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Cd, Hg, and Pb Compounds of Benzene-1,3-diamidoethanethiol ($BDETH_2$)

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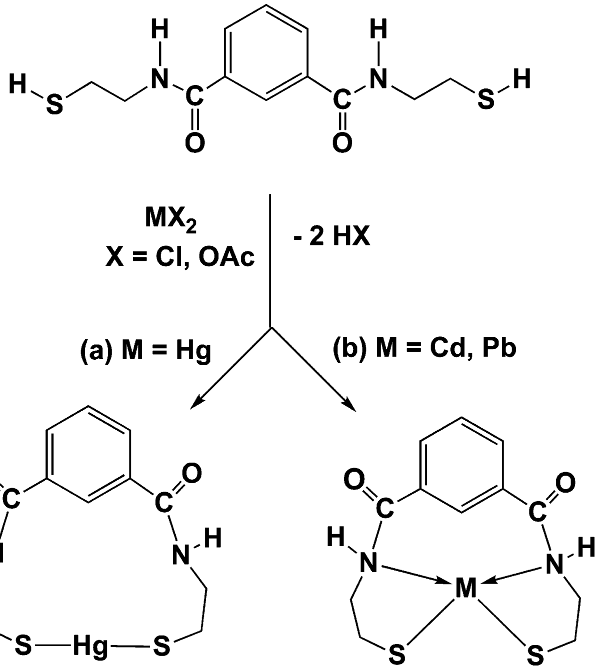
Benzene-1,3-diamidoethanethiol ($BDETH_2$) is an exceptional precipitant for removing soft heavy metals from water. The present work will detail the bonding arrangement of $BDETH_2$ to the metals Cd, Hg, and Pb, along with the full characterization data of the BDET–M compounds. It was found that the Hg compound has a linear S–M–S geometry. The characterization data consisted of Mp, EA, IR, Raman, MS, XANES, EXAFS, and solid-state multinuclear NMR.

Introduction

Benzene-1,3-diamidoethanethiol ($BDETH_2$) which has the trade name MetX was originally designed and synthesized for use as a precipitation agent for the removal of soft metals from water.[1−6] It can be delivered as either the sodium salt or as an ethanolic solution of the unmetallated ligand. The ligand was found to be very effective at removing metals from water and in producing nonleaching precipitates. The reaction that occurs between $BDETH_2$ and a divalent metal cation is shown in Scheme 1.

In aqueous solutions at 50 ppm Pb or Hg, the addition of $BDETH_2$ in EtOH at pH 4 and 6 levels drops the metal concentration to below either ICP-OES (for Pb) or CVAF (for Hg) detection limits in 6 h.[1,2]

Scheme 1. Reaction between $BDETH_2$ and a Metal Cation.



In actual applications, $BDETH_2$ was effective in metal removal from gold mining effluent, lead battery recycling, and acid mine drainage. When samples collected from an active gold-mining site in South America were treated with the sodium salt of this ligand, mercury from solutions containing cyanide was found to be irreversibly bound and precipitated.[3] For samples taken from lead battery recycling sites (LBRS), it was observed that more than 99.4% of lead could be removed within 15 min starting with an average initial concentration of 3.61 ppm using a stoichiometric 1:1 molar dose of $BDETNa_2$ to lead.[4] When acid mine-drainage (AMD) solutions were treated with $BDETH_2$, it was found that the divalent metals were almost completely precipitated.[5] The Fe concentration was reduced to <0.009 ppm from an

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initial concentration of 2.70 ppm and that of Mn to <0.001 ppm from an initial concentration of 0.913 ppm.

In summary, $BDETH_2$ has been shown to remove soft heavy metals from water under a variety of conditions. However, the chemical identity of the metal compounds that were formed in the treatment process were not determined. The ligand was designed to provide a linear S−M−S geometry in binding and precipitating mercury (Scheme 1a), while providing two strong covalent bonds, along with additional coordination by the nitrogens, to give at least a four-coordinate bonding environment for Cd and Pb (Scheme 1b). The present work will present the complete characterization data for the BDET compounds of Cd, Hg, and Pb.

