Inorg. Chem. **2004**, *43*, 7094–7100

Inorganic Chemistry
Article

Stabilization of a Subvalent Oxidation State of Bismuth in *N,N*-Dimethylthioformamide Solution: An EXAFS, UV–Vis, IR, and Cyclic Voltammetry Study

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Received June 10, 2004

At the dissolution of anhydrous bismuth(III) trifluoromethanesulfonate in *N*,*N*-dimethylthioformamide (DMTF) a deep red-orange complex, $\lambda_{max} = 457$ nm, is formed. Bismuth(III) is reduced by the solvent to a low-valent oxidation state stabilized by the sulfur-coordinating solvent DMTF. The obtained complex is weakly solvated seen by a low EXAFS amplitude and a slightly higher absorption energy of the L_{III} edge than of the DMTF-solvated bismuth(III) ion. The EXAFS data reveal a dimeric bismuth complex solvated by a single DMTF molecule, which sulfur atom bridges the bismuth atoms. The Bi–S bond distance is 2.543(2) Å, and the Bi···Bi distance is 3.929(7) Å giving a Bi–S–Bi angle of 101.2(4)°. The very low number of coordinated solvent molecule shows that the lone electron pairs of the reduced bismuth ions are stereochemically active. Cyclic voltammetry investigations provide evidence that at least one bismuth atom in the dimer exists in an oxidation state lower than +III, seen by two peaks at approximately –0.36 and –0.57 V in the reduction half-cycle. The absence of EPR signals excludes the presence of bismuth(II) radicals.

Introduction

Due to the relativistic stabilization of the 6s orbitals the most stable oxidation state of the heaviest elements of the p-block is two below the (old) group number. Additionally, splitting of 6p orbitals into $6p_{1/2}$ and $6p_{3/2}$ and relativistic stabilization of the $6p_{1/2}$ orbital stabilize the bismuth(I), polonium(II), and astatine(III) cations. In the case of bismuth the most common oxidation states are +III and +V. The existence of the very unstable bismuth(II) and bismuth(IV) ions in aqueous hydrochloric acidic solution has been shown by means of the pulse radiolysis technique.[1,2] The formation of subvalent bismuth cations, e.g., bismuth(I) ions and some bismuth cluster cations, has been identified in molten salts containing bismuth(III) chloride and metallic bismuth.[3,4] Moreover, monovalent bismuth cations were obtained under vacuum in concentrated hydrochloric acid solution saturated with bismuth chloride and presence of metallic bismuth.[5] The bismuth(I) ion is a very interesting example among p-block elements (besides polonium(II) and astatine(III)) with respect of having two lone electron pairs, $6s^2$ and $6p_{1/2}{}^2$.

One of the aims in the present project is find stable compounds and complexes of subvalent heavy metal ions. It is well-known that typically soft electron-pair donor solvents stabilize low oxidation states of metals. In this paper the sulfur donor solvent *N*,*N*-dimethylthioformamide (DMTF) was used. DMTF has high dipole moment ($\mu = 4.44$ D), high permittivity ($\epsilon = 47.5$),[6] and some hydrogen bonding ability[7] and is therefore a suitable solvent for metal salts. These properties allow highly charged species to be dissolved

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10.1021/ic0400787 CCC: $27.50

without ion-pair formation. DMTF has a soft Lewis base character, $D_S = 52$,[7] which results in strong interactions with soft electron-pair acceptors.

A number of metal ions, such as zinc, cadmium,[8,9] mercury(II),[8−11] copper(I), silver(I), gold(I),[12] and thallium(I),[13] solvated by DMTF have been investigated. The structures of the solvates of metal ions with DMTF have been determined in solution using large-angle X-ray scattering (LAXS)[9,10,12,13] and extended X-ray absorption fine structure (EXAFS)[6,13] and in solid state using single-crystal X-ray diffraction.[8,10,12] Furthermore, some solvates have also been studied by means of vibrational spectroscopic methods.[9−12] Previously, it was found that lower oxidation states of some metal cations were stabilized in DMTF; e.g., thallium(III) is spontaneously reduced to thallium(I)[13] and copper(II) to copper(I).[12]

