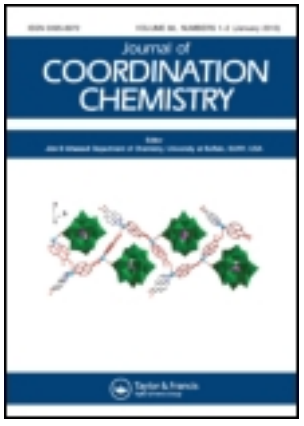

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A spectroscopic and *ab initio* study on Bi(III) complex formation with 3-mercaptopropanesulfonic acid

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This article deals with complex formation of Bi(III) with 3-mercaptopropanesulfonic acid (H_2MPS) in aqueous perchloric acid solutions, with synthesis and characterization of a solid 3-mercaptopropanesulfonate complex of bismuth(III). The stoichiometry and structures of Bi-MPS species in aqueous solution and of a solid complex have been studied by UV–Vis, ^{1}H-NMR, ICP-AES, Raman, and EXAFS spectroscopic methods; the structures have also been simulated with DFT/PBE0 calculations. The Bi(III) L_{III}-edge EXAFS oscillation for a solid compound with the empirical formula $[Bi(HMPS)_2(ClO_4)]^0$ was simulated with two Bi–S interatomic distances at 2.50 ± 0.01 Å, two Bi–O distances at 2.56 ± 0.02 Å and two Bi–O distances at 2.75 ± 0.02 Å. Implementation of the same approach for aqueous solutions on the assumption of S_3BiO_3 coordination at the H_2MPS : Bi(III) mole ratio ≥ 3.0 revealed three Bi–S bonds at 2.53 ± 0.02 Å and three Bi–O bonds at 2.68 ± 0.02 Å, respectively. Optimized geometries, electronic structures of $Bi(HMPS)_3$ and $[Bi(HMPS)_2ClO_4]^0$, vibrational properties of $[Bi(HMPS)_2ClO_4]^0$, and electronic absorption spectrum of $Bi(HMPS)_3$ species obtained by DFT and TD–DFT modeling are consistent with empirical parameters. In the UV–Vis spectrum of $Bi(HMPS)_3$ the LMCT and MLCT $S^{2-} \leftrightarrow Bi^{3+}$ band appears at 268 nm.

Keywords: Bismuth(III); 3-Mercaptopropanesulfonic acid; Molecular spectroscopy; DFT

Introduction

Pharmaceutical properties of bismuth(III) are governed by complex-formation processes, specifically with O,N,S-donor ligands exerting various physiological and biological effects [1]. In cancer therapy, pretreatment by bismuth(III) compounds reduces carboplatin-related and cisplatin-related nephrotoxicity without introducing serious side effects. Hence, research on complex-formation of Bi(III) with S-donor amino acids and peptides enhances notions and conceptual foresight of bismuth(III) biochemistry, specifically of compounds possessing antiulcer activity – such as of CBS – colloidal bismuth subcitrate (De-Nol) [2]. The neutral molecule of H_2MPS – $HS–CH_2–CH_2–SO_3H$ is a S, O-donor that is capable of bidentate coordination. Though mercaptoalkanesulfonate acids and their salts are extensively used in

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drug industry and analytic chemistry, there is only few data available on their complexation with various metal ions.

Recently, Petrov *et al.* have studied complex-formation of Bi(III) with 2-mercaptoethanesulfonatic (H_2MES) and 3-mercaptopropanesulfonatic acids in aqueous perchloric acid solutions at $C_{Bi} >> C_L$. The stability constants and electronic structures of $Bi(H_2O)_3(HMES)^{2+}\cdot H_2O$ and $Bi(H_2O)_3(HMPS)^{2+}\cdot H_2O$ "monocomplex" species have been determined [3]. Ioannou and Tsivgoulis have reported synthesis and properties of the Bi(III)–H_2MES complex [4].

It is noteworthy that there is a critical lack of published and verified data on complex-formation of Bi(III) with mercaptoalkanesulfonic acids in aqueous solutions and, particularly, on distances of Bi–S and Bi–O coordination bonds. Hence, the current article deals with determination of stoichiometry, geometry, and research on electronic structure of Bi(III) 3-mercaptopropanesulfonate species both in aqueous solutions and in the solid state.

The chemicals

All chemicals were of analytical grade: Bi_2O_3, $HClO_4$, Na_2CO_3, and disodium EDTA. Sodium 3-mercaptopropanesulfonate (MPSNA) was available from Sigma–Aldrich.