Experimental Section

General Considerations. All chemicals were purchased from commercial sources and used without further purification. Solvents were of reagent grade. Elemental analyses and Raman spectra (using a Nicolet FT-Raman 906 ESP Spectrometer) were obtained at the University of Kentucky's Center for Advanced Energy Research. Infrared spectra were recorded as KBr disks, using a Nicolet 320 FTIR spectrophotometer. ^1H NMR spectra were run on a Varian INOVA 400 MHz instrument, and ^{13}C NMR spectra were run on a Varian Gemini 200 MHz instrument. XAFS experiments were performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Long Island, NY. A Finnigan Incos 50 Quadrupole instrument was used for recording EI mass spectra. Thermogravimetric analyses were carried out on a TA instruments TGA 2950 thermogravimetric analyzer. Solid-state MAS NMR with cross polarization was performed on a Varian INOVA 400wb Solids NMR spectrometer. Spectrometer/Larmor frequencies for the ^{113}Cd, ^{199}Hg, and ^{207}Pb nuclei were 88.8, 60.8, and 41.58 MHz, respectively, with magic angle spinning at 3 kHz. Metal analyses were obtained on a Varian Vista-Pro Simultaneous ICP-OES (Cd and Pb) and a Varian CETAC M6000A CVAA (Hg).

Leaching Studies. Two 100 mL aqueous solutions (100 ppm) of each of the metal salts of mercury, lead, and cadmium were prepared using deionized water. To these were added an equimolar amount of $BDETH_2$ dissolved in 95% ethanol. The reaction mixtures were stirred for one hour, and the resulting precipitates were filtered under gravity and dried overnight open to air. The precipitates were transferred into Erlenmeyer flasks, followed by addition of 100 mL of deionized water to each. The flasks were divided into two categories. The pH values of one category of flasks (labeled A) were adjusted to 1 and those for the other category (labeled B) were adjusted to 3 by adding concentrated HCl with continuous stirring. The pH values were measured using a pHTestr (Sigma-Aldrich). Ten milliliter aliquots were transferred by syringe into tubes after 1, 7, 14, and 28 days for metal concentration measurements. The metal concentrations of the Cd and Pb solutions were measured using ICP-OES, and those of Hg were measured by CVAA.

Synthesis and Characterization of BDET−Metal Compounds. BDET−Cd (1). A solution of $CdCl_2$ (0.916 g, 0.005 mol) in deionized (DI) water (10 mL) was added to a stirred solution of $BDETH_2$ (1.42 g, 0.005 mol) in 50 mL of 95% ethanol. A white precipitate formed immediately which was filtered under vacuum and dried in air to yield 1.28 g (65%) of the product. mp: 196 °C. Anal. Calcd for $C_{12}H_{14}N_2S_2O_2Cd$: C, 36.5; H, 3.6; N, 7.1; S, 16.3. Found: C, 35.9; H, 4.3; N, 6.9; S, 15.6. IR (KBr, cm^{-1}): 3414s (νNH), 2926m [νC−H(methylene)], 1632ss (νCO), 1541ss (δNH), 1479 (νC═C), 1274m [in-plane bending C−H(arom)], 729m [out-of-plane bending C−H(arom)]. Raman (cm^{-1}): 205, 174 (Cd−S). The compound was found to be insoluble in water, methanol, ethanol, water/methanol, water/ethanol, dimethylsufoxide, dimethylsulfoxide/water, dimethylformamide, acetone, ethyl acetate, tetrahydrofuran, diethyl ether, acetonitrile, acetonitrile/water, chloroform, dichloromethane, hexanes, toluene, nitrobenzene, nitromethane, carbon disulfide, and 10% acetic acid.