At the study of the solvation of the DMTF solvated bismuth(III) ion it was found that the use of bismuth(III) perchlorate resulted in a very pale pink solution, while the dissolution of anhydrous bismuth(III) trifluoromethanesulfonate gave a deep red-orange solution. An EXAFS study of a DMTF solution of bismuth(III) perchlorate showed an octahedral bismuth(III) solvate complex with a Bi−S bond distance of 2.794(8) Å,[14] which was in coherence with previous studied bismuth(III) complexes with sulfur donor ligands as, e.g., tris(diisopropyldithiophosphato)bismuth(III), $[Bi((C_3H_7O)_2PS_2)_3]$ (a),[15] tris(diethyldithiophosphinato)bismuth(III), $[Bi((C_2H_5O)_2PS_2)_3]$ (b),[16] tris(diethyldithiophosphinato)bismuth(III) benzene, $[Bi((C_2H_5O)_2PS_2)_3 \cdot C_6H_6]$ (c),[17] tris(diethyldithiocarbamato)bismuth(III), $[Bi((C_2H_5)_2NCS_2)_3]$ (d),[18] and tris(methyl-*n*-hexyldithiocarbamato)bismuth(III), $[Bi(CH_3)(C_6H_{13})NCS_2)_3]$ (e).[19] These complexes have distorted octahedral or distorted triangular antiprism geometry. In the coordination compounds b and c the average Bi−S bond distance is equaled to 2.804 and 2.788 Å, respectively. In the remaining complexes there are three short and three longer Bi−S bonds. The average Bi−S bond lengths are 2.702 and 2.874 Å for complex a, 2.700 and 2.943 Å for complex d, and 2.705 and 2.881 Å for complex e, respectively. In oxygen donor solvents as water, dimethyl sulfoxide, and *N*,*N*-dimethylpropyleneurea, bismuth(III) forms geometrically regular solvates with coordination numbers of 8, 8, and 6, respectively.[14] The unusual behavior of bismuth(III) ions in a DMTF solution of bismuth(III) trifluoromethanesulfonate is certainly a reduction of bismuth(III) to a lower oxidation state. It is well-known that soft donor ligands as sulfur and phosphorus stabilize lower oxidation states, and as described above, DMTF exhibits reducing properties.[12,13] The trifluoromethanesulfonate ion seems to promote the reaction between bismuth(III) and DMTF, probably due to weak interaction to bismuth(III), while the perchlorate ion seems not to interact at all, thereby not promoting any reduction reactions. The silver(I) and mercury(II) trifluoromethanesulfonate systems in DMTF and liquid ammonia show a similar behavior with formation of black precipitates with trifluoromethanesulfonate salts while the perchlorate systems are completely stable.[9,12]

The EXAFS study of the deep red solution, obtained at the dissolution of bismuth(III) trifluoromethanesulfonate, showed a much lower EXAFS amplitude and a significantly shorter Bi−S bond distance than in the hexakis(*N*,*N*′-dimethylthioformamide)bismuth(III) complex. This shows clearly that bismuth(III) had undergone a reaction. In this paper the results of the studies of this deep red bismuth DMTF complex in solution using EXAFS, UV−vis, IR, and electrochemical techniques to characterize this complex are presented.

Experimental Section

Preparation of Samples. In spectroscopic and electrochemical measurements *N*,*N*-dimethylthioformamide (Aldrich) and *N*,*N*-dimethylformamide (Merck) were used as purchased. For EXAFS studies DMTF was prepared by reacting its oxygen analogue *N*,*N*-dimethylformamide with phosphorus pentasulfide (Merck) in benzene, as described by Gutmann et al.[20] Anhydrous bismuth(III) trifluoromethanesulfonate, $Bi(CF_3SO_3)_3$, in the form of white powder, was prepared by drying an aqueous acidic solution in an oven at 465 K for 1 week to completely evaporate off excess water and acid as described elsewhere.[14] Because of high hygroscopicity, bismuth(III) trifluoromethanesulfonate should be stored in an oven at 465 K or in a small airtight vessel in a desiccator. Immediately before all measurements anhydrous bismuth(III) trifluoromethanesulfonate was dissolved in DMTF and the obtained solution was filtered. Momentarily at the dissolution in DMTF the solution turns deep reddish-orange. After about 3 days at room temperature a black-brown precipitate, probably bismuth(III) sulfide, is formed. However, this deep reddish-orange solution can be stored for longer time at temperatures below 273 K without formation of any precipitate. An attempt to crystallize the deep red bismuth DMTF complex resulted in formation of orthorhombic elemental sulfur as characterized by X-ray crystallography.

Vis Spectroscopy. Visible absorption spectra were recorded in the range 360−600 nm with a scan rate of 100.0 nm/min on a GBC Cintra 40 UV−vis spectrometer. Because of the very high absorption of the deep red-orange DMTF solution, either glass cuvettes with a path length of 2 mm or thin films of the solution with a path length of about 0.01 mm were used. The thickness of the film was calculated from the mass of solution enclosed between two glass plates. The spectra were collected using air or pure DMTF as a reference.