The stock solution of bismuth(III) triperchlorate was prepared by dissolution of an accurate weight of Bi_2O_3 in concentrated $HClO_4$ that had been standardized before with 0.1 N Na_2CO_3 solution. The acid was taken in excess to prevent bismuth(III) hydrolysis and 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 the stock $Bi(ClO_4)_3$ solution was determined by Gran titration [5]. The MPSNA solution was obtained by dissolution of accurate dry salt weight; excess $HClO_4$ amount was added to provide C_{H+} = 0.5 M.

Equipment

The UV–Vis spectra were measured with an Evolution 300 scanning spectrophotometer (ThermoScientific, UK) using 1 cm quartz cells. Cell thermostating (±0.1 K) was performed with a Haake K15 thermostat connected to Haake DC10 controller.

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 ^{1}H-NMR spectra of aqueous solutions of Bi(III)-MPS compounds were measured with a Bruker Avance III spectrometer (600 MHz ^{1}H-resonance gradient coil). The D_2O/H_2O mixture served as external standard with deuterium signal being the reference one. The spectra were obtained with 17-ms 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 32 K points and consequent convolution with exponential function with 0.8 Hz broadening.

The EXAFS transmittance spectra both of a solid compound and of aqueous Bi(III)/MPSNA solution were collected at the synchrotron radiation channel of the VEPP-3 storage ring (The Budker Institute of Nuclear Physics of SB RAS). The ring energy and current 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 in a 10 mm Teflon cell with Mylar window.

Sample preparation

UV–Vis spectroscopy. The stoichiometry of Bi-MPS species was determined by three methods: of mole ratio – at invariant $C_{H_2MPS} = 1 \times 10^{-4}$ M, of isomolar ratio – at invariant $C_{Bi} = 1 \times 10^{-4} - 4 \times 10^{-4}$ M and of Job – at invariant $C_{Bi} + C_{H_2MPS} = 1 \times 10^{-3}$ M. Perchloric acid was taken in excess to prevent bismuth(III) hydrolysis ($C_{H^+} = 0.5$ M). The UV–Vis electronic absorption spectra (EAS) were measured within 220–450 nm.

Raman, ^{1}H-NMR, and EXAFS spectroscopy. Each solution was prepared with 0.8 M excess acidity ($HClO_4$). The Raman spectra were recorded for three solutions: of bismuth (III) perchlorate ($C_{Bi} = 0.1$ M), of ligand ($C_{H_2MPS} = 0.3$ M), and of both reagents at the same concentrations. The NMR spectra were measured for ligand and bismuth-ligand solutions ($C_{Bi} = 0.1$ M; $C_{H_2MPS} = 0.3$ M). The EXAFS study required a single solution containing 0.1 M of $Bi(ClO_4)_3$, 1 M of H_2MPS, and 1 M of $HClO_4$.

The solid complex was obtained from solution containing 0.1 M of $Bi(ClO_4)_3$, 0.2 M of H_2MPS, and 0.6 M of $HClO_4$. The yellow precipitate appeared after salting the solution out with acetone. 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 34.05% of Bi and 20.71% of S (calculated for $[Bi(HMPS)_2(ClO_4)]^0$: Bi = 33.77%, S = 20.73%).

EXAFS spectra analysis

The XAS BiL_{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 wave vectors, and consequent Fourier transformation to construct the atomic radial distribution function (figure 1).

All of these spectrum processing procedures were performed using VIPER software [6]. The local environment of the Bi(III) atom was modeled with EXCURV 98 software [7] for