BDET−Hg (2). A solution of $HgCl_2$ (1.36 g, 0.005 mol) in DI water (30 mL) was added to a stirred solution of $BDETH_2$ (1.42 g, 0.005 mol) in 50 mL of 95% ethanol. A white precipitate formed immediately which was filtered under vacuum and dried in air to yield 2.51 g (100%) of the product. mp: 156 °C. Anal. Calcd for $C_{12}H_{14}N_2S_2O_2Hg$: C, 29.8; H, 2.9; N, 5.8; S 13.3. Found: C, 29.2; H, 2.4; N, 5.4; S, 12.6. IR (KBr, cm^{-1}): 3300s (νNH), 3062m [νC−H(arom)], 2923m [νC−H(methylene)], 1642ss (νCO), 1533ss (δNH), 1478m (νC═C), 1275m [in-plane bending C−H(arom)], 728m [out-of-plane bending C−H(arom)]. Raman (cm^{-1}): 293 (Hg−S). The compound was found to be insoluble in the same solvents as compound **1**.

BDET−Pb (3). A solution of $Pb(CH_3COO)_2 \cdot 3H_2O$ (0.9490 g, 0.0025 mol) in DI water (10 mL) was added to a stirred solution of $BDETH_2$ (0.71 g, 0.0025 mol) in 25 mL of 95% ethanol. A yellow precipitate formed immediately which was filtered under vacuum and dried in the air to yield 1.14 g (93%) of the product. mp: 178 °C. Anal. Calcd for $C_{12}H_{14}N_2S_2O_2Pb$: C, 29.4; H, 2.9; N, 5.7; S, 13.1. Found: C, 28.6; H, 2.7; N, 5.7; S, 12.7. IR (KBr, cm^{-1}): 3318s (νNH), 3079m [νCH(arom)], 2887m [νCH(methylene)], 1633ss (νCO), 1535ss (δNH), 1478m (νC═C), 1277m [in-plane bending C−H(arom)], 693 [out-of-plane bending C−H(arom)]. Raman (cm^{-1}): 306, 164 (Pb−S). The compound was found to be insoluble in the same solvents as compound **1**.

Results and Discussion

Synthesis and Characterization. In a typical reaction, an aqueous salt solution of a metal was added to an ethanolic solution of $BDETH_2$. Precipitates formed immediately after combination of the two solutions. Compounds **1** (BDET−Cd), and **2** (BDET−Hg) were white, while compound **3** (BDET−Pb) was yellow. Yields of the products ranged from 65% for compound **1** to 100% for compound **2**.

Infrared spectroscopy data obtained for all three compounds show that the peak at 2556 cm^{-1} from the S−H stretching (νSH) is absent from the spectra indicating that the protons of the thiol groups in $BDETH_2$ were displaced by the metals and that the metals formed bonds with the S atoms.

Raman spectroscopy exibited metal−sulfur stretches for all of the compounds. For example, the band at 205 cm^{-1} in compound **1** was attributed to Cd−S. This is similar to values found in the literature for νCd−S in tetrahedral cadmium compounds like $Cd(TAA)_2$ (TAA = monothioacetylacetone)[7] and $[Cd(Et_2dtc)_2]_2$ (Et_2dtc = diethyldithiocarbamate).[8] The band at 293 cm^{-1} for compound **2** can be attributed to a linear Hg−S bond very similar to linear Hg−S bonds

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reported in the literature.[9] For example, for the Hg−S bands in $Hg(SMe)_2$, the values 297,[10] 295,[11] and 298[12] cm^{-1} have been reported by different groups. The band at 164 cm^{-1} was assigned to νPb−S. These values are similar to values for νPb−S reported in the literature for tetrahedral lead compounds such as $(C_6H_5)_3PbSC_6H_5$.[13]

The compounds were found to be very stable in air, light, and water. They were found to be insoluble in over twenty-two common laboratory solvents/solvent systems such as water, methanol, ethanol, water/methanol, water/ethanol, etc. Therefore, no solution NMR experiments could be performed with these compounds.

In the mass spectroscopic data for BDET−Cd, the peak at 282 corresponds to $[M^+ - Cd]$, while the peaks at 112, 111, and 110 correspond to the isotope peaks of Cd. In the spectrum for BDET−Hg, peaks at 204−198 correspond to the isotopic peaks of Hg. The peak at 282 corresponds to $[M^+ - Hg]$. Similarly, in the spectrum for BDET−Pb, peaks at 208, 207, and 206 correspond to the isotope peaks of Pb. The peak at 282 corresponds to $[M^+ - Pb]$.

