

A pH-Metric, UV, NMR, and X-ray Crystallographic Study on Arsenous Acid Reacting with Dithioerythritol

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The aqueous solutions of arsenous acid with the meso and racemic forms of 1,4-dithiol-butane-2,3-diol, namely, dithioerythritol (dte) and dithiothreitol (dtt), respectively, were titrated pH-metrically in different molar ratios. The pK_a values determined for $As(OH)_3$, and dtt were in good accordance with the literature data, and we determined for the first time the pK_a value of dte. The deprotonation steps of both M ($As(OH)_3$ considered as a central metal ion) and H_2L components dte and dtt (considered as ligands) appeared at a higher pH in the titration curves of the ternary systems (M, H_2L , H^+) than in the individual component. This unusual observation is explained by the condensation reactions between the reagents taking place in the $pH < 8$ range. In the solutions of $c_{As(III)} > 5 \cdot 10^{-3}$ M, the precipitate formed upon mixing the arsenous acid and H_2L solutions in neutral medium, and the formation of the precipitate shifted toward acidic pH on the increase of the total concentrations. This indicated that pH-metry can follow the reactions only in an indirect way. Useful, but not satisfactory, information can be obtained by means of this method alone. Combined with NMR and UV spectroscopic measurements it is revealed that depending on the $As(III)/H_2L$ molar ratio, different complexes form in the solutions. In the species with 1:2 composition, one of the ligands is strongly bound to the arsenic(III) probably via its two thiolate, while the second one is attached only weakly. The crystal structure of an $As(III)$ –dte crystal of 1:1 composition, grown from ethanolic solution, shows that $As(III)$ binds the ligand through its three p-orbitals in a manner similar to that expected in aqueous solution. While the uptake of the second ligand cannot be detected by pH-metry, the decomposition of thioether bonds above $pH \sim 10$ is confirmed by the change in UV spectra at ~ 265 nm to be a base-consuming process. In such alkaline solutions, most probably, rearrangement of the bonding scheme occurs, resulting in ligands being bound to the arsenic(III) through the oxygen donor atoms.

Introduction

A survey of the chemistry of arsenic is important because of its well-known toxic effect, which is prevented by limiting the arsenic concentration in drinking water as low as $10 \mu g/L$. Still more than 50 million people have to drink water

containing arsenic in concentrations well above this limit.^{1–4} The toxicity also depends on the oxidation state, that is, $As(III)$ is 25–60 times more toxic than $As(V)$.⁵ Removal of arsenic from drinking water is possible only for $As(V)$ by ion-exchange or as a precipitate of $AlAsO_4$ or $FeAsO_4$.

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Despite the existing sophisticated methods, there is no efficient, selective, and economic way to eliminate As(III) from drinking water.^{6–8} Robins et al. state in their review:⁹ “There have not been any significant and innovative improvements in the methods for removing arsenic from process and effluent solutions, or indeed from drinking water, in the last decade or so. The current needs to remove arsenic from drinking water is now a world problem, and so must be addressed as a matter of great urgency.”

To learn more about the behavior of As(III), it seemed to be a good idea to find a ligand that forms a stable complex with As(OH)₃. In neutral aqueous solution, As(III) is present as As(OH)₃. On the basis of this similarity to boric acid, one might expect that also As(OH)₃ can form stable esters with hydroxy-group-containing ligands (tartaric acid, ascorbic acid, ethylene glycol, glycerine, and hydroquinone) However, our trial to detect such adducts by pH-potentiometry failed, in agreement with previous literature data.¹⁰

Recent investigations showed that As(III) has high affinity to sulfur-containing molecules, and it has been used for a specific and sensitive assay for dithiols already almost 40 years ago.¹¹ Although thiolates may exert several disadvantages, that is, they are easily oxidized or bound strongly to heavy metal ions, their use in biotechnological water purification could be a promising perspective. Indeed, there are already results in the literature about engineered arsenic-accumulating bacteria.^{12–14}

Among the sulfur-containing molecules interacting with As(III), glutathione (H₃gs), as one of the most important examples in the living cell, has been studied. Scott et al. isolated the tris(glutathionate)–As(III) complex and characterized it by mass spectrometry.¹⁵ The equilibrium study of the complex formation of As(III) with cysteine (H₂cys) and glutathione was also published recently.¹⁶ pH-metric, UV, and ¹H NMR measurements showed the formation of [As(Hcys)₃] and [As(Hgs)₃]^{3–} complexes, where the ligands bind to the As(III) via their sulfur atoms forming thioester bonds. In case of both ligands in alkaline solutions (pH > 10), the complexes break up, and hydroxide groups partly replace the thiolate ions in the As(III) coordination sphere

resulting in [As(cys)(OH)₂][–] or [As(gs)(OH)₂]^{2–} species. Most of these suggestions were, however, based on indirect results.

On the other hand, the biological effect of arsenic can be assigned to its binding potential to the thiolate-containing functional groups of biomolecules. The possible mechanism of action is suggested to be the modulation of protein phosphorylation¹⁷ or the inhibition of steroid binding to glucocorticoid receptors¹⁸ on binding of arsenic to the vicinal thiols of the participating enzymes. Dithiothreitol (dtt) has been shown in biological experiments to enhance arsenic trioxide-induced apoptosis in several different leukemia cell lines, a promise of an effective drug for leukemia.¹⁹ The synergistic role of dtt has not yet been clarified.

There are no published data on the solution chemistry of arsenic(III) with dtt and dithioerythritol (dte). The two ligands are stereoisomers, dte being the meso isomer and dtt the racemate of 1,4-dithiol-butane-2,3-diol. To get better insight into the interaction of arsenous acid and these ambidentate ligands containing two thiolate and two hydroxy groups, we have undertaken a pH-metric, UV, and NMR spectroscopic study, being presented below, together with the crystal structure determination of [As(H₃dte)].

Experimental Section

Materials and Methods. Measurements were performed using dithioerythritol (dte) from Fluka and dithiothreitol (dtt) from Sigma-Aldrich. Two kinds of As(III) solution were used: anhydrous As₂O₃ (Merck) was dissolved in 0.1 M sodium hydroxide solution (Sigma-Aldrich) and a commercial sodium arsenite solution (Sigma-Aldrich). NaOH stock solution (Sigma-Aldrich) was standardized against potassium hydrogen phthalate. The concentration of the As(III) solution was determined pH-metrically by simultaneous refinement of the pK_a and the concentration of the arsenous acid from at least three parallel titrations.