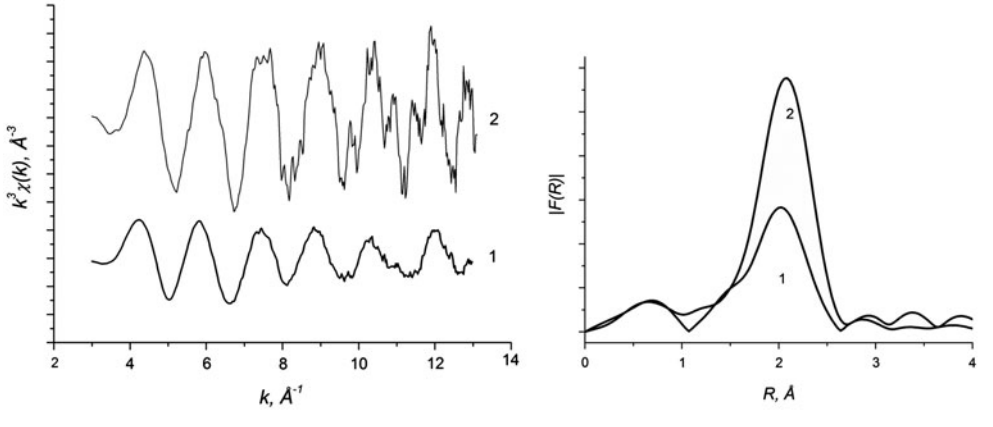

Figure 1. BiL_{III} EXAFS-spectra $\chi(k)\ k^3$ and their Fourier transformation modules for the solid complex and its aqueous solution.

Fourier-filtered (ΔR = 1.0–3.0 Å) k-weighed data within 3–13 $Å^{-1}$ range of wave vectors for solid compound and k^2-weighed data within 3–11 $Å^{-1}$ range of wave vectors for liquid solution.

During 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 (S_0^2 = 0.8) and fixed during the spectrum modeling of solutions.

Ab initio *study*

Calculations were carried out using the GAMESS-US program package [8] with the Supercomputer of Institute of Space and Information Technologies (SFU) [9]. Geometry optimization was performed by density functional theory (DFT) with the hybrid functional PBE0 [10] under Grimme's empirical correction. The def2-TZVPP basis set including ECP pseudo-potential for Bi was applied to every atom in the complex during every computational procedure. The PBE0 functional and the TZVPP basis set have been proven as the appropriate ones in the case of Bi(III) compounds [11–14].

Solvent effects were evaluated using the non-equilibrium implementation of the C-PCM solvation model (water built-in parameters were used). The 2.07 Å Van-der-Waals atomic radius was picked up for the Bi atom. The built-in radii were assigned to the other atoms.

The UV–Vis spectra of complex species were reproduced from the vertical excitation energies for the first 21 singlet excited states (TD-DFT/PBE0/C-PCM). The optimized geometries and molecular orbitals were visualized with the ChemCraft software [15]. The MO's percentage composition was found with the QmForge software [16].

Results and discussion

Solid $[Bi(HMPS)_2ClO_4]^0$ complex

Complexation of Bi(III) by 3-mercaptopropanesulfonic acid in aqueous perchloric acid solutions and the final product are governed by the initial mole ratio of reagents. Recently, Petrov *et al.* reported formation of soluble $Bi(H_2O)_3(HMPS)^{2+}\cdot H_2O$ "monocomplex" species at H_2MPS : Bi(III) ratio ≤ 1 [3]. The current study reveals honey-dew colored precipitate in solutions at H_2MPS : Bi(III) = 2. This precipitate dissolved at higher L : M ratios.

The yellow solid complex was separated, dried, and characterized by Raman and EXAFS spectroscopy. A similar Bi(III) complex with 2-mercaptoethanesulfonic acid had been synthesized recently [4]. The $[Bi(HMPS)_2ClO_4]^0$ complex was found to be X-ray amorphous according to XRD analysis.

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 $[Bi(HMPS)_2ClO_4]^0$ solid complex are compared on figure 2.

The Raman spectra (figure 3) gave evidence of ligand coordination via sulfur atom of thiol functional group. The band at 313 cm^{-1} referring to ν(Bi–S) vibrations was present in the Raman spectrum in the case of solid $[Bi(HMPS)_2ClO_4]^0$ and was absent in the case of solid MPSNA. On the contrary, the band at 2562 cm^{-1} corresponding to ν(S–H) vibrations was found in the Raman spectra of the ligand and was absent in the Raman spectra of the complex.