Efforts were made to run solid-state NMR since it has been reported in the literature that ^{199}Hg MAS solid-state NMR could be utilized to determine the coordination geometry of Hg-containing compounds from the shielding anisotropic shifts.[9] The anisotropic shift for tetrahedral Hg is small ($<$1200 ppm); for trigonal, it is intermediate (1200−1400 ppm), and for linear, it is large ($>$4000 ppm). The ^{199}Hg MAS solid-state NMR for BDET−Hg resulted in a spectrum with no detectable ^{199}Hg signal. Linear Hg compounds tend to feature high anisotropic shifts that are large and broad, often to the point of being undetectable. In the literature, there is evidence that Hg signals are not observed for Hg-thiolates containing linear Hg−S bonds.[9,14,15] In one study it was reported that no Hg signals were obtained in the solid-state ^{199}Hg NMR of $Hg(Ph)_2$, $CH_3HgO_2CCH_3$, or $PhHgO_2CCH_3$.[14] This was attributed to excessive sideband patterns ($\gg$125 kHz) which result from the large shift anisotropy expected for linear compounds. Similarly, ^{199}Hg NMR signals for $[Hg(18S6)](PF_6)_2$ (18S6 = 1,4,7,10,13,16 (hexathiacyclooctadecane)) were not observed because of the identical length (2.689(2) Å) of all six Hg−S bonds.[15] The lack of a ^{199}Hg NMR signal provided indirect evidence that compound **2** contained a linear S−Hg−S bonding unit. By comparison, the *solution* structure of the MerP protein, where the Hg is bound by two cysteine groups,[16] the geometry of the S−Hg−S bond was found to be 177 °C with a ^{199}solution Hg NMR shift of −816 ppm.[17,18] It is important to note that BDETH2 provides the same binding environment and geometry for Hg as the MerP protein. However, no signals were also detected for **1** and **3** in the ^{113}Cd and ^{207}Pb MAS solid-state NMR. This can be attributed to the lack of any proton near the metal center resulting in very long relaxation times and not to the presence of a linear S−M−S (M = Cd, Pb) bond since these compounds are expected to be ligated in a T_d geometry by the BDET ligand.

Table 1. Results of Leaching Studies for BDET−Cd, BDET−Hg, and BDET−Pb

metal	pH	concentration (ppm) 1d	7 d	14 d	28 d
Cd	1	$<0.008^a$	$<0.008^a$	$<0.008^a$	$<0.008^a$
Cd	3	$<0.008^a$	$<0.008^a$	$<0.008^a$	$<0.008^a$
Hg	1	$<0.0005^b$	$<0.0005^b$	$<0.0005^b$	$<0.0005^b$
Hg	3	$<0.0005^b$	$<0.0005^b$	$<0.0005^b$	$<0.0005^b$
Pb	1	$<0.020^a$	$<0.020^a$	$<0.020^a$	$<0.020^a$
Pb	3	$<0.020^a$	$<0.020^a$	$<0.020^a$	$<0.020^a$

[a] ICP-OES detection limit; [b] CVAA detection limit

The coordination geometries of many model compounds have also been examined.[9,19] The most common primary coordination number for Hg(II) is 2. These compounds have covalent bond lengths that vary between 2.316 and 2.361 Å and bond angles that vary between 180.0° and 167.4°.[9] Recently, it was demonstrated that a linear compound, $[Hg\{S(CH_2)_2NH_3\}_2](Cl)_2$, is formed when $HgCl_2$ reacts with cysteamine hydrochloride.[20] Cysteamine forms the side chains of $BDETH_2$. The observed Hg−S bond lengths are 2.333(9) and 2.338(9) Å, and the S−Hg−S bond angle is 168.53(3)°. Distortions from linearity are generally caused by longer secondary bonding interactions found in the solid state.

Single-crystal X-ray analyses could not be performed because of the insolubility of the compounds in all the solvent combinations tested.

