ± 0.1
2.0	1.0 HClO_4 + 1.0 NaClO_4 + 0.5 HClO_4 + 1.5 NaClO_4	3	6.51 ± 0.08	5450 ± 200	17.8 ± 0.1
		1	2.77 ± 0.02	4560 ± 150	13.2 ± 0.1
		1	3.08 ± 0.06	4864 ± 150	13.2 ± 0.1

The $\log \beta_n$ and $\epsilon_{\text{Bi}(\text{HMPA})_n}^{267}$ have been considered as constants within the range of $I = 0.5 - 2.0$. The very similar $\log \beta_1$ value is observed for triple-charged $\text{In}(\text{III})$ while double-charged $\text{Zn}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cd}(\text{II})$ metal ions form weaker species with H_2MPA . Despite the lack amount of data, one may conclude that strength of complex species of transition metals with H_2MPA is governed by ionic potential of metal ion. The experimental “true” and conditional stability constants have been used for the construction of distribution diagrams (Figures 3 and S2). It can be seen that mono- and tris-ligand complexes are dominating species.

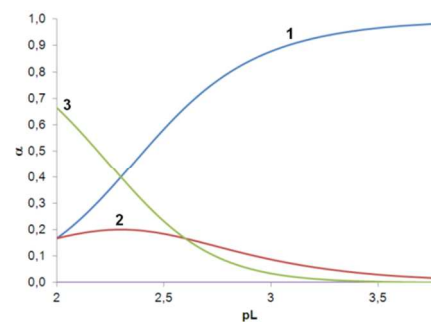


Fig. 3 Distribution diagram obtained using experimental “true” stability constants; 1 – $[\text{MHL}]$, 2 – $[\text{M}(\text{HL})_2]$, 3 – $[\text{M}(\text{HL})_3]$

RAMAN SPECTROSCOPY

Raman spectroscopy has indicated apparent formation of Bi-S bond, hence 3-mercaptopropionic acid coordinates via sulfur atom of thiol group (Figure S3). The band at 2585 cm^{-1} corresponding to $\nu(\text{S-H})$ vibrations was found in the Raman spectrum of H_2MPA solution. No such band was present in the spectrum of $\text{H}_2\text{MPA-Bi}(\text{III})$ solution while the new band at 304 cm^{-1} corresponding to $\nu(\text{Bi-S})$ vibrations clearly indicated binding of bismuth(III) to sulfur.

$^1\text{H-NMR}$ SPECTROSCOPY

The decrease in intensity of the peak located at 2.24 ppm in the $^1\text{H-NMR}$ spectrum of $\text{H}_2\text{MPA-Bi}(\text{III})$ aqueous solution (Figures

S4 and S5) assigned to the S-H group supports the coordination of the ligand via sulfur of thiol group.

EXTENDED X-RAY ABSORPTION FINE STRUCTURE AND DFT CALCULATIONS

The distribution diagram (Figure 3) evidently shows tris-ligand complex being the most dominating species under the condition of ligand excess. Thus, EXAFS investigation has been performed to establish the structure of the complex species.

According to EXAFS data, bismuth(III) under condition of ligand excess (molar ratio $H_2L:M \geq 3$) is coordinated by three oxygen and three sulfur atoms. The experimental Fourier-filtered and simulated EXAFS spectra in aqueous perchloric solution are compared in Figure 4A.

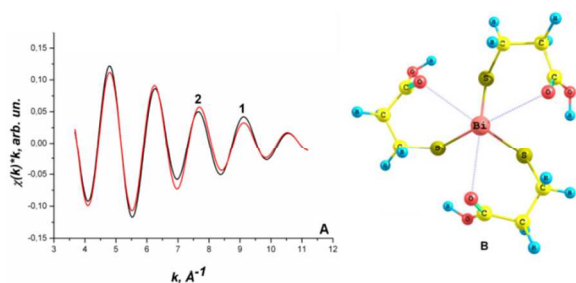


Fig. 4 The experimental Fourier-filtered (1) and simulated Bi L_{III} EXAFS spectra (2) (A) of $Bi(HMPA)_3$ complex species (B) in aqueous perchloric solution

Density functional theory (DFT) calculations were carried out in the present work to interpret the thermodynamic data. Besides the DFT study has highlighted the relationship between the intrinsic affinity of a given metal ion for the target ligand and the solvating effects.