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IR Spectroscopy. Far- and mid-infrared absorption spectra of the deep red bismuth DMTF solution and pure DMTF were recorded at room temperature with a Bruker Equinox 55 FT-IR spectrometer. This instrument was equipped with deuterated triglycine sulfate (DTGS) detectors. Spectra of the solutions were recorded in the range 900−4000 cm^{-1} with the resolution of 1 cm^{-1} using a liquid cell with CaF_2 windows. Potassium bromide windows could not be used due to formation of a dark precipitate on the KBr surface. In the range 650−900 cm^{-1} at 1 cm^{-1} resolution and in the range 50−650 cm^{-1} at a resolution of 2 cm^{-1} the spectra were recorded with polyethylene windows placed in the liquid cell with a 0.1 mm Teflon spacer. Polyethylene windows absorbs strongly in the region 700−740 cm^{-1}, due to vibrations of the CH_2 groups in polyethylene.[21] Additionally, in the range 650−4000 cm^{-1}, at a resolution of 1 cm^{-1}, an IR spectrum of the deep red bismuth DMTF solution was recorded by means of an accessory designed for attenuated total reflectance (ATR) technique equipped with ZnSe crystal.

EXAFS. The EXAFS spectra of saturated deep red bismuth DMTF solutions, obtained by dissolving bismuth(III) trifluoromethanesulfonate in DMTF, were collected at two occasions in transmission and fluorescence mode simultaneously, at room temperature, at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA. The transmission data were found to have the lowest S/N ratio and used in the data treatment. SSRL operates at 3.0 GeV and a maximum current of 100 mA. The measurements were performed at the wiggler beam-line 4-1 using a Si(220) double-crystal monochromator, which was detuned to 50% of maximum intensity at the end of the scans, to remove higher order harmonics. For the internal energy calibration a thin bismuth metal foil was recorded simultaneously. The ionization energy of Bi L_{III} electrons in the metal is defined as 13 419 eV.[22] Five scans were recorded, energy calibrated, and averaged. The EXAFS functions were extracted using standard procedures for preedge subtraction, spline removal, and data normalization.[23] To obtain quantitative information the k^3-weighted EXAFS oscillations were analyzed by nonlinear least-squares fitting of the model parameters. All data treatment was made by the use of the EXAFSPAK program package.[24] Model fitting was performed with theoretical phase and amplitude functions including both single and multiple scattering paths using the ab initio code FEFF (version 6.01).[25]

Cyclic Voltammetry. Cyclic voltammetric experiments were carried out using an Autolab potentiostat (ECO Chemie, Utrecht, The Netherlands) in a three-electrode arrangement with a Ag/AgCl electrode as reference, a platinum foil as counter electrode, and a glassy-carbon electrode (GCE, BAS, 3 mm diameter) as working electrode. Argon was used to deaerate the solution, and an argon blanket was maintained over the solution during the experiments. In all electrochemical measurements performed, tetrabutylammonium trifluoromethanesulfonate, $(C_4H_9)_4N(CF_3SO_3)$ (Aldrich), was used as supporting electrolyte. A dark precipitate, identified as Bi_2S_3, had to be frequently cleaned off the working electrode.

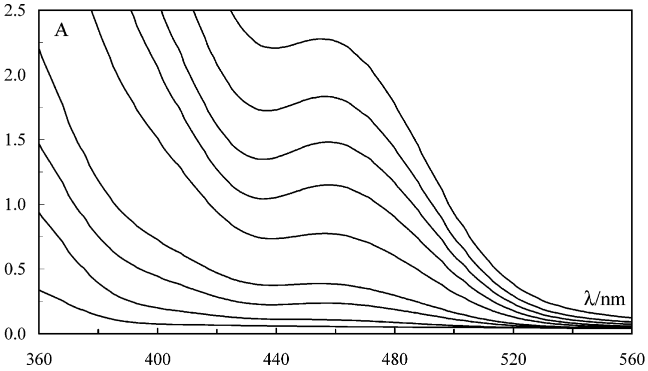

Figure 1. Absorption spectra of the DMTF solutions of the bismuth complex prepared by dissolution of $Bi(CF_3SO_3)_3$ in DMTF. From below: pure DMTF, 0.01, 0.03, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 $mol \cdot dm^{-3}$ solutions, respectively (thickness of the films about 0.01 mm). Air was used as a reference.