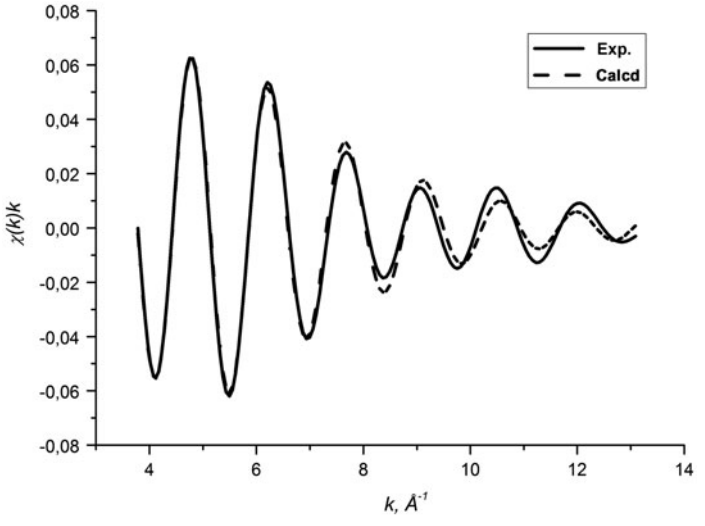

Figure 2. The experimental Fourier-filtered and simulated BiL_{III} EXAFS spectra of the solid $[Bi(HMPS)_2ClO_4]^0$.

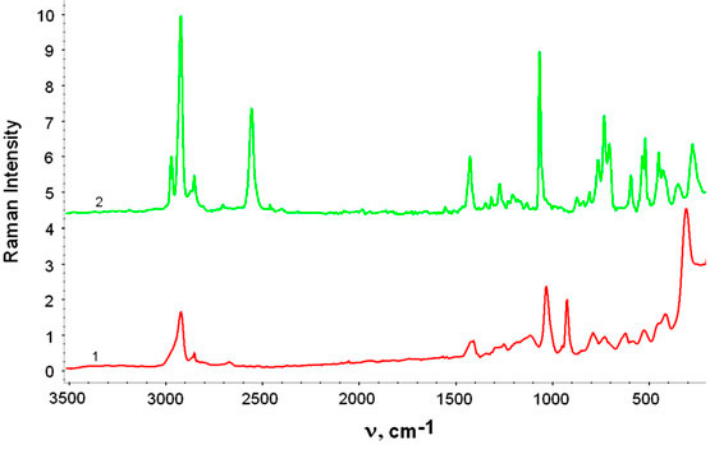

Figure 3. Raman spectra of solid $[Bi(HMPS)_2ClO_4]^0$ and solid MPSNA.

Bands at 1256, 1189, 1036, and 929 cm^{-1} corresponding to ν(O–Cl) vibrations were present in the Raman spectra of $[Bi(HMPS)_2ClO_4]^0$ thus providing evidence of ClO_4^- ion presence in the inner coordination sphere of bismuth(III). The bands in the Raman spectra of MPSNA and of $[Bi(HMPS)_2ClO_4]^0$ are listed in table S1.

A structure of $[Bi(HMPS)_2ClO_4]^0$ was suggested considering the high affinity of bismuth(III) to sulfur and oxygen. Such structure and stoichiometry were consistent with and resulted from elemental analysis (ICP-AES), Raman, and EXAFS spectroscopy. The suggested geometry, optimized by DFT/PBE0/def2-TZVPP computations, is shown on figure 4.

Figure 4 shows that $HMPS^-$ and ClO_4^- ions are bound to bismith(III) as bidentate chelating ligands. The optimized geometry belongs to C_2 point symmetry group. The

EXAFS and DFT data provided the same Bi–S bond distance, 2.50 ± 0.01 Å (table 1). There are two types of Bi–O bonds in the $[Bi(HMPS)_2ClO_4]^0$ complex: the bismuth(III) is bound to an oxygen atom of the SO_3-group of each $HMES^-$ ligand and to two oxygen atoms of ClO_4^-. The Bi–O bonds are 2.56 ± 0.02 Å (EXAFS) or 2.51 Å (DFT) in the case of MPS coordination and 2.75 ± 0.02 Å (EXAFS) or 2.84 Å (DFT) in the case of ClO_4^- coordination. Hence, EXAFS and DFT study provided Bi–O and Bi–S bond distances in the solid $[Bi(HMPS)_2ClO_4]^0$, consistent with previous report for Bi(III)-thiolate complexes: 2.4–2.7 and 2.5–2.6 Å, respectively [17].

Complex-formation of Bi(III) with H_2MPS in aqueous perchloric acid solutions

According to UV–Vis spectroscopy of aqueous solutions at H_2MPS/Bi(III) mole ratio = 3.0, the dominating species under such conditions has M : L stoichiometry = 1 : 3 (figures S1–S3 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.863283)).