Leaching Study. The compounds were stirred at pH 1 and 3 for 1, 7, 14, and 28 days and extracts taken for ICP and CVAA analyses. The extracts were found to contain essentially no metals (Table 1). The exceptional stability of the compounds may be attributed to the hydrophobic nature of the ligand environment which would prevent access to the metal atoms by water soluble species such as H_3O^+. Table 1 summarizes the results of this study.

XAFS and XANES Study. To examine the Hg bonding environment in compound **2**, X-ray absorption fine structure (XAFS) spectroscopy was performed at the K-edge of sulfur and the L_{III}-edge of Hg on $BDETH_2$ and BDET−Hg. HgS (cinnabar) was used as a reference material; elemental sulfur and elemental mercury were used as energy calibration standards. Figure 1 shows the sulfur K-edge XANES spectra for $BDETH_2$, BDET−Hg, and HgS (cinnabar). The onset

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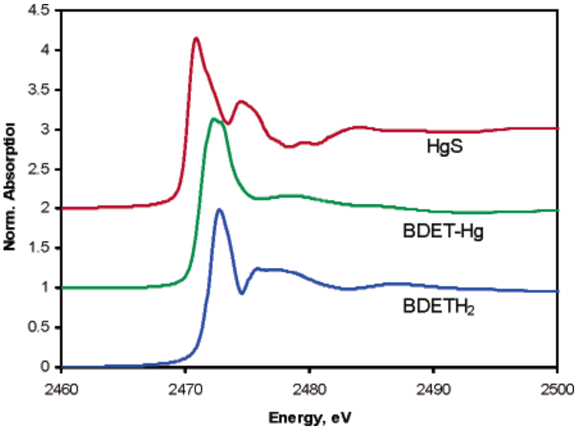

Figure 1. Sulfur XANES spectra for HgS, BDET−Hg, and for BDETH$_2$.

of absorption shifts to higher energy in the order of HgS (2470.9 eV) < BDET−Hg (2472.3 eV) < BDETH$_2$ (2472.7 eV). It is well-known[21−23] that the position of the first peak (white line) in the K-edge XANES spectra of sulfur compounds is a measure of the sulfur oxidation state. The peak position observed for BDETH$_2$ relative to that of elemental sulfur, which is assumed to occur at 2,472.0 eV, is similar to those observed[21−23] for aliphatic monosulfides containing C−S−H functional groups (thiols, mercaptans) and significantly removed from the peak position for the sulfide anion in HgS. BDET−Hg, which involves sulfur bonded between carbon and Hg^{2+}, is appropriately intermediate in peak position between those for HgS and BDETH$_2$.

Figure 2a shows the mercury L$_{\text{III}}$-edge XANES spectra for both HgS (cinnabar) and BDET−Hg. The spectra are similar, although HgS has more pronounced fine structure as a consequence of the smaller and more regular unit cell and three-dimensionally ordered crystal structure.

Figure 2b shows the first derivative XANES spectrum that accentuates the two inflection points on the rising edge in the XANES spectrum. A parameter known as the inflection point difference, IPD, is defined as the separation in electron volts of the two prominent peaks that occur in the derivative XANES spectrum. This separation appears to reflect the nature of the anion to which the Hg is bound.[24,25] Both HgS (cinnabar) and BDET−Hg have similar values for IPD (7.7 ± 0.3 eV for HgS and 7.5 ± 0.3 eV for BDET−Hg), reflecting the fact that Hg^{2+} is principally bound to sulfur atoms in both materials.

Figure 3 compares the EXAFS region of the Hg XAFS spectra for HgS and BDET−Hg. Figure 3a shows the isolated EXAFS oscillations converted to a reciprocal space representation (k-space, in Å^{-1}) and weighted by k^3. As can be seen, these oscillations occur at regular intervals in k-space, and the amplitude of the oscillations is significantly greater for HgS. The spacing of the oscillations is similar for both materials, although the two curves are offset from each other.