The first step of the crystallization of the As(III) H₃dte^{3–} coordination compound was to obtain the white, powdered precipitate from the aqueous solution of the components. This precipitate was filtered and washed with distilled water. Boiling ethanol was added to the precipitate until it dissolved. The solution was left to cool, and the recrystallized product was filtered and dried.

The compositions of all solid products were checked by inductively coupled plasma atomic emission spectroscopy (ICP-AES), complemented by organic elemental analysis. The latter was done on the recrystallized single crystals. These crystals from which one was selected for X-ray diffraction measurements showed the following composition (the theoretically expected values for C₄H₇O₂S₂As in parenthesis): As, 31.6% (33.1%); C, 21.4% (21.2%); H, 2.96% (3.12%); S, 27.8% (28.4%).

ICP-AES Spectrometry. The As content of the samples was determined by inductively coupled plasma atomic emission (ICP-AES) spectroscopy. Prior to the analysis, the samples were digested using 0.1 M HCl (Merck). The resulting solutions were then transferred into volumetric flasks, which were filled using Millipore

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MilliQ quality deionized water. The analysis was performed at the As I 193.26 nm emission wavelength and using a Jobin-Yvon 24-type all-argon spectrometer equipped with a Teflon V-groove nebulizer and a Gilson Minipuls III peristaltic pump. Three determinations from each sample solutions were carried out using two-point background correction, 4-point direct calibration, and Gaussian spectral-drift compensation. Standard solutions for calibration were prepared from a 1 g/L commercial As stock solution (Merck) through dilution with Millipore MilliQ quality deionized water.

pH-metric Measurements. pH-potentiometric titrations in aqueous solutions were performed at 298.0 ± 0.1 K; the ionic strength was adjusted to 0.1 M with NaClO_4 (Fluka). High-purity argon gas served to remove carbon dioxide and molecular oxygen from samples and to provide an inert gas atmosphere during all measurements. The measurements were conducted in parallel at two different laboratories. An ABU93-type (Radiometer) autoburette with a built in pH-meter and a Titrino GP 736 (Metrohm) autoburette with an Orion 710A pH meter were used to perform the potentiometric titrations using standard NaOH, HClO_4 , and As(III) solutions. The homemade titration program adjusted the titration steps to the slope of the titration curve by decreasing the addition increments on increase of the slope. The minimum step was 0.005, while the maximum step 0.05 mL (for a total added volume of 3–5 mL). Semimicro combined pH electrodes (Orion 9103 BN and Metrohm 6.0234.100) were calibrated²⁰ before each measurement. The emf values were converted to pH values with the aid of a four-parameter extended Nernst equation (eq 1).

$$E = E_0 + K \log[\text{H}^+] + J_{\text{H}}[\text{H}^+] + \frac{J_{\text{OH}}K_{\text{w}}}{[\text{H}^+]} \quad (1)$$

where J_{H} and J_{OH} are fitting parameters in acidic and alkaline media for the correction of experimental errors, mainly from the liquid junction and the alkaline and acidic errors of the glass electrode; $K_{\text{w}} = 10^{-13.75}$ M² is the autoprotolysis constant of water under the applied measurement conditions.²¹ The parameters were calculated by a homemade program based on the nonlinear least-squares method. The concentration of arsenous acid fell in the $1\text{--}5 \cdot 10^{-3}$ M interval, while the As(III)/ H_2L ratio was between 1:1 and 1:3.

Electronic Absorption Measurements. UV spectra were recorded by means of a Hewlett-Packard 8452A diode-array spectrophotometer in the 190–300 nm wavelength interval in a 0.5 cm quartz cuvette. The concentration of arsenous acid fell in the $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ M interval, while the As(III)/ H_2L ratio was between 2:1 and 1:10.

NMR Measurements. ¹H NMR spectra were measured with a Bruker Avance DRX-500 set. DSS was used as an internal standard (0 ppm). The sample aliquots included 10% D_2O . The water peak was suppressed by the presaturation method. The spectra of the free ligand and the As(III)/ LH_2 1:1 and 1:2 systems were recorded at three different pH values (3.0, 6.0, 11.0). The free ligand concentration was 0.135 M, while in the arsenic-containing systems, the total ligand concentration was ~ 0.01 M, because of the limited solubility of the species formed.

Solid state ¹³C NMR spectra were recorded at room temperature operating at 11.7 T magnetic field (¹³C 125.7 MHz). Samples were packed in 4 mm diameter ZrO_2 rotors and were spun at 5 kHz speed, ¹³C CP-MAS spectra were referenced to external DSS sample. ¹³C CP-MAS experiments were acquired with the following parameter

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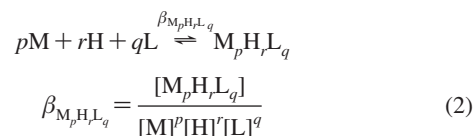
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Table 1. Crystallographic Data for [As(HL_3dte)]

formula	$\text{C}_4\text{H}_7\text{O}_2\text{S}_2\text{As}$
formula mass	226.149 g/mol
cryst syst	orthorhombic
space group	<i>Fdd2</i> (No. 43)
<i>a</i>	12.634(1) Å
<i>b</i>	33.360(1) Å
<i>c</i>	6.547(1) Å
<i>V</i>	2759.4(1) Å ³
<i>Z</i>	16
<i>T</i>	122.4(5) K
λ	0.71073 Å
D_{calcd}	2.237 g cm ⁻³
μ	5.455 cm ⁻¹
R_{int}	0.0598
$R(F_o)$	0.0171
$wR(F_o^2)$	0.0435

sets: ¹H 90 ° pulse was 4.0 μs ; cross polarization contact time was 2 ms, and an ¹H decoupling 62.5 kHz, 2s repetition delay was applied. A 300 ppm spectral region was recorded with a carrier frequency placed at 110 ppm; the ¹H frequency was positioned to 4.7 ppm, and 1 K transients were recorded in 2 K complex data points resulting in 27.3 ms of acquisition time. Lorentzian window function (with 50 Hz broadening factor) was applied prior to Fourier transformation.