EPR Spectroscopy. The EPR measurement of the deep red DMTF solution in the temperature of liquid nitrogen was carried out with a Bruker ESP 300E X-band EPR spectrometer.

Results

Vis Spectroscopy. The highly concentrated solutions of the deep red bismuth DMTF complex are optically transparent above 400 nm when thin films, ca. 0.01 mm thick, were prepared for investigation by means of visible spectroscopy. However, below this wavelength measurements became impossible because of very high absorption even with thin films. The maximum of absorption was observed at 457 nm for a wide range of concentrations of the solution (Figure 1). Using thin sample films this band can be observed at concentrations above 0.01 $mol \cdot dm^{-3}$. With regard to the very high absorption in this range of concentrations we could not use a cuvette even with path length of 2 mm. However, at lower concentrations the band with maximum at 457 nm could not be recorded (Figure 1). At considerably lower concentrations ($<10^{-3}$ $mol \cdot dm^{-3}$) the complex decomposed in the course of some minutes resulting in formation of a black precipitate, identified by dissolution in hydrochloric acid as Bi_2S_3. After centrifugation the spectrum of the remaining solution became very similar to pure DMTF showing that in principle all bismuth had precipitated.

Infrared Spectroscopy. The bands observed in the vibrational spectra can be attributed to internal vibrations of the DMTF molecule, the trifluoromethanesulfonate anion, and the metal−ligand bond. A full assignment of bands on the basis of normal coordinate analyses in combination with quantum chemical calculations has been performed for the DMTF molecule.[11] Moreover, the spectra of the solvated zinc, cadmium, silver(I) trifluoromethanesulfonate, cadmium, mercury(II), copper(I) perchlorate, and gold(I) tetrafluoroborate in DMTF solution and in the solid state have also been analyzed.[8,9,12] As the bismuth concentration is approximately 0.2 $mol \cdot dm^{-3}$ in this study, the solvent dominates the

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spectrum. In the far-infrared region liquid DMTF shows three marked bands: a scissoring-rocking mode of the N−C′ entity at 407 cm^{-1}, the out-of-plane vibration N−C′ at 364 cm^{-1}, and a smaller band originating from a bending mode of the NCS entity and from a rocking mode of the NC'_2 entity at 277 cm^{-1}.[11] Because of the large contribution from the solvent, the Bi−ligand bands are difficult to recognize. However, in the presence of the deep red bismuth DMTF complex a new band appears at 288 cm^{-1} overlapping partially with the band at 277 cm^{-1}. Moreover, there are some changes between 380 and 400 cm^{-1} in the form of shoulders on the lower frequency side of the band at 407 cm^{-1}. The bismuth−ligand vibrations appear at frequencies similar to those observed for the metal−ligand vibrations in DMTF solutions of cadmium (299, 394 cm^{-1}), mercury(II) (317 cm^{-1}),[9] silver(I) (285, 382 cm^{-1}), and copper(I) (382 cm^{-1}).[12] The main frequencies ascribed to solid Bi_2S_3 are found at 282, 235, and 205 cm^{-1}.[26] Some other reported values for Bi−S stretching vibrations are 222 and 197 cm^{-1} in $Bi(SCH_2CH_2OH)_2ClO_4$,[27] 320 and 305 cm^{-1} in $C_6H_5Bi(SC_6H_4NH_2)_2$,[28] a series of weak bands between 290 and 250 cm^{-1} in $Bi(SC_6H_4NH_2)_3$,[29] and 180 cm^{-1} in $Bi(SC_6H_5)_3$.[30] The Bi−S stretching in our system contributes strongly to the band around 288 cm^{-1}. Furthermore, we observe around 299 cm^{-1} a weak shoulder on the higher frequency side of the band at 288 cm^{-1}. We suppose that it may result from the presence of two bands belonging to Bi−S vibrations in this region of spectrum. The main bands derived from vibrations of the $CF_3SO_3^-$ ion are located in the middle part of the infrared spectrum just as for solutions of other metal trifluoromethanesulfonate salts in DMTF[9] and for some solid trifluoromethanesulfonate salts.[31] No significant frequency shifts in the presence of the bismuth salt were found for the anions, as expected for a noncoordinating or weakly interacting species. Also no significant wavenumber shifts are observed for the bands belonging to DMTF molecules.

In the studied solutions, as in pure solvent, the application of normal absorption IR spectroscopy gave us during our measurements in mid-infrared region three strong and broad bands in the regions 2800−3020, 1350−1600, and 1080−1180 cm^{-1}, which composition was precisely the same as described previously.[7,11] Using the ATR technique, we obtained the bands mentioned above but with lower intensities and better separated. These bands consist only of the vibrations of the DMTF molecule.