The radial structure function (RSF) spectra shown in Figure 3b were obtained by applying a Fourier transform to the spectra in Figure 3a. One main peak is observed in the RSF of both materials; it represents the first coordination shell between Hg and sulfur. The peak occurs at about the same position in both spectra, but its amplitude is almost twice as high in HgS than in BDET−Hg. By application of FEFF 6.0 fitting procedures[26] to the EXAFS region data, it is possible to estimate the bond distance (R in Å) between Hg and S and the coordination number (CN) for the Hg. This was achieved using HgS (cinnabar) as a model compound for the EXAFS data for BDET−Hg. Cinnabar has a distorted NaCl-type structure (space group, $P3_221$); each Hg^{2+} cation is surrounded by two S^{2-} anions at a distance of 2.37 Å, and the S−Hg−S bond angle is 172°.[27] The FEFF fitting can be achieved using the RSF (R) or the $k^3\chi$ spectrum (k) or the back-transform of the major peak in the RSF, which separates the contribution of the Hg−S shell from the overall $k^3\chi$ spectrum (q). The FEFF least-squares fitting of cinnabar is summarized in Table 2.

These values were then used to model the EXAFS region data for BDET−Hg. The resulting least-squares values are shown in Table 3. The comparison of data and fit returned by this procedure is shown in Figure 4 for cinnabar and BDET−Hg. Also indicated in Figure 4 is the close correspondence of the k-space EXAFS spectrum for Hg in BDET−Hg and the k-space EXAFS spectrum derived from back-transform of the Hg−S shell in the RSF.

The agreement among the different fitting bases, R, k, and q, is reasonable and within anticipated experimental errors. Interestingly, despite the apparent factor of almost 2 in amplitude of the Hg−S peaks in the RSF (Figure 3), the FEFF fitting indicates that the coordination numbers of Hg in both HgS and BDET−Hg are the same. The bond distance for the Hg−S bonds in BDET-Hg is about 0.04 Å longer and the Debye−Waller factor, σ^2, is significantly higher; both of which will result in less amplitude in the RSF peak. The distance estimated for the Hg−S bonds in BDET−Hg was 2.42 Å, which falls in the range of values (2.34−2.53 Å) previously reported in the literature.[27−29]

The derived Hg−S bond distance is relatively long for two-coordinated Hg^{2+} in mercury−sulfur complexes and such elongation may indicate additional secondary interactions with other ligands.[6] More complex FEFF modeling was attempted to assess, in particular, the possibility that oxygen or carbon was in the first coordination sphere. However, such fitting did not improve the fits significantly nor did it return any meaningful results. Hence, it can be concluded that,

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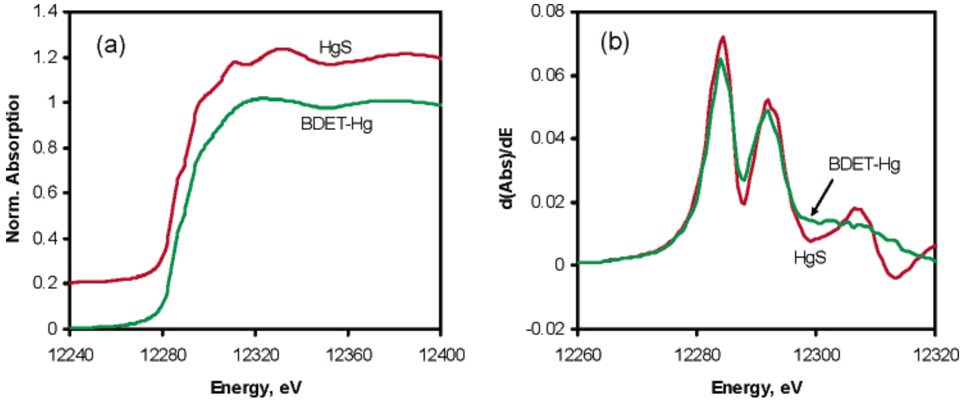

Figure 2. (a) Hg L_{III}-edge XANES spectra for HgS and BDET−Hg. (b) The first derivative Hg L_{III}-edge XANES spectra.