Equilibrium Constant Calculations. The species formed in the systems were characterized by a general equilibrium process (eq 2).



where M is As(OH)₃, L is the thiol-deprotonated form of the dte or dtt, and the charges are omitted for simplicity. The corresponding constants were calculated by the computer program PSEQUAD.²² The set of titration curves as pH versus volume of titrant was input to the program.

X-ray Data Collection and Analysis. Diffraction data were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo K α radiation. The temperature was kept at 122.4(5) K using an Oxford Cryosystems low-temperature liquid nitrogen cooling device. The data reduction was performed using the Nonius Collect suite of programs.²³ A numerical absorption correction was applied on the basis of the crystal shape. The structure was obtained by direct methods using SIR97²⁴ and was refined by full-matrix least-squares against F^2 using the SHELXL-97 program.²⁵ Positions and anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located using difference maps, and their positions and isotropic displacement parameters were refined. The crystallographic data are summarized in Table 1.

Results and Discussion

pH-Metric Measurements. Binary Systems. The $\text{p}K_{\text{a}}$ values of the arsenous acid and the two ligands, dte and dtt,

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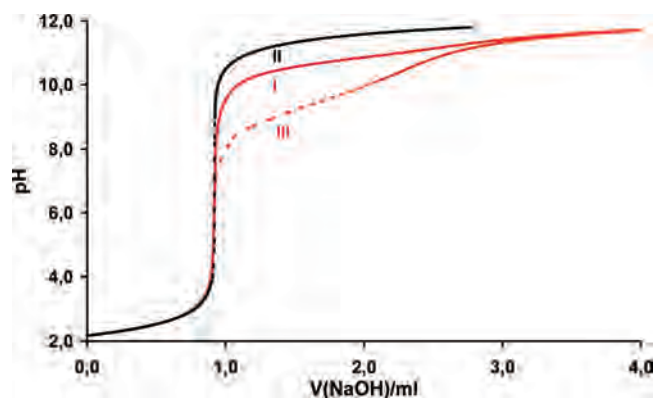
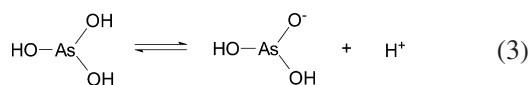


Figure 1. Experimental titration curve of the As(III)–dte system at 1:1.1 metal to ligand molar ratio (I, red full line): $1.1 \times c_{\text{As(III)}} = c_{\text{dte}} = 2.2 \cdot 10^{-3}$ M. Curve II (black dashed line) is the titration curve of the initially added excess strong acid with strong base, and curve III (red dashed line) shows the titration curve calculated on the basis of the assumption that no interaction between As(OH)₃ and dte occurred.

were determined by means of pH-potentiometric titrations. Solid As₂O₃ was dissolved in ~0.1 M NaOH solution. Initially, an excess of HClO₄ solution was added to the aliquot of the arsenic(III) solution to start the titration from acidic pH. The pH was rising quickly after the neutralization of the excess of the strong acid. Around pH ~8 a buffered region started because of the deprotonation process of the arsenous acid. The pK_a value was calculated to be 9.11(2), the ambiguity of the last digit given in the parenthesis, that corresponds well to the data found in the literature (pK_a = 9.00; *I* = 0.1 M NaClO₄,²⁶ 9.25; *I* = 0).²⁷ This process yields H₂AsO₃⁻ according to eq 3. The organic ligands dtt and dte

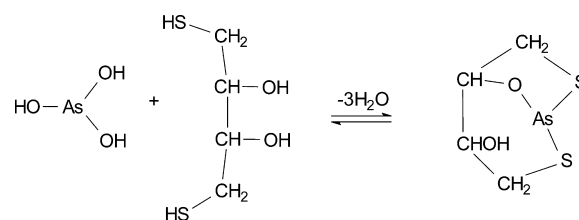


were titrated similarly: the deprotonation processes in both cases took place above pH 8 in two overlapping steps. The determined macroscopic deprotonation constants for dte were pK_{a1} = 9.17(2) and pK_{a2} = 10.17(2), and for dtt, they were pK_{a1} = 9.03(2) and pK_{a2} = 10.07(2). The latter value is in good agreement with the already published data (pK_{a1} = 8.99, pK_{a2} = 10.00; *I* = 0.1 M KNO₃).²⁸

Titration of the As(OH)₃/H₂L ~1:1 System with Base. The titrations of the As(III), H₂L, H⁺ ternary systems also started from the acidic pH as a consequence of the addition of an initial excess of strong acid to the reaction mixture. The behavior of the two organic ligands (dtt and dte) toward arsenous acid was essentially the same. In the following discussion, they will not be distinguished, and as components, both will be denoted by H₂L = dte or dtt.

The experimental titration curve of the As(III)–dte system at 1:1.1 metal to ligand molar ratio, shown as I in Figure 1, seems at first to not give much information on the chemical reactions taking place during the titration. To help the

Scheme 1



understanding of the situation, we have added curve II, which is a separate titration of the added initial excess of perchloric acid alone, and curve III, which is a simulated curve for a system with the same initial parameters as the experimental curve based on the assumption that no interaction between As(OH)₃ and dte occurred.

Evaluation of the Titration Curves in the pH ~8–10 Range. The titration curves in the pH 8–10 range must reflect the combined effect of the acidity constants of As(OH)₃, of the various thiol groups and of the coordination ability or the (thio)ester formation if one prefers this way of naming of the condensation reactions between the As(III) and the ligands. In the following, we approached the experimental titration curve (I) in Figure 1 assuming the process depicted in Scheme 1. The reaction here leads to the formation of a 1:1 complex. This product has earlier been crystallized with dtt,²⁹ and now its existence has been confirmed by a crystal structure determination of [As(H₃dte)] (vide infra). In this case, the coordination ability has to win over the very weak acidity of an alcohol.