EXAFS. The amplitude of the EXAFS function of the deep red-orange bismuth DMTF solution is unusually small indicating a very low coordination number of bismuth. Besides the main contribution of a Bi−S interaction, significant Bi--Bi, Bi--C, and Bi--N single scattering and a Bi−S−C three leg scattering path give significant contributions to the EXAFS function. The model fitting the experimental data best is a dimer with a single DMTF molecule bridging the bismuth atoms through the sulfur atom. When mononuclear models were tested, it was impossible to get rid of a sinusoidal residual above $k = 6$ Å^{-1}, with a maximum at ca. $k = 9$ Å^{-1}. This problem was completely solved by the introduction of a dimeric complex. Only a model with one DMTF molecule/bismuth, from an EXAFS point of view, gives an amplitude reduction factor, S_o^2, close to the expected value of 0.8−1.0. Higher numbers of DMTFs/bismuth give S_o^2 values below 0.5, which is very hard to explain for an ordinary transmission experiment, and models with more than one DMTF bound to each bismuth were therefore excluded. The two Bi−S bond distances seem to be identical as the Debye−Waller factor is quite small and as the Bi--C, Bi−N, and Bi--C_{methyl} distances are all well-defined with relatively small Debye−Waller factors and very close to the distances expected for a symmetric complex. This indicates strongly that the $Bi_2SCHN(CH_3)_2$ complex must be rigid with high symmetry. This seems very likely as the DMTF molecule is almost planar, and rotation around the bond axes are only allowed for the methyl groups, which causes results in the Bi--C, Bi−N, and Bi--C_{methyl} distances being all well-defined. The Bi−S and Bi--Bi distances of 2.543(2) and 3.929(7) Å, respectively, give a Bi−S−Bi angle of 101.2(4)°. Assuming that the S−C bond distance in the coordinated DMTF molecules is 1.68 Å,[32] an observed Bi--C distance of 3.479(15) Å gives an Bi−S−C angle of 109.2(8)°, which is in very good agreement with the observed three-leg Bi−S−C scattering path distance, 3.79(2) Å. This Bi−S−C angle is very similar to the corresponding angles in DMTF-solvated borderline metal ions as copper(I) and cadmium(II),[32] and the obtained Bi--N and Bi--C_{methyl} distances are in very good agreement with an almost planar DMTF molecule and the intramolecular bond distances and angles in coordinated DMTF molecules. This result shows clearly that the two lone electron pairs on bismuth atoms in the deep red bismuth DMTF complex are stereochemically active, which is in accordance with previous observations that the lone electron pairs are more often stereochemically active on low charged metal ions than on metal ions with high charge.[13] The structural parameters of the deep red bismuth DMTF solution are summarized in Table 1, the fits of the experimental EXAFS data are shown in Figure 2, and the Fourier transform is presented in Figure 3.

Table 1. Mean Bond Distances, *d*/Å, Debye−Waller Factor Terms, σ^2/Å^2, Number of Distances, *N*, and the Amplitude Reduction Factor, S_o^2, of the Deep Red Bismuth DMTF Complex in Solution As Determined by EXAFS at Ambient Room Temperature

interactn	N	d	σ^2	S_o^2
Bi−S	1	2.543(2)	0.0048(2)	0.81(2)
Bi--Bi	1	3.929(7)	0.0094(6)	
Bi--C	1	3.479(15)	0.011(2)	
Bi−S−C	2	3.79(2)	0.002(1)	
Bi--N	1	4.40(2)	0.0059(14)	
Bi--C_{methyl}	2	5.39(2)	0.013(3)	

The positions of the absorption edges of the deep red bismuth complex and the hexasolvated bismuth(III) DMTF

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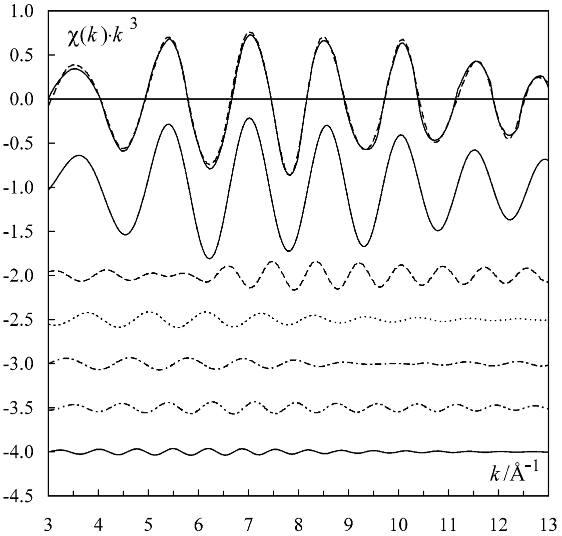