Raman spectroscopy indicated the apparent formation of Bi–S bond, hence 3-mercaptopropanesulfonate ligand coordinates via sulfur of thiol (figure 5). The band at 2583 cm^{-1} corresponding to ν(S–H) vibrations was found in the spectrum of H_2MPS solution. No such band was present in the spectrum of H_2MPS/Bi(III) solution, while the new band at 315 cm^{-1} corresponding to ν(Bi–S) vibrations clearly vindicated binding of bismuth(III) to sulfur.

No chemical shift of 1.85 ppm with respect to the free SH-group was found in the ^{1}H-NMR spectrum of H_2MPS/Bi(III) aqueous solution (Supplementary material, figures S4 and S5). Such fact also proves coordination of ligand to bismuth(III) via sulfur of thiol.

According to EXAFS data, bismuth(III) in the complex is surrounded by three oxygen and three sulfur atoms. A bidentate O, S-coordination of three 3-mercaptopropanesulfonate ligands has been suggested. The experimental Fourier-filtered and simulated EXAFS spectra for the $Bi(HMPS)_3$ species in aqueous perchloric acid solution are compared in figure 6.

A structure of non-charged $Bi(HMP)_3$ species was suggested according to combined evidence of Raman, ^{1}H-NMR, and EXAFS data. Such geometry has been optimized by DFT/PBE0/def2-TZVPP/C-PCM calculations (figure 7).

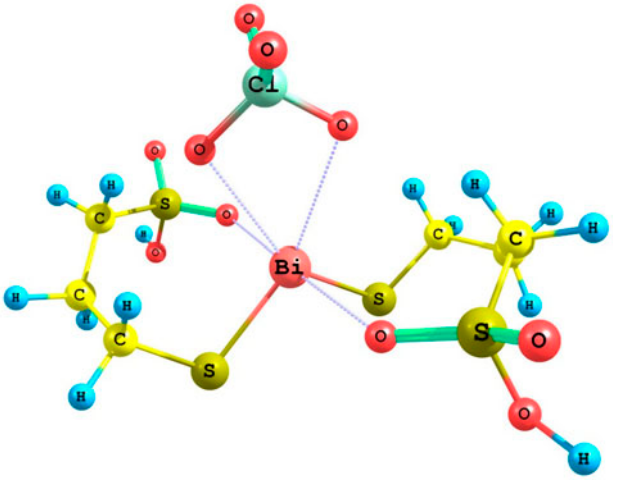

Figure 4. Optimized geometry of $[Bi(HMPS)_2ClO_4]^0$.

Table 1. Coordination numbers and interatomic distances according to EXAFS spectra and DFT-optimized geometries.

	$[Bi(HMPS)_2ClO_4]^0$ – solid			$Bi(HMPS)_3$ – aqueous solution		
	Interatomic distance			Interatomic distance		
Bond	EXAFS	DFT	N	EXAFS	DFT/C-PCM	N
Bi–S	2.50 ± 0.01 Å	2.50	2	2.53 ± 0.01 Å	2.57 ± 0.05 Å	3
Bi–O	2.56 ± 0.02 Å	2.51	2	2.68 ± 0.02 Å	2.95 ± 0.05 Å	3
	2.75 ± 0.02 Å	2.84	2			

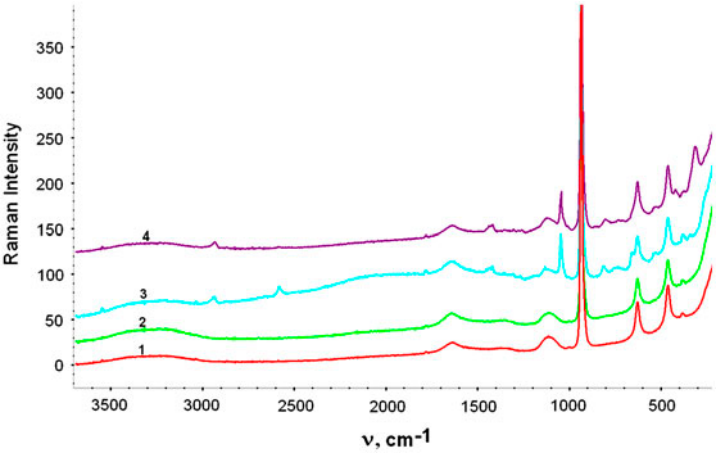

Figure 5. Raman spectra of aqueous perchloric solutions at $C_{Bi(III)}$ = 0.1 M, C_{MPSNA} = 0.3 M and C_{HClO4} = 0.8 M.