If the 1:1 species was formed in a system with a total concentration ratio of 1:1 As(III):L, the expected condensation reactions, like the thioester or ester formation, would result in water but not in proton release, and this kind of complexation can not be directly followed by pH-metry. At the same time, all the donor groups that deprotonate in the pH range of 8–10 in the binary systems lose this ability upon condensation reactions. Therefore the pH-metric titration curve of this system should look like a titration curve of the initially added excess of the strong acid (curve II in Figure 1). However, as the figure shows this is true only up to pH ~9. On the other hand, the comparison of the experimental curve (I) with the simulated one, assuming no interaction between the components (III) makes one realize that all the deprotonation processes of the free components disappeared up to pH ~10 (only the small ligand excess consumes hydroxide ions). Thus, considering the formation of [As(H₁L)] species, one can describe the titration curves between pH ~8 and 10 well.

We shall show below that the crystal structure of the isolated single crystals is in complete agreement with the product shown in Scheme 1, supporting the above discussion.

Evaluating the Titration Curves at pH > 10. No simple agreement was achieved between the titration curves I and II for pH values in the range of 10–11.5. Here the experimental curve shows a buffering effect of the solution, despite all the donor groups (with the exception of one of the hydroxy groups of the ligand) having lost their protons

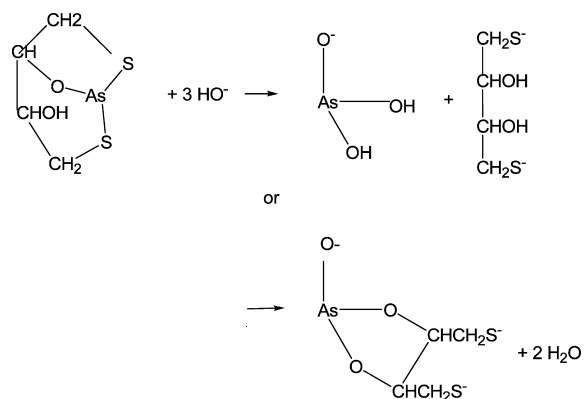
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Scheme 2



in the above reaction (Scheme 1). To explain this behavior, one might consider the reaction in Scheme 1 as being reversed: while the formation of condensation products described in Scheme 1 did not result in proton release, the decomposition as shown by Scheme 2 requires hydroxide ions because the reaction takes place at $\text{pH} > 10$. Under such conditions, the free HS-groups and $\text{As}(\text{OH})_3$ must be deprotonated according to the above results on the binary systems.

The number of hydroxide ions consumed upon the formation of either products in reaction Scheme 2 is three. Because the assumption of the formation of $[\text{As}(\text{H}_1\text{L})]$ species gave satisfactory fit up to $\text{pH} 10$, we calculated the difference between this simulated curve (including only the excess of the strong acid and the small excess of the ligand over the arsenous acid) and the measured titration curve, which, indeed, corresponds to the consumption of 3 equiv of hydroxide ions related to the total amount of arsenous acid at $\text{pH} 11.3$ (Figure 2).

Taking this result into account, the experimental titration curve (I) can be perfectly fit by introduction of three further deprotonation steps in the pH range of 10–11.5. These processes occur in a strongly cooperative manner with $\text{p}K_{\text{a}1} = 10.27$ and the $\text{p}K_{\text{a}2} + \text{p}K_{\text{a}3} = 21.78$.

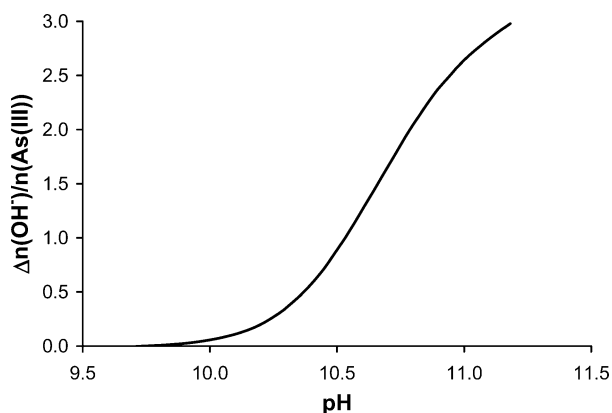
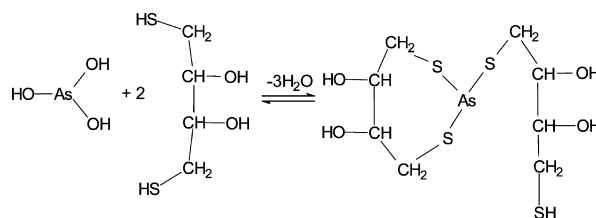
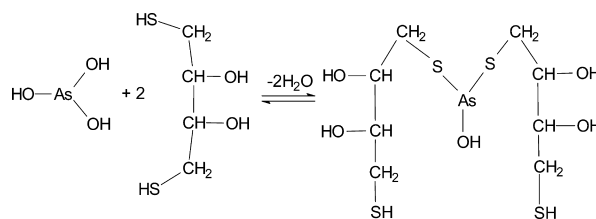


Figure 2. Difference of the experimental and simulated titration curves based on assumption of the formation of $[\text{As}(\text{H}_1\text{L})]$ species related to the total amount of arsenous acid as a function of the pH . This curve has been constructed by subtraction of the base volumes at the identical pH values, from which the amount of the difference in consumed base ($\Delta n(\text{OH}^-)$) is determined.

Scheme 3



Scheme 4



Titration of the $\text{As}(\text{OH})_3/\text{H}_2\text{L} = 1:2$ Systems with Base. With ligand in excess, species other than the one shown in Scheme 1 may also form. Schemes 3 and 4 present such suggestions for condensations using presumably the more potent ligand thiolate instead of alcoholate. In Figure 3, titration curve of acidified solutions of $\text{As}(\text{OH})_3$ and dte in the molar ratio 1:2 with sodium hydroxide is shown as curve IV. An enhanced buffering effect is seen above $\text{pH} 8$, as one would expect if free thiol groups were present with a metal to ligand ratio of 1:2.