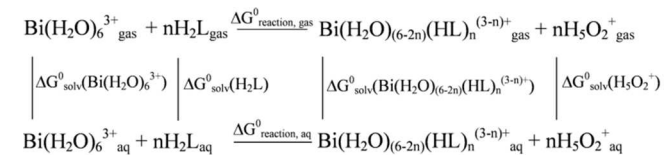
Previous research [52] dedicated to study of S,O-chelate complex formation of Bi(III) with 3-mercaptoethansulfonic (H_2MES) and 3-mercaptopropanesulfonic acids (H_2MPS) has found $Bi(H_2O)_3(HL)^{2+} \cdot H_2O$ species to be more stable rather than $Bi(H_2O)_4(HL)^{2+}$ one. The solvation model SMD was found the best to fit the thermodynamics calculations for complexation of main groups elements.

In strong acidic medium the ligand coordinates via sulfur atom of thiol group, while carboxyl group remains protonated being involved in formation of Bi-O ionic bond via carbonyl oxygen atom. Thus a bidentate O,S-chelation of 3-mercaptopropionic ligands has been suggested during the current research. Optimized geometries of complexes are shown in Figure 5 and Figure 4B.

Thermodynamic properties of the complex species were theoretically investigated aiming to check consistence with experimental stability constants. The calculation was based on the thermodynamic cycle (Scheme 1) suggested by Bryantsev et al [53]. The best calculation of stability constant for $Bi(HL)_2^+$ complex species has been achieved using $H_7O_3^+$ leaving group contrary to mono and tris complex species. It is worth separating the reaction free energy in aqueous solution as the sum of three parts: electronic plus nuclear repulsion energy (ΔE^{ele}), thermal contribution (ΔG^T), and solvation free energy ($\Delta \Delta G^{sol}$), as given in Equation 4. The thermal contribution is

estimated using the ideal gas model, the calculated harmonic vibrational frequencies to estimate the zero point energy correction (ZPE), and the correction due to the thermal population of vibrational levels (Table S3).

$$\Delta G_{aq}^{tot} = \Delta E^{ele} + \Delta G^T + \Delta \Delta G^{Sol}. \quad (4)$$



Scheme 1 Thermodynamic cycle for interaction of Bi(III) with H_2MPS in aqueous solution

According to the previous research [52], the PBE0 hybrid functional has been chosen as the reference one. Also Zhao et al recommend Minnesota group density functionals, especially M06, for calculation of molecular structures and thermochemistry of main group elements [54]. Results have been obtained using various density functionals on DFT/Def2-TZVPP level are compared in Table 4.

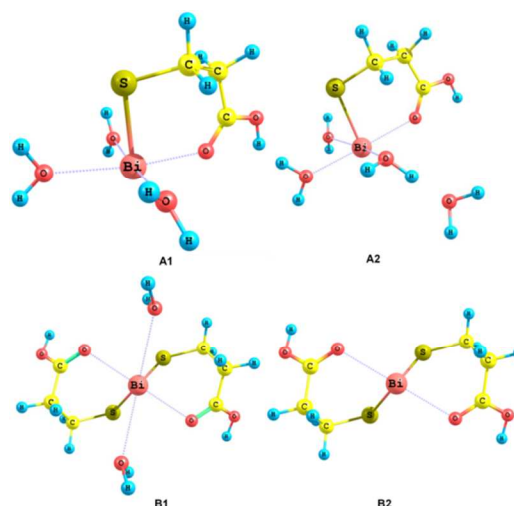


Fig. 5 Optimized geometries of $Bi(H_2O)_3(HMPA)_2^+$ (A1), $Bi(H_2O)_3(HMPA)_2^+ \cdot H_2O$ (A2), $Bi(HMPA)_2(H_2O)_2^+$ (B1) and $Bi(HMPA)_2^+$ (B2) complex species