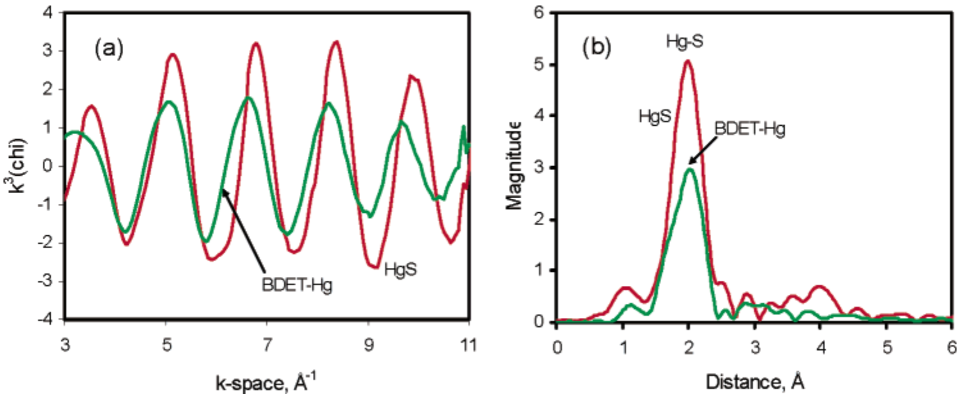

Figure 3. (a) EXAFS oscillations isolated from the XAFS spectrum and displayed as $k^3\chi$ vs k. (b) Radial structure function obtained by applying a Fourier transform to the $k^3\chi$ spectra shown in panel a. The single main peak represents the first Hg−S coordination shell, uncorrected for the phase shift.

Table 2. FEFF Parameters Derived for Cinnabar (hexagonal HgS)

	S_0^2	CN[a]	e_0	R (Å)	σ^2	R_{fact}
crystallography[17]		2		2.37		
R (1.3−2.6 Å)	0.41	2	8.4	2.386	0.003	0.008
k (3−13 Å^{-1})	0.41	2	8.2	2.385	0.003	0.044
q (Hg−S)	0.40	2	8.1	2.385	0.003	0.006
error (q)	±0.005		±1.2	±0.005	±0.0006	

[a] A value for CN of 2 was assumed for the fitting to derive values for S_0^2.

Table 3. FEFF Parameters Derived for BDET−Hg on the Basis of the Cinnabar Parameters

	S_0^{2a}	CN	e_0	R (Å)	σ^2	R_{fact}
R (1.3−2.6 Å)	0.41	2.15	5.4	2.42	0.008	0.024
k (3−13 Å^{-1})	0.41	2.16	5.9	2.42	0.008	0.032
q (Hg−S)	0.40	2.08	5.9	2.42	0.008	0.020
error (q)		±0.25	±1.6	±0.01	±0.001	

[a] A value for S_0^2 of 0.41 was assumed for the fitting to derive values for CN.

although such interactions may indeed be present to account for the longer Hg−S bond, they are not reflected in the EXAFS data presumably because of their nonsystematic nature. Such a result is more consistent with the BDET−Hg mercury complex being polymeric rather than crystalline.

TGA Study. Thermogravimetric analyses (TGA) were conducted on **1**−**3** to gain further information on the stability and composition of the compounds. The thermogram for **1** shows that the compound is fairly stable up to 77 °C, after which it begins to lose mass. The observed weight loss of 3.19% between 77 and 272 °C indicates that the compound may be hydrated. However, the absence of broad bands at 3415 (νOH) and 1642 cm^{-1} (δH_2O) in the IR spectrum and the results of elemental analysis do not support this possibility. The thermogram of **2** shows that the compound is very stable up to 239 °C. The observed weight losses of 13.76 (between 239 and 303 °C) and 62.32% (between 303 and 383 °C) did not correspond to any structural feature of the compound. The thermogram for **3** shows that the compound is fairly stable up to 280 °C, after which it begins to lose mass. The weight losses observed indicate that all three compounds decompose without producing any stable intermediates. This could be an indication that the compounds are polymeric rather than molecular (Figure 5a), an observation in keeping with the insolubility of the compounds.