It shall be noted, that the number of the released protons in the $\text{pH} 8$ –10 range is different for the reactions in Schemes 1, 3, and 4. In Scheme 3, one ($-\text{SH}$) and, in Scheme 4, three functional groups (two $-\text{SH}$, and an OH bound to arsenic(III)) deprotonate from the noncoordinating components, while in the case of formation of $[\text{As}(\text{H}_1\text{L})]$, two protons are released from the $-\text{SH}$ groups of the free ligand between $\text{pH} 8$ and 10. Using the $\text{p}K_{\text{a}}$ values from the binary systems, the simulated curves VII (yellow dashed line), VIII (green dashed line), and VI (blue dashed line) in Figure 3 are obtained, respectively. It should be mentioned, that one can only speculate about these $\text{p}K_{\text{a}}$ values because the complex

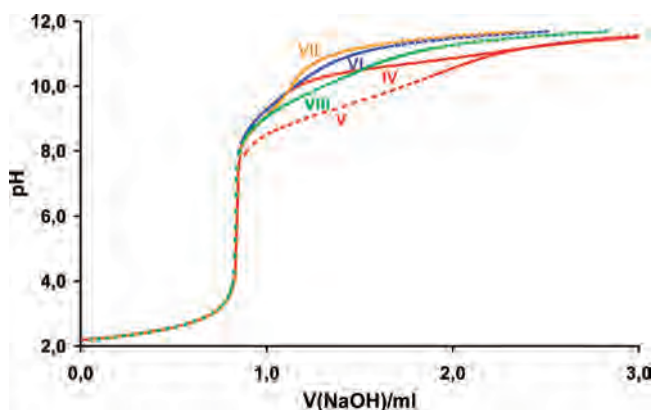


Figure 3. Experimental titration curve of the $\text{As}(\text{III})$ –dte system at 1:2 metal to ligand molar ratio (IV, red full line): $2 \times c_{\text{As}(\text{III})} = c_{\text{dte}} = 4.0 \cdot 10^{-3}$ M. The dashed lines show calculated titration curves based on the assumption of the formation of different condensation adducts below $\text{pH} \sim 8$: (V, red dashed line), no interaction between the components; (VI–VIII), assumption of reactions of Schemes 1, 3, and 4, respectively.

formation may affect them, resulting in an ambiguity of the simulations.

Because the assumption of the formation of $[\text{As}(\text{H}_1\text{L})]$ species even in the $\text{As}(\text{III})/\text{H}_2\text{L} = 1:2$ systems gave the best fit (curve VI) up to pH 10, we calculated the difference between this fit and the measured titration curve (curves IV and VI in Figure 3), and it corresponds exactly to the curve depicted in Figure 2. In fact this difference is the same for all initial metal to ligand ratios when the same reaction (Scheme 1.) is assumed. Thus experimental titration curves at any metal to ligand ratio can be explained satisfactorily including the formation of $[\text{As}(\text{H}_1\text{L})]$ species, the simple neutralization reactions of the remaining free donor groups of free ligand excess, and the destruction shown in Scheme 2.

The above results underline that the arsenous acid unlike boric acid is a simple Brønsted acid and is not prone to accept HO^- , resulting in the addition product $\text{As}(\text{OH})_4^-$. The two acids are thus totally different in their behavior contrary to earlier expressed views.³⁰ It appears that the total bonding to As(III) happens when ligands donate electronic charge to the three empty p-orbitals of As^{3+} . Therefore other ions with the electronic structure $nd^{10}(n+1)s^2(n+1)p^0$ are dominated by three-coordination, and they are seldom able to achieve a symmetric coordination number 4.^{30–32} The two s-electrons thus behave as one would expect from a closed shell and have little influence on bonding.

In conclusion, the above results suggest that in condensation reaction the $[\text{As}(\text{H}_1\text{L})]$ complex is formed. At high pH, the process is reversed, and decomposition of this thioester-type product occurs. However, because at this pH, both the ligand and the arsenous acid exist in their corresponding deprotonated forms, 3 equiv of hydroxide ions are needed for the equilibrium state. As also indicated in Scheme 2, the outcome is either the free, negatively charged ligand and the monoanionic arsenite or the coordination compound (diester) of the glycol part of the organic molecule. On the basis of the pH-metric results, we can not make decision between the latter processes. Although, the experimental titration curves obtained pH-metrically can be perfectly described by the above considerations, this method only provides indirect information on the systems.

When a titration is performed in a system with $c_{\text{As}(\text{III})} > 0.005$ M, a precipitate appears when the pH reaches ~ 6 . When the concentration is increased, the precipitation process occurs in a slightly acidic range. This supports the conclusion that the condensation products form below pH 8. These and the above observations show that the chosen system is rather complicated. For this reason, NMR and UV spectroscopy, as well as X-ray diffraction, have been undertaken to further substantiate the unusual reactions.

Crystal Structure of $[\text{As}(\text{H}_3\text{dte})]$. Dithioerythritol with arsenous acid crystallizes in the orthorhombic spacegroup

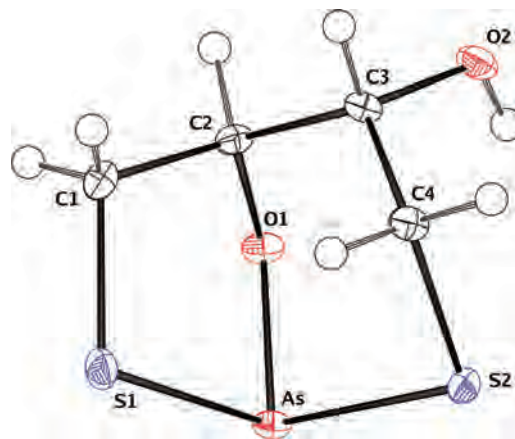


Figure 4. ORTEP drawing of $[\text{As}(\text{H}_3\text{dte})]$ with numbering corresponding to that of Table 2.

Fdd2 with 16 molecules in the unit cell. Infinite chains of $\text{O1}\cdots\text{H2}-\text{O2}$ hydrogen bonds (2.912 Å) are the only strong intermolecular bonds present. The arsenic atom in the $[\text{As}(\text{H}_3\text{dte})]$ structure (Figure 4) is bound covalently to the ligand atoms O1, S1, and S2, in a manner similar to that for the $[\text{As}(\text{H}_3\text{dtt})]$ structure.²⁹ In both structures, the S–As–O and S–As–S angles approach 90° (Table 2), suggesting that As(III) binds the ligand with σ -bonding through its three π -orbitals similar to what is expected to happen in aqueous solution.