Table 4. Estimated Gibbs energies (kJ mol^{-1}) and stability constants of Bi(III)- H_2MPS complex species (DFT/Def2-TZVPP)

Species	DFT	ΔE^{ele}	ΔG^T	$\Delta \Delta G^{Sol}$	ΔG^{tot}	$\log \beta_{calc}$	$\log \beta_{exp}$
$M(HL)^1$	PBE0	-822.5	8.8	721.8	-91.9	16.1	
	PBE0	-816.8	7.5	721.6	-87.6	15.3	
	M06	-792.6	5.2	711.3	-76.1	13.3	
$M(HL)^2$	M11	-803.3	-4.4	730.0	-77.7	13.6	13.1
	M06L	-783.6	5.6	715.6	-62.4	10.9	
	M11L	-802.0	3.8	739.2	-59.0	10.3	
$M(HL)_2^1$		-1009	13.6	925.6	-69.8	12.2	
$M(HL)_2^2$	M06	-1095	12.1	1001	-81.6	14.3	15.2
$M(HL)_3$		-912.4	15.6	792.6	-104.2	18.3	17.8

Obviously, M06 density functional and def2-TZVPP basis set provide the most accurate calculation of complexation thermodynamics. Literally – the least discrepancy between $\log\beta_{\text{calc}}$ and $\log\beta_{\text{exp}}$ values. Thus DFT/M06/def2-TZVPP level has been chosen for further calculations.

The final sequence of cumulative stability constants $\beta_1 < \beta_2 < \beta_3$ agrees both with theoretical and empirical data. It should be noted that $\log\beta_1$ value for $\text{Bi}(\text{H}_2\text{O})_3(\text{HMES})^{2+}\cdot\text{H}_2\text{O}$ [52] with the similar structure (sulfonic group instead of carboxylic) (11.7) is close to one for $\text{Bi}(\text{H}_2\text{O})_3(\text{HMPA})^{2+}\cdot\text{H}_2\text{O}$ (13.1).

The DFT calculations provide increasing Bi-O bond distance from 2.40 Å (M(HL)) to 2.49 Å (M(HL)₂) and up to 2.94 Å (M(HL)₃). This fact is consistent with decreasing charge of complex species: $\text{MHL}^{2+} < \text{M(HL)}_2^+ < \text{M(HL)}_3^0$.

The combination of EXAFS and DFT data (Table 5) on $\text{Bi}(\text{HMPA})_2^+$, $\text{Bi}(\text{HMPA})_3$ structure provided quite consistent Bi-S bond distances matching with previously reported Bi-S distances for bismuth-thiolate complexes in aqueous solutions – 2.5-2.6 Å [55, 56]. On the contrary, the Bi-O bond distances rather mismatched. The similar difference in experimental and calculated Bi-O bond distances was observed in [56].

Table 5. Coordination numbers (N) and interatomic distances for $\text{Bi}(\text{HMPA})_3$ according to EXAFS spectra and DFT-optimized geometries (DFT/M06/Def2-TZVPP)

Bond	N	$2\sigma^2$ (Å ²)	Interatomic distance (Å)	
			EXAFS	DFT
Bi-S	3	0.012±0.008	2.51 ± 0.01	2.53
Bi-O	3		2.70 ± 0.02	2.94

$2\sigma^2$: Debye – Waller factor

Discrepancy between Bi-O bond distances from EXAFS (2.70) and DFT calculations (2.94) for tris complex species can be explained in assumption of contribution of bi-ligand complex species (2.43 from DFT). Theoretical methods have been widely applied to interpret experimental spectroscopic data. Since authors of [57, 58] consider PBE0 density functional appropriate for calculations of vertical excitation spectrum, it has been chosen for TD-DFT simulations. The optimized geometry for TD-DFT study was taken from DFT/M06 calculation. A TD-DFT study has been carried out on electronic structure of the every complex species to investigate charge transfer process (Table 6).