This is further supported in the literature where $BDETH_2$ is used in passivating gold surfaces in self-assembled monolayers. In these studies the mode of bonding is either “open” (Figure 5b) or with the two sulfurs bonded to two metals (Figure 5c).[30] For the present compounds, then, a bridging, polymeric structure is most likely.

The elemental analyses clearly indicate that the compound formulations are $C_{12}H_{14}N_2S_2O_2Cd$, $C_{12}H_{14}N_2S_2O_2Hg$, and $C_{12}H_{14}N_2S_2O_2Pb$ for **1**, **2**, and **3**, respectively. For **1** (anal. calculated for $C_{12}H_{14}N_2S_2O_2Cd$), the experimental values agreed very well with that of the calculated ones. While the

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(30) Vance, A. L.; Wiley, T. M.; Nelson, A. J.; van Buuren, T.; Bostedt, C.; Terminello, L. J.; Fox, G. A. *Langmuir* **2002**, *18*, 8123−8125.

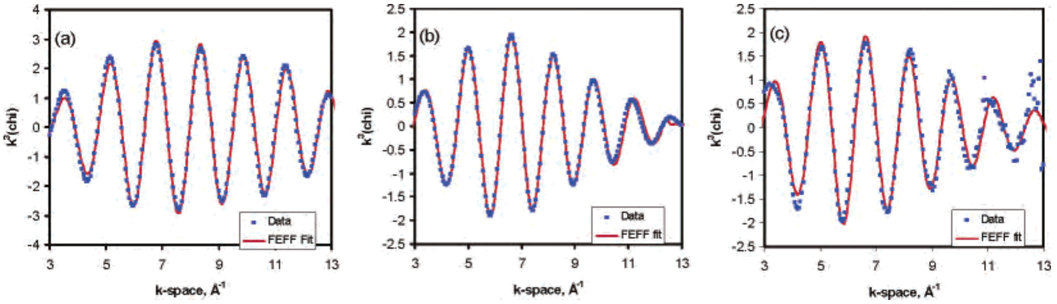

Figure 4. Comparison of FEFF model function and data for (a) the Hg−S shell in RSF back-transformed to *k*-space for cinnabar, HgS, (b) the Hg−S shell in RSF back-transformed to *k*-space for BDET−Hg, and (c) the total *k*-space EXAFS oscillations for BDET−Hg.

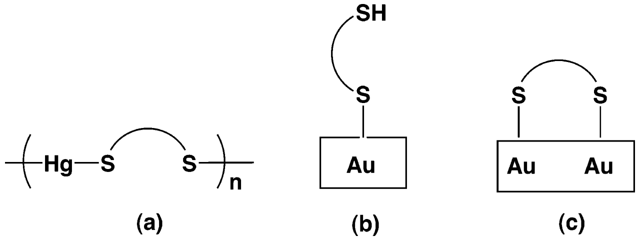

Figure 5. (a) Mercury binding to sulfurs, polymeric, (b) gold binding, open mode, and (c) gold binding through two sulfur atoms.[30]

calculated values for C, H, N, and S were 36.51, 3.58, 7.10, and 16.25%, respectively, the corresponding experimental values were 35.91, 4.29, 6.94, and 15.60%. The elemental analysis data found experimentally for the other compounds, namely, BDET−Hg, and BDET−Pb also agree well with the calculated values.

Conclusions

The previous observations and the results of the current study support the presence of a linear coordination environment for BDET−Hg (**2**). It is likely that the BDET−Cd (**1**) and BDET−Pb (**3**) structures are four-coordinate and distorted tetrahedral. Scheme 1 illustrates the possible structures for **1**, **2**, and **3**. However, it should be mentioned here that although Pb(IV) compounds have a tendency to be four-coordinate and tetrahedral, Pb(II) compounds exist as both discrete and polynuclear complexes exhibiting a broad range of coordination numbers from 2 to 12.[31] It has also been reported that the most common coordination numbers are two [16% of all Pb(II) compounds reported in the CSD], four [24% of all Pb(II) compounds], and six [15% of all Pb(II) compounds].[31]

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