Bond lengths and angles are in accordance with $[\text{As}(\text{H}_3\text{dtt})]$ and with the generally observed ones for similar molecules. The only major difference to the $[\text{As}(\text{H}_3\text{dtt})]$ structure is the axial hydroxyl group in the six-membered ring, a consequence of the stereochemically different C3 atoms. A discrepancy between the C2–C3–O2 and C4–C3–O2 angles found for $[\text{As}(\text{H}_3\text{dtt})]$ is not observed in the present structure of $[\text{As}(\text{H}_3\text{dte})]$. A short intermolecular contact of 2.93 Å between As(III) and O2 is not unusual according to a search in the CSD database.³³

The As–S1–C1 and As–S2–C4 angles are 94.54° and 99.27° , respectively, similar to those of the $[\text{As}(\text{H}_3\text{dtt})]$ structure. A search in the Mogul database³⁴ revealed that the As–S1–C1 angles in $[\text{As}(\text{H}_3\text{dtt})]$ and $[\text{As}(\text{H}_3\text{dte})]$ are small in comparison to the 22 C–C–S–As–S five-membered ring systems found in the CSD. The mean value for these systems is 100° with a standard deviation of 2° . However, $[\text{As}(\text{H}_3\text{dte})]$ and $[\text{As}(\text{H}_3\text{dtt})]$ are the only C–C–S–As–O five-membered ring systems in the CSD.

¹H NMR Spectra. ¹H NMR spectra of neutral dte solutions show a set of three distinct proton signals at 2.678, 2.871, and 3.700 ppm (Figure 5, spectrum II). This corresponds to half the number of protons bound to carbons, and it thus reflects the presence of mirror image symmetry of the ligand. The two CH_2 protons are magnetically inequivalent, thus the signals of the CH_2 protons appear as an AB quartet each signal being further split into doublets as a consequence of the coupling with the neighboring CH

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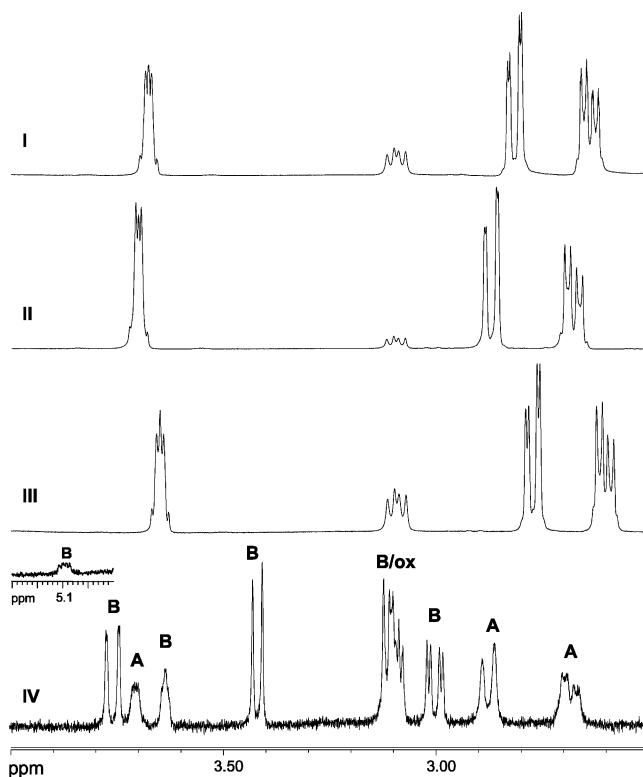
Table 2. Selected Bond Distances, d , Bond Angles, α , and Torsion Angles, t , for [As(H₃dte)] Where the Numbering Is That of Figure 4

	d (Å)
As–S1	2.2524(4)
As–S2	2.2579(4)
As–O1	1.8200(8)
S1–C1	1.8332(11)
S2–C4	1.8238(10)
O1–C2	1.4376(12)
O2–C3	1.4229(12)
C1–C2	1.5334(14)
C2–C3	1.5389(13)
C3–C4	1.5285(14)
	α (deg)
S1–As–S2	100.08(1)
S1–As–O1	90.12(2)
S2–As–O1	96.01(2)
As–S1–C1	94.54(3)
As–S2–C4	99.27(3)
As–O1–C2	113.74(5)
S1–C1–C2	111.06(6)
O1–C2–C1	108.76(8)
O1–C2–C3	111.84(7)
C1–C2–C3	115.26(8)
O2–C3–C2	109.68(8)
O2–C3–C4	111.42(8)
C2–C3–C4	115.82(8)
S2–C4–C3	113.79(7)
	t (deg)
S2–As–S1–C1	87.78(3)
O1–As–S1–C1	–8.34(4)
S1–As–S2–C4	–41.20(3)
O1–As–S2–C4	49.99(4)
S1–As–O1–C2	35.12(6)
S2–As–O1–C2	–65.03(6)
As–S1–C1–C2	–16.25(7)
As–S2–C4–C3	–53.97(7)
As–O1–C2–C1	–53.31(8)
As–O1–C2–C3	75.13(8)
S1–C1–C2–O1	42.69(9)
S1–C1–C2–C3	–83.80(9)
O1–C2–C3–O2	58.42(10)
O1–C2–C3–C4	–68.74(10)
C1–C2–C3–O2	–176.67(8)
C1–C2–C3–C4	56.17(11)
O2–C3–C4–S2	–63.18(9)
C2–C3–C4–S2	63.11(10)

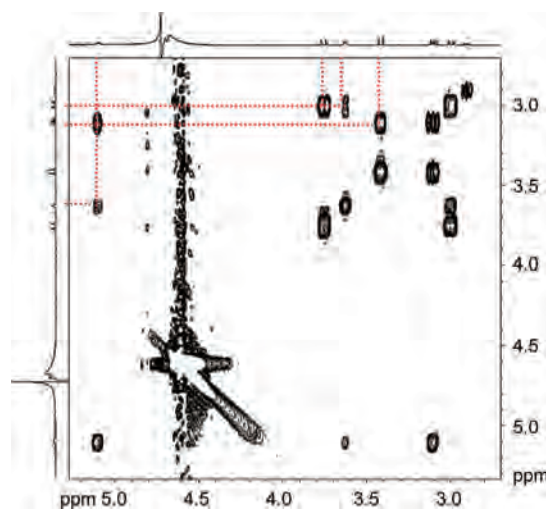
protons. The chemical shifts of the proton resonances and the coupling constants measured at pH 6.0 are reported in Table 3.