Table 6. Contribution of different electronic charge transfers to the 267 nm absorbing band of $\text{Bi}(\text{H}_2\text{O})_3(\text{HMPA})^{2+}\cdot\text{H}_2\text{O}$, $\text{Bi}(\text{HMPA})_2^+$ and $\text{Bi}(\text{HMPA})_3$ species

Species	λ_{exp} , nm	λ_{calc} , nm	f	MO	Transition
M(HL)		270	0.009	H→L (83.2 %)	
		267	0.01	H-1→L+1 (36.8 %) + H→L+2 (47.1 %)	
M(HL) ₂	267 (max) broad	273	0.008	H→L+1 (70.5 %)	LMCT
		289	0.014	H→L (30.9 %) + H→L+1 (45.6 %)	
		271	0.011	H-1→L (27.4 %) + H→L+2 (35.0 %)	
M(HL) ₃		265	0.013	H-1→L+1 (60.4 %)	

The band at 267 nm corresponds to the main electronic transition occurring from the HOMO to the LUMO for M(HL). The spreading of absorbance band for M(HL)_3 complex species has been confirmed by TD-DFT calculations. Figure 6 exhibits MO's (SMD/DFT/PBE0) contributing to charge transfer for M(HL) (see Figures S6 and S7 for $\text{Bi}(\text{HL})_2^+$ and M(HL)_3 , respectively). Atomic orbital population analysis is given in the Table S4 providing evidence of electronic transition from sulfur to bismuth. These data give solid evidence of $\pi \rightarrow \pi^*$ charge transfer from thiol sulfur atom to bismuth(III) in both complex species. Recently we reported of the same $\pi \rightarrow \pi^*$ S→Bi charge transfer at 268 nm in the $\text{Bi}(\text{H}_2\text{O})_3(\text{HMPS})^{2+}\cdot\text{H}_2\text{O}$ and $\text{Bi}(\text{HMPS})_3$ species in aqueous perchloric solutions [52, 58].

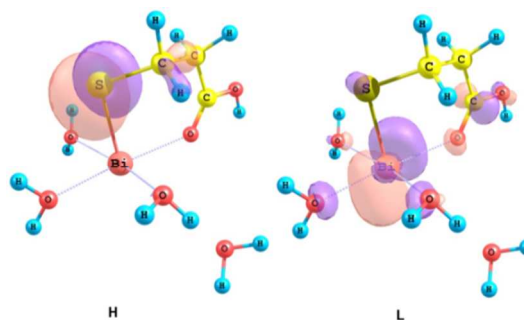


Fig. 6 Rendered HOMO and LUMO of $\text{Bi}(\text{H}_2\text{O})_3(\text{HMPA})^{2+}\cdot\text{H}_2\text{O}$

Hence, SMD/TD-DFT/PBE0 model and Def2-TZVPP basis set provide good accordance of theoretical and experimental EAS. Actually more accurate structural, spectroscopic and thermodynamic data might be obtained by direct calculation of relativistic and specific solvation effects or by application of different diffusion basis sets. Nevertheless, such calculations were considered as a very resource-intensive operation and thus had not been performed during our current research.

Solid $\text{H[Bi(MPA)}_2]\cdot\text{H}_2\text{O}$ complex

The final product of complexation of Bi(III) by 3-mercaptopropanesulfonic acid in perchloric acid aqueous solutions are governed by initial mole ratio of reagents. The current study revealed yellow colored precipitate in solutions at $\text{H}_2\text{L}:\text{M}$ ratio = 2.0. This precipitate is found to dissolve at higher $\text{H}_2\text{L}:\text{M}$ ratios.