Figure 2. Fit of the individual contribution of the different scattering paths of the EXAFS data of the deep red DMTF solution prepared by dissolution of anhydrous solid bismuth(III) trifluoromethanesulfonate: solid line, experimental data; dashed line, model. Individual contributions: Bi−S single scattering (offset −1); Bi--Bi single scattering (offset −2.0); Bi--C single scattering (offset −2.5); Bi−S−C three leg multiple scattering (offset −3.0); Bi--N single scattering (offset −3.5); Bi--C_{methyl} single scattering (offset −4.0).

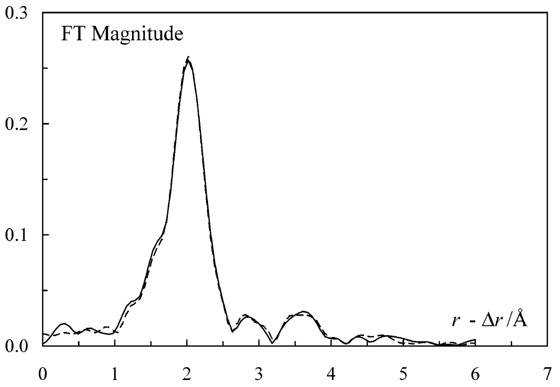

Figure 3. Fourier transform and the fit of the deep red bismuth DMTF complex using the structure parameters in Table 1.

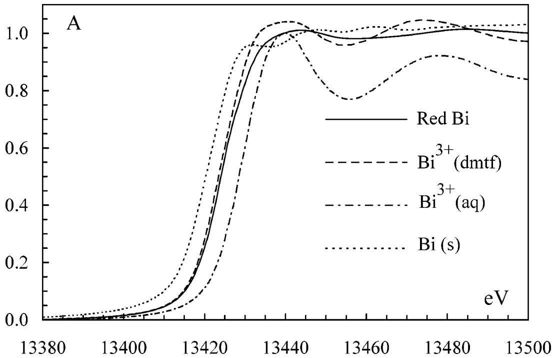

Figure 4. Edge structure of bismuth metal: DMTF solution of the deep red bismuth complex (labeled red Bi); hexakis(*N*,*N*-dimethylthioformamide)-bismuth(III) ion in solution (labeled Bi^{3+}(dmtf)); hexaaquabismuth(III) ion in aqueous solution (labeled Bi^{3+}(aq)); metallic bismuth (labeled Bi(s)).

complex ions at 13 424.1 and 13 423.5 eV (half-height edge energies), respectively, Figure 4, indicate that the actual charge on bismuth in the red complex ion is higher than on the bismuth(III) ion, which is hexasolvated in DMTF.[14] This shows that the charge reduction through the solvation on the

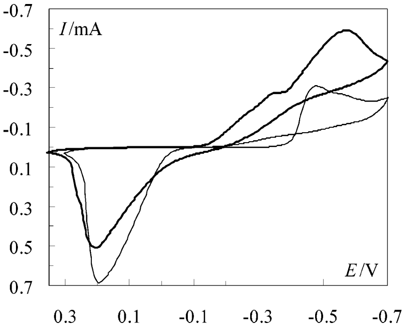

Figure 5. Cyclic voltammogram for the solution of 0.05 mol·dm^{-3} $Bi(CF_3SO_3)_3$ in DMTF/0.5 mol·dm^{-3} $(C_4H_9)_4N(CF_3SO_3)$ [thick line (scan rate: 50 mV·s^{-1})]. For comparison the solution of 0.05 mol·dm^{-3} $Bi(CF_3SO_3)_3$ in DMF/0.5 mol·dm^{-3} $(C_4H_9)_4N(CF_3SO_3)$ is shown as the thin line.

red bismuth complex in DMTF is very poor, which is in complete agreement with the observed structure with only 1 solvent molecule/2 bismuth's in the red complex, which shall be compared with 6 DMTF molecules/bismuth(III) ion.