The ¹H NMR spectrum of the free dte molecule depends on pH. Between pH 3 and 6 a slight downfield shift of the signals could be observed in spite of the lack of deprotonation processes in this pH range. This might be the result of the slight changes in the intramolecular hydrogen bonding. The shift of the signals especially for those of CH₂ protons is more pronounced when going from pH 6.0 to 11.0. In this pH range, the proton resonances are shifted upfield because of the deprotonation of the thiol groups. It has to be noted that there is a fourth group of the signals (near 3.1 ppm) with small intensity that is not affected by pH change, and according to Krezel et al.,²⁸ it might be assigned to a specific oxidation product of the ligand.

Complex formation is well reflected by the ¹H NMR spectra. At 1:1 metal ion to ligand ratio the spectrum shows six independent signals. ¹H–¹H COSY experiments (Figure

**Figure 5.** ¹H NMR spectra of the dte solutions at pH values of (I) 3.0, (II) 6.0, and (III) 11.0. Part IV presents the ¹H NMR spectrum of the As(III)/dte 1:2 system at pH 6.0.**Table 3.** Characteristic ¹H NMR Parameters for Free and Complexed dte in Aqueous Solution at pH 6.0

sample	¹ H chemical shifts (ppm)			J_{HH} (Hz)		
	H (CH)	H _A (CH ₂)	H _B (CH ₂)	² J_{AB}	³ $J_{\text{H(CH),H}_A}$	³ $J_{\text{H(CH),H}_B}$
free dte	3.71	2.86	2.69	14.1	2.5	7.0
As/dte 1:1 complex	5.1/3.65	3.1/3.0	3.43/3.8	14.5/11.0	4.5/7.0	3

**Figure 6.** ¹H–¹H COSY experiment on the As(III)/dte 1:1 system at pH 6.0.

6) revealed that all six signals belong to the same molecule. On coordination to As(III), the ligand protons become strongly affected, and those having identical chemical shifts in the free ligand become very different. This means that upon reaction with As(III), the symmetry of the ligand is

broken up (all protons are in different magnetic environment) indicating an asymmetric coordination of dte to As(III), as shown in Figure 4, depicting one stereoisomer of $[\text{As}(\text{H}_3\text{dte})]$. The signal assignment, chemical shift values, and coupling constants for the 1:1 complex are given in Table 3. It can be seen that one of the CH signals has been significantly shifted as compared to that of the free ligand, as a consequence of the deprotonation and coordination of one of the alcoholate ions, while the second CH signal is only slightly affected by the formation of the $[\text{As}(\text{H}_3\text{dte})]$ species.

An interesting feature of the COSY spectrum is that the cross peak between the methine proton and one of the methylene protons (H_B) is missing for one of the CH–CH₂ pairs. This means that the vicinal coupling constant $^3J_{\text{H}(\text{CH}),\text{H}_\text{B}}$ is too small (usually less than 1 Hz) and could not be resolved in the 2D spectrum. On the basis of the semiempirical Karplus equation,³⁵ the very small value of the vicinal $^3J_{\text{HH}}$ coupling constant suggests a molecular geometry in which the dihedral angle between the hydrogen atoms are close to 90° (gauche position). Indeed, this angle determined in the crystal structure of $[\text{As}(\text{H}_3\text{dte})]$ is found to be 91° ($\pm 1^\circ$).

At pH 6.0 and with 1:2 metal to ligand ratio, two sets of signals were detected indicating slow ligand exchange processes (Figure 5, spectrum IV). Integration of the peak areas proved that each set of signals corresponds to one equivalent of ligand. The set denoted B is identical to the 1:1 complex, and it can be assigned to the coordinating, tridentate ligand. The pattern of the other set of signals denoted with A is similar to the free dte. These signals appear at the same chemical shift values as the free ligand at pH 6.0, but they are broader and do not vary with pH. If we assign them as free dte, they should be shifted upfield with decreasing pH (see Figure 5, spectra I and II). Instead, at pH 3.0, the position of both groups of signals A and B remain the same as at pH 6.0. This may be explained by the assumption that the signals denoted with A belong to a weakly bound dte (probably through the OH groups of the organic ligand). This weak binding maintains the symmetry of the free dte but fixes the ligand in the same conformation in the pH 3.0–6.0 range. On the basis of this, we suggest that at 1:2 metal to ligand ratio a 1:2 complex is formed with one strongly and one weakly bound dte molecule. This is in line with the solid state precipitate investigations (see below).

The ¹H NMR spectra of As(III)/dte systems recorded at pH 11.0 are completely different and less informative, than the previous ones. The number of signals decreases considerably. At a 1:1 ratio, only two very broad signals are detected in the spectrum. This might be consistent with the decomposition of $[\text{As}(\text{H}_1\text{L})]$ complex in alkaline solution, suggested by potentiometry. Nevertheless, the signals are unlike those for the free dte (Figure 5, spectrum III). Temperature-dependent measurements revealed that these peaks sharpen with increasing temperature, which may suggest the presence of fast ligand-exchange processes at this pH. However, the NMR measurements could not provide any detailed information about these exchange reactions. At 1:2 metal to ligand

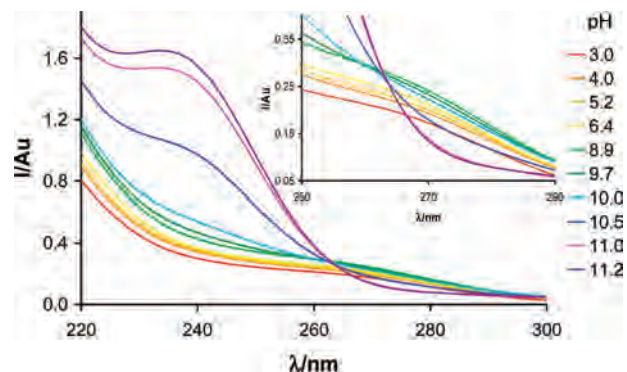


Figure 7. pH dependence of the UV absorption spectra the As(III)/dte 1:1.1 system ($c_{\text{As(III)}} = 5 \cdot 10^{-4}$ M) in a 0.5 cm quartz cuvette. The insert shows the region of the band system near 270 nm.

ratio the signals of the oxidation product of the ligand could only be detected. The signals of dte are probably so broad that they fall into the baseline. On the basis of these results, we suggest that second process depicted in Scheme 2 is favored against the complete decomposition of $[\text{As}(\text{H}_1\text{L})]$ complex at high pH.