A structure of $\text{H[Bi(MPA)}_2]\cdot\text{H}_2\text{O}$ was consistent with and resulted from elemental analysis (ICP-AES), Raman and EXAFS spectroscopy. This complex was found to be X-ray amorphous according to XRD analysis.

The Raman spectra (Figure S8) have given evidence of ligand coordination via sulfur atom of thiol functional group. The band at 304 cm^{-1} referring to $\nu(\text{Bi-S})$ vibrations was present in the Raman spectrum in the case of solid $\text{H[Bi(MPA)}_2]\cdot\text{H}_2\text{O}$ and was absent in the case of free ligand. On the contrary, the band at 2585 cm^{-1} corresponding to $\nu(\text{S-H})$ vibrations was found in the Raman spectra of the ligand and was absent in the Raman spectra of the complex.

According to EXAFS data, the central Bi(III) atom is surrounded by four neighbor oxygen atoms and by two sulfur

atoms. The experimental Fourier-filtered and simulated EXAFS spectra for the $\text{H}[\text{Bi}(\text{MPA})_2]\cdot\text{H}_2\text{O}$ solid complex are compared in Figure 7A.

3-mercaptopropionic acid commonly forms complex species of cyclic S,O-chelate structures [8, 18]. However, it also forms polymeric S-bridged structures with Pd(II) and Pt(II) [16, 17] and O-bridged polymers with Gd(III), Eu(III) and Tb(III) [15].

No bidentate coordination of carboxylic functional group in $[\text{Bi}(\text{MPA})_2]^-$ is observed (DFT) so this complex is likely to have polymeric structure. However, this assumption can not be confidently confirmed by EXAFS data, because the objective conditions do not allow with certainty to detect the appropriate feature on the curve of Fourier transform module of corresponding spectrum. The suggested geometry has been optimized by DFT/M06/Def2-SVP computations (Figure 7B). Figure 7B shows that MPA^{2-} ions are bound to bismuth(III) as bidentate (S,O) chelating ligands forming a polymeric structure. Coordination number of six is achieved by binding of Bi(III) with other two complex fragment by bridging COO-group. Such ligand coordination is consistent with previous reports [8, 15, 16 - 18]. The optimized geometry corresponds to the C_2 point symmetry group. The results of EXAFS spectroscopy investigation and of DFT simulation are given in Table 7.

Table 7. Coordination numbers (N) and interatomic distances according to EXAFS spectra and DFT-optimized geometries (DFT/M06/Def2-SVP)

Bond	$2\sigma^2(\text{\AA}^2)$	N	Interatomic distance (\AA)	
			EXAFS	DFT
Bi-S	0.023 ± 0.002	2	2.50 ± 0.01	2.65
Bi-O		2	2.36 ± 0.02	2.35
		2	2.75 ± 0.02	2.80

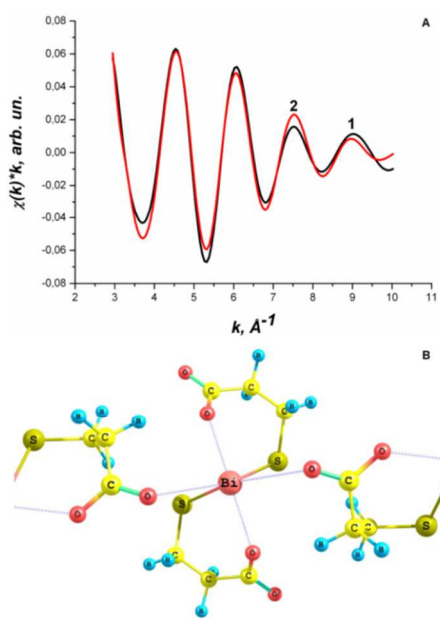


Fig. 7 The experimental Fourier-filtered (1) and simulated Bi L_{III} EXAFS spectra (2) of the solid $[\text{Bi}(\text{MPA})_2]\cdot\text{H}_2\text{O}$ (A) and optimized fragment of polymer $[\text{Bi}(\text{MPA})_2]^-$ (B)