The combination of EXAFS and DFT methods provided quite consistent Bi–S bond distances at 2.53 ± 0.01 Å (EXAFS) and at 2.57 ± 0.05 Å (DFT) being a good match with previously reported Bi–S distances for bismuth-thiolate complexes in aqueous solutions: 2.5–2.6 Å [18]. On the contrary, the Bi–O bond distances rather mismatched: 2.95 ± 0.05 Å (DFT) and 2.68 ± 0.02 Å (EXAFS). The structure of $Bi(HMPS)_3$ is stabilized by a hydrogen bond Bi–S···H–O_3S at 2.05 Å. Despite relativistic effects are taken into account in Def2-TZVPP basis set by pseudopotential ECP, and C-PCM model includes nonspecific solvation effects, the difference between Bi–O bond lengths, obtained from EXAFS data and DFT calculations, can be observed. Though it might be useful for direct calculation of relativistic and specific solvation effects, it was considered as a very resource-intensive operation.

A TD–DFT study has been carried out on electronic structure of the $Bi(HMPS)_3$ species investigate charge transfer process. The band at 268 nm corresponds to the main electronic transition occurring from the HOMO to the LUMO and LUMO+1 (table 2). Figure 8 exhibits MO's (C-PCM/DFT/PBE0) contributing to charge transfer. Atomic orbital population analysis is given in table 3 providing evidence of electronic transition from sulfur to bismuth. These data give solid evidence of major $\pi \rightarrow \pi^*$ charge transfer from thiol sulfur atom to bismuth(III) and of minor $n \rightarrow \pi^*$ reverse charge transfer. Recently, we reported the same $\pi \rightarrow \pi^*$ S→Bi charge transfer in the $Bi(H_2O)_3(HMPS)^{2+}\cdot H_2O$ "monocomplex" species in aqueous perchloric acid solutions.

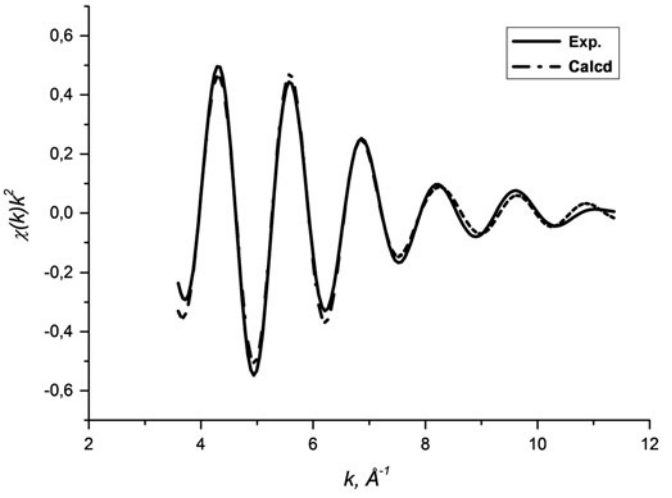

Figure 6. The experimental Fourier-filtered and theoretical-modeled BiL_{III} EXAFS spectra of Bi(HMPS)$_3$ species in aqueous perchloric acid solution.

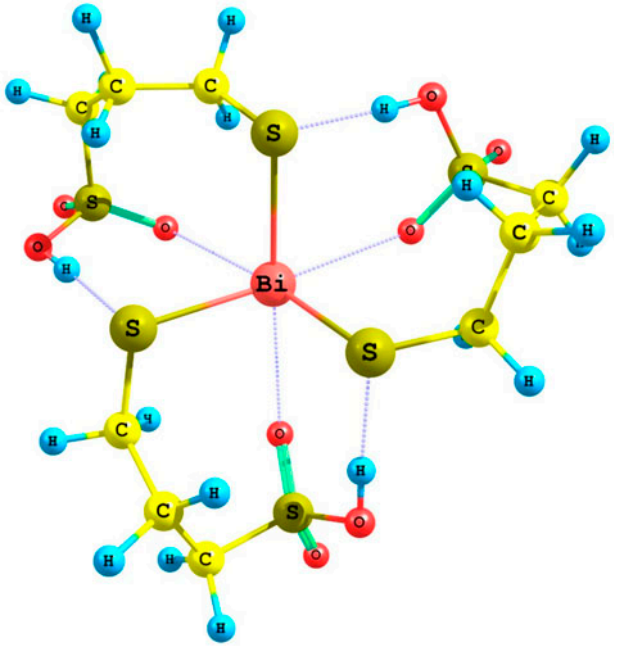

Figure 7. Optimized geometry of Bi(HMPS)$_3$.