Another dimeric structure in a DMTF complex solution has been found for silver(I) in the solid state, $[Ag_2(SCHN(CH_3)_2)_6]^{2+}$, which contain two asymmetric sulfur bridges with one short and one long Ag−S bond, 2.529 and 2.930 Å, respectively.[12] Moreover, many complexes in which sulfur is a bridging atom for metals are known. The μ_2 bridging S mode is present, e.g., in $(Et_3P)Au-S-Au(PEt_3)$ and $[(Ph_3P)_2Pt]_2S$, the triply bridging S mode (μ_3) present, e.g., in $[(Ph_3P)Au]_3S$ and $[(CO)_3Co]_3S$, and the quadruply bridging S mode (μ_4) present, e.g., in $[(CH_3)SFe_2(CO)_6]_2S$.[33] In the $[Co(NCS)_6Hg_2]\cdot C_6H_6$ complex the NCS group acts as tridentate ligand forming a Co−N bond and an S bridge between two Hg atoms.[34]

Cyclic Voltammetry. To confirm the existence of a lower oxidation state than +III of bismuth in DMTF, cyclic voltammograms were recorded in solutions containing different concentrations (up to 0.05 mol·dm^{-3}) of the deep red bismuth complex. The performed experiments provided evidence for more than one oxidation state of deep red bismuth complex in DMTF solution. As shown in Figure 5, two partially overlapping peaks can be detected in the reduction half-cycle. They probably correspond to the following reduction processes: (1) bismuth(I) to bismuth metal; (2) bismuth(III) to bismuth metal. The observed potentials are approximately −0.36 and −0.57 V for peaks 1 and 2, respectively. The peak currents are difficult to measure due to the overlap of the signals. After reduction of the two forms of bismuth in the dimer, an oxidation peak corresponding to the oxidation of bismuth metal to bismuth(III) was observed at +0.21 V. A considerable difference between the anodic and cathodic peaks shows that the metallic bismuth layer is oxidized with large overpotential. In addition, a dark precipitate of a bismuth-containing compound becomes visible on the surface of the working electrode showing that bismuth metal is oxidized into the Bi_2S_3 deposit.

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(33) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: London, 1984; Chapters 15 and 17.

(34) Gronbaek, R.; Dunitz, J. D. *Helv. Chim. Acta* **1964**, *47*, 1889.

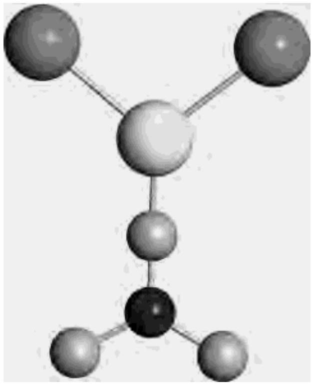

Figure 6. Model of the deep red dimeric bismuth *N,N′*-dimethylthioformamide complex.

The obtained voltammogram was compared to that recorded for bismuth(III) trifluoromethanesulfonate solution in *N,N*-dimethylformamide (a similar ligand but with oxygen instead of sulfur as a donor atom). In this case only one maximum at −0.49 V due to reduction of bismuth(III) to bismuth metal in the reduction half-cycle was found (Figure 5). With increasing total concentration of bismuth, the reduction processes occur at more negative potentials, the oxidation process occur at more positive potential, and the peaks become broader for both solvents (DMTF and DMF). Unfortunately, due to instability of our product we did not use bulk chronocoulometry experiments, which could give us direct information of charge of bismuth cations.

EPR. No signals were observed in EPR experiments, showing that neither radicals nor other paramagnetic species are present in the deep red bismuth DMTF complex. This absence of EPR signals strongly suggests that the dimer contains the bismuth(III) and bismuth(I) (or both bismuth(I)) cations which are inactive in EPR because of their s^2 and $s^2p_{1/2}^2$ electron configuration, respectively.

Discussion

The EXAFS measurements show that dissolution of bismuth(III) trifluoromethanesulfonate in DMTF results in formation of a very unusual dimeric structure (Figure 6) in which the sulfur atom in the DMTF molecule bridges two bismuth ions with a mean Bi−S bond distance of 2.543(5) Å. Bi−S stretching frequencies are found at 288 cm^{-1} and as a weak shoulder at about 299 cm^{-1}. In visible spectroscopy a very strong absorption at 457 nm is observed ($\epsilon \approx 1.4 \times 10^4$ $dm^3 \cdot mol^{-1} \cdot cm^{-1}$). The formation of the intensively colored solution upon dissolving bismuth(III) trifluoromethanesulfonate in DMTF, while the color is absent at dissolution in *N,N*-dimethylformamide, DMF, suggests that significant amounts of bismuth(III) ions are reduced by DMTF to a lower oxidation state. The source of strong absorption at 457 nm could be the transfer of electron between $p_{1/2}$ and $p_{3/2}$ orbitals as observed for Bi^+ in aqueous solutions[5] or from charge-transfer transition. In our system, $\epsilon \approx 1.4 \times 10^4$ $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, in contrary to $p_{1/2}$−$p_{3/2}$ transition where ϵ is only 1.3×10^2 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, which strongly indicates that the high absorption band results from charge-transfer transition. The electrochemical studies show two reduction steps, which also strongly support the view that in the red bismuth system at least one bismuth atom is present in an oxidation state lower than +III. EPR results exclude the presence of species with unpaired electrons.