There are two types of Bi-O bonds in the $[\text{Bi}(\text{MPA})_2]^-$ complex according to EXAFS data analysis: the covalent ($2.36 \pm 0.02 \text{ \AA}$) and the ionic ($2.75 \pm 0.02 \text{ \AA}$) ones. The DFT simulation has provided Bi-O bond distances of 2.35 \AA and 2.80 \AA , respectively. Hence, EXAFS and DFT study provided Bi-O and Bi-S bond distances in the solid $[\text{Bi}(\text{MPA})_2]^-$ being consistent with previous report for Bi(III)-thiolate complexes: $2.4\text{-}2.7 \text{ \AA}$ and $2.5\text{-}2.6 \text{ \AA}$ long respectively [58, 59].

Some curious behaviour can be observed making comparison between $\text{M}(\text{HL})_3$ and $\text{H}_3\text{O}^+[\text{ML}_2]^-$ complex species: tris complex has not participated from solution during any time, despite the fact that this complex has no charge. It may be associated with specific contributions of solvation effects in total Gibbs energies. The similar pattern has been reported previously [56] for Bi(III)-2-mercaptopropanesulfonic acid (H_2MPS). Further investigations on biological activity seem to be curious and valuable [22, 23].

Conclusions

The aim of the current research has been achieved successfully and the following conclusions have been drawn:

- Complex formation of Bi(III) with 3-mercaptopropionic acid has been studied in the aqueous perchloric solutions at $C_{\text{H}^+} = 0.5 - 2.0 \text{ M}$. Equilibrium study had been performed by spectrophotometry at 298 K within $I = 0.5 - 2.0$. Formation of $\text{Bi}(\text{HMPA})_3$ species under ligand dominance ($C_{\text{H}_2\text{L}} \gg C_{\text{M}}$) condition has been vindicated by Raman, $^1\text{H-NMR}$, UV-Vis and EXAFS spectroscopy. Each 3-mercaptopropionato ligand (HMPA^-) is coordinated to bismuth(III) via sulfur atom of thiol group and via carbonyl oxygen atom of carboxylic group. The novel solid complex ($\text{H}[\text{Bi}(\text{MPA})_2]\cdot\text{H}_2\text{O}$) has been obtained and characterized by Raman and EXAFS spectroscopy and DFT simulation. The polymeric structure formation with Bi-O bridging via carboxyl group of MPA^{2-} species has been suggested.
- Among the PBE0, M06, M06-L, M11 and M11-L density functionals which have been tested, the M06 has been chosen as the most appropriate one for calculations of H_2MPA complexation thermodynamics and molecular geometries. The SMD/M06/def2-TZVPP model provided the most accurate prediction of stability constants of bismuth(III)-thiolate species with discrepancies within ± 1.0 logarithmic unit. The TD-DFT (PBE0) study proved that 267 nm bands in the UV-Vis EAS of $[\text{Bi}(\text{H}_2\text{O})_3(\text{HMPA})^{2+}]\cdot\text{H}_2\text{O}$, $\text{Bi}(\text{HMPA})_2^+$ and $\text{Bi}(\text{HMPA})_3$ species correspond to $\pi \rightarrow \pi^*$ charge transfer from thiol sulfur atom to bismuth(III).

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Listing of ¹H-NMR, Raman and UV-Vis spectral data, distribution diagram, Cartesian coordinates for DFT/M06-optimized geometries and energies, atomic percentage and rendered molecular orbitals. See DOI: 10.1039/b000000x/
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