Hence, C-PCM/TD-DFT/PBE0 functional and def2-TZVPP basis set provide good accordance of theoretical and experimental EAS.

Table 2. Contribution of different electronic charge transfers to the 268 nm absorbing band of $Bi(HMPS)_3$ species.

λ_{exp}, nm	λ_{Calcd}, nm	*F*	MO	Transition
268	266	0.033	HOMO → LUMO (74.5%)	LMCT + MLCT
	265	0.030	HOMO → LUMO+1 (70.2%)	

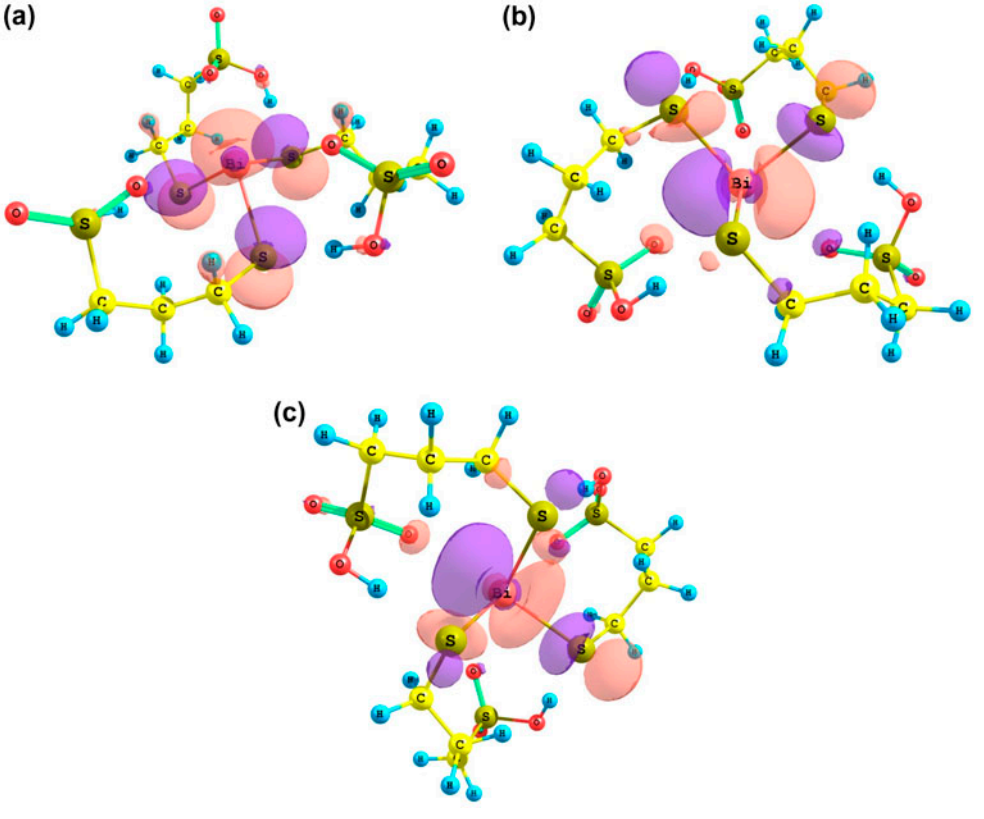

Figure 8. Rendered HOMO, LUMO and LUMO+1 of $Bi(HMPS)_3$ species.

Table 3. Percentage composition of $Bi(HMPS)_3$ molecular orbitals.

MO	Energy, eV	Bi	3S
HOMO	−7.265	17.88 (s)	38.06 (p_z)
LUMO	−1.439	40.52 (p_x)	7.21 (p_x)
			4.64 (p_y)
			6.45 (p_z)
LUMO+1	−1.404	40.78 (p_y)	4.74 (p_x)
			7.57 (p_y)
			6.14 (p_z)

Conclusions

(1) Complex-formation of Bi(III) with 3-mercaptopropanesulfonic acid has been studied in aqueous perchloric acid solutions at C_{H+} = 0.5 M. Formation of $Bi(HMPS)_3$ species under ligand dominance ($C_L >> C_M$) condition has been vindicated by Raman, ^{1}H-NMR, UV–Vis, and EXAFS spectroscopy. Each 3-mercaptopropanesulfonate ligand ($HMPS^-$) is coordinated to bismuth(III) via sulfur of thiol and via oxygen of sulfonic group. The Bi–S and Bi–O bonds are 2.53 ± 0.01 and 2.68 ± 0.02 Å, respectively.