In principle, two models of our unusual dimeric complex can be proposed. According to the first one, both bismuth atoms in the dimer are in oxidation state +I. This model explains the presence of only one Bi−S distance and a very low coordination number due to two lone electron pairs/bismuth as strongly indicated by the EXAFS studies. The presence of two peaks in the reduction half-cycle in the voltammogram could be then ascribed to the separate reduction processes: bismuth(I) to bismuth(0) occurred at two different potentials with regard to the dimeric structure. The bismuth(I) ions have the coordination number 3 owing to possession of two stereo active lone pairs, $6s^2$ and $6p_{1/2}^2$. The presence of these lone electron pairs prevents coordination of bismuth by other solvent molecules or trifluoromethanesulfonate ions.

According to the second model, the dimer contains bismuth in both +I and +III oxidation states. The absence of EPR signals and in particular the presence of two peaks in cycle voltammetry support the second model. At first sight the existence of not two but only one Bi−S bond distance contradicts the proposed structure. The Bi(I)−S and Bi(III)−S bond distances should be different, because bismuth(I) in the dimer shows the sp^2 hybridization with the bonding pair, the 6s pair, and the $6p_{1/2}$ pair in the hybrid orbitals. In contrast, bismuth(III) shows sp hybridization, where the hybrid orbitals are occupied by the bonding pair and by the 6s pair. In accordance with a general rule, one can expect a shorter distance for lower hybridization and vice versa. This contradiction can be removed by assuming that the real structure is a resonance hybrid between two structures. In the first, two electron pairs are localized at one bismuth atom (bismuth(I)) and one pair at the another bismuth atom (bismuth(III)). The second structure is formed by transfer of one electron pair from bismuth(I) to bismuth(III), which results in an exchange of positions of the bismuth ions. The appearance of such a resonance hybrid well explains the presence of only one Bi−S bond distance in the dimer. The problem of bond length in our dimer can also be explained indirectly by the analogy to the I_3^- ion. We postulate that the part of the studied complex which consists of two bismuth ions connected through a bridging sulfur atom can be considered as a system similar to the I_3^- ion. This anion is an example of intervalence charge-transfer transition[35] and in solution and in some salts has symmetrical structure with equal I−I bond distances (e.g. 2.90 Å in $As(C_6H_5)_4I_3$).[33] As in the case of the bismuth dimer, it is also difficult to assign unambiguous oxidation numbers to the iodine atoms in I_3^-. The intensive color of our solution results probably from the formation of an intervalence charge-transfer transition[35,36] in the dimer containing two bismuth atoms in different

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(35) Kettle, S. F. A. *Physical Inorganic Chemistry. A Coordination Chemistry Approach*; Oxford University Press: New York, 1996; Chapter 8.

oxidation states connected through a bridging sulfur atom from the DMTF molecule.

Acknowledgment. We gratefully acknowledge the support given to these investigations by the State Committee for Scientific Research (Poland) Grant No. 7T 09A 073 20 and by the Swedish Research Council. The authors thank Prof. Slawomir Siekierski for helpful discussions and Dr. Agnieszka Wieckowska for help in electrochemical studies. Stanford Synchrotron Radiation Laboratory (SSRL) is gratefully acknowledged for allocation of beam time and placement of laboratory facilities at our disposal. SSRL is operated by the Department of Energy, Office of Basic Energy Sciences. The SSRL Biotechnology Program is supported by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and by the Department of Energy, Office of Biological and Environmental Research.

Supporting Information Available: A table of IR frequencies, IR, IR-ATR, and EXAFS spectra, and Fourier transforms of EXAFS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Robin, M. B.; Day, P. Mixed Valence Chemistry-A Survey and Classification. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeléus, H. J., Sharpe, H. J., Eds.; Academic Press: New York, 1967; Vol. 10, p 248.