(2) $[Bi(HMPS)_2ClO_4]^0$ has been obtained and characterized by Raman and EXAFS spectroscopy. Vibrational assignment has been performed for Raman spectra of $[Bi(HMPS)_2ClO_4]^0$ and MPSNA. The Bi–S bond is 2.50 ± 0.01 Å, while the Bi–O distances are 2.56 ± 0.02 and at 2.7 ± 0.02 Å for sulfonic group and perchlorate, respectively.

(3) The geometries of $[Bi(HMPS)_2ClO_4]^0$ and $Bi(HMPS)_3$ have been optimized with DFT/PBE0/Def2-TZVPP and DFT/PBE0/Def2-TZVPP/C-PCM calculations, respectively. The TD-DFT study proved that 268 nm band in the UV–Vis electronic absorption spectrum of $Bi(HMPS)_3$ species corresponds to $\pi \rightarrow \pi^*$ charge transfer from thiol sulfur atom to bismuth(III) and of $n \rightarrow \pi^*$ reverse charge transfer.

Supplementary material

^{1}H-NMR and UV–Vis spectral data, cartesian coordinates for DFT-optimized geometries, experimental and calculated bands in the Raman spectra.

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References

[1] G.G. Briand, N. Burford. *Chem. Rev.*, **99**, 2601 (1999).
[2] H. Sun, H. Li, I. Harvey, P.J. Sadler. *J. Biol. Chem.*, **274**, 29094 (1999).
[3] A.I. Petrov, N.N. Golovnev, I.D. Dergachev, A.A. Leshok. *Polyhedron*, **50**, 59 (2013).
[4] P.V. Ioannou, G.M. Tsivgoulis. *Main Group Chem.*, **11**, 89 (2012).
[5] D. Midgley, K. Torrance. *Potentiometric Water Analysis*, Wiley, New York (1978).
[6] (a) K.V. Klementiev. VIPER. Available online at: http://www.cells.es/Beamlines/CLAESS/software/viper.html (accessed 1 June 2013); (b) K.V. Klementev. J. Phys. D: Appl. Phys., **34**, 209 (2001).
[7] S. Tomic, B.G. Searle, A. Wander, N.M. Harrison, A.J. Dent, J.F.W. Mosselmans, J.E. Inglesfield. *CCLRC Technical Report DL-TR-2005-001*, ISSN 1362-0207 (2005). Available online at: http://www.cse.clrc.ac.uk/cmg/EXCURV/ (accessed 1 June 2013).
[8] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery. *J. Comput. Chem.*, **14**, 1347 (1993).

[9] Available online at: http://www.cluster.sfu-kras.ru (accessed 1 June 2013).
[10] C. Adamo, V. Barone. *J. Chem. Phys.*, **110**, 6158 (1999).
[11] F. Weigend, R. Ahlrichs. *Phys. Chem. Chem. Phys.*, **7**, 3297 (2005).
[12] A.A. Auer, D. Mansfeld, C. Nolde, W. Schneider, M. Scheurmann, M. Mehring. *Organometallics*, **28**, 5405 (2009).
[13] K.Y. Monakhov, G. Linti. *Inorg. Chem.*, **48**, 6986 (2009).
[14] L.M. Reith, M. Stiftinger, U. Monkowius, G. Knör, W. Schoefberger. *Inorg. Chem.*, **50**, 6788 (2011).
[15] G.A. Zhurko, *ChemCraft Version1.6*. Available online at: http://www.chemcraftprog.com (accessed 1 June 2013).
[16] A.L. Tenderholt. *QMForge: A Program to Analyze Quantum Chemistry Calculations*, Version 2.1 2007. Available online at: http://qmforge.sourceforge.net (accessed 1 June 2013).
[17] G.G. Briand, N. Burford, M.D. Eelman, N. Aumeerally, L. Chen, T.S. Cameron, K.N. Robertson. *Inorg. Chem.*, **43**, 6495 (2004).
[18] J. Naslund, I. Persson, M. Sandstrom. *Inorg. Chem.*, **39**, 4012 (2000).