UV Absorption Spectroscopy. The UV absorption spectroscopy measurements were based on the intense transition of the thiolate ion at 236 nm ($\epsilon_{\text{dte}} \approx 4480 \text{ M}^{-1} \text{ cm}^{-1}$) and the less intense sulfur \rightarrow As(III) charge transfer around 266 nm ($\epsilon_{\text{complex}} \approx 510 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁶ While arsenous acid and $\text{As}(\text{OH})_2\text{O}^-$ have low absorption at the latter wavelength, the thiolate band has a residual absorbance that interferes with the charge transfer band. Figure 7 shows the pH dependence of the UV spectra in As(III)/L 1:1.1 system. The intensity of the maximum at 266 nm first grows with increasing pH because of the more complete formation of the $[\text{As}(\text{H}_1\text{L})]$ complex. The spectra show that this process starts below pH 4.

Concerning the assignment¹⁶ of these absorption bands, we made DFT calculations on $[\text{As}(\text{H}_3\text{dte})]$ and $[\text{AsO}(\text{H}_5\text{dte})]^{3-}$ using the Gaussian program³⁶ installed on personal Linux and Windows computers. The geometry was optimized using the b3lyb functional and the 6–31 g basis set. For the resulting structures, time-dependent DFT was computed using the same functional and basis set. For $[\text{AsO}(\text{H}_5\text{dte})]^{3-}$, we calculated relatively intense (oscillator strength, $f > 0.01$) transitions at 276 nm ($f = 0.018$, origin oxygen to arsenous charge transfer) and at 232 nm ($f =$

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0.011, origin O,S \rightarrow As CT). For [As(H₃dte)], we saw relatively intense transitions at 245 nm ($f = 0.059$, origin S,O \rightarrow As CT) and at 223 nm ($f = 0.028$, origin S,O \rightarrow As CT). These findings confirm the earlier assignments¹⁶ of the absorption bands.

The variation of the As(III) to ligand total concentration ratio at a constant pH = 6.0 showed that upon increasing of the arsenic content, the [As(H₁L)] complex is gradually formed up to the ratio of 1:1, and there is no further change in the spectra on addition of arsenic excess to this solution.

Above pH \sim 7, the effect of the deprotonation of the slight excess of the ligand thiol groups can be observed. However, when the pH exceeds 9.0, the intensity of the band around 266 nm starts to decrease, and above pH \sim 11, it disappears, in parallel with the rising intensity of the maximum at 236 nm. This behavior refers to the decomposition of the complex species being held together by As–S bonds and the appearance of free thiolate groups. A similar pattern was observed in the spectra of As(III)–glutathione complex, where a partial rearrangement of the coordination sphere was suggested into a mixed hydroxo complex already around pH \sim 7, while the complete decomposition into free components was achieved around pH \approx 10.5.¹⁶ In the case of dtt and dte, these processes occur at higher pH indicating a stronger coordination because of chelation. On the basis of the above measurements, we can only state that the thiolate groups become uncoordinated in strongly alkaline solutions. Either a simple decomposition or the rearrangement of the coordination sphere involving glycolate-type binding occurs. The latter process is suggested by the fact that in alkaline medium we could not obtain the same ¹H NMR spectrum in the presence and absence of As(III). The spectrophotometric measurements also showed that, even under careful exclusion of elementary oxygen, the oxidation of the ligand takes place to a small extent in alkaline medium. This process dramatically influences the intensity of the band at 236 nm.

¹³C NMR Spectra of the Solid-State Complex. As we pointed out earlier, at concentrations above 5 mM precipitate was formed, and ¹³C NMR spectroscopy was not applicable for the solution measurements. However, the precipitate formed in 1:2 system was investigated by solid-state ¹³C NMR by CP-MAS method. In the resulting spectrum, in a manner similar to that of the ¹H NMR solution spectra, two groups of signals were observed. The chemical shifts of one of these correspond well to that of free dte, but the ¹³C NMR spectrum of the latter contains considerably narrower bands than in the presence of the As(III) with a quadrupole moment ($I = 3/2$). The ratio of the two different ligand signals is 1:1. It is not a usual observation that a free ligand is coprecipitated with a coordination compound in an equimolar ratio. Therefore we assume that a dte-molecule binds to the entity [As(H₃dte)] by weak coordinative interactions, probably through its OH groups. Since such interactions do not result in pH change, they can not be detected by pH-metry. The solid-state NMR lines are too broad to yield further informations.

ICP-AES Measurements. The As(III) contents of the precipitates from the solutions of the different As(III)/L ratios have been determined by the ICP-AES method. The compositions of precipitates obtained from 1:1 and 1:2 systems were in good correspondence with the solution composition As 28–37% (expected: 33.1%) and As 16–21% (expected: 19.7%), respectively, for 1:1 and 1:2 adducts. From solutions with higher ligand excess, only a precipitate with 1:2 composition could be obtained. All the precipitates yielded the same single crystal of the [As(H₃dte)] species after recrystallization from ethanol.

Conclusions

In the present work, we could prove that the dtt and dte molecules can bind As(III) with high affinity around pH 6–7 in aqueous solutions with their OH and SH functional groups. Although the indirect detection of the adduct formation prevented the determination of stability constants, the results showed quantitative binding already at 1:1 As(III)/L ratio, contrary to the As(III) cysteine or glutathione systems, where even in the presence of 3-fold ligand concentrations 50 and 35% of the As(III) remained free at pH 7, respectively.¹⁶ The structural investigations in solution demonstrated that the main species exhibits the same binding mode as it is determined by X-ray diffraction for the crystal obtained by recrystallization from ethanolic solution. The structure of the [As(H₃dte)] single crystal shows that the ligand donor groups appear to donate electronic charge to the three empty p orbitals of As³⁺. Thus the difference between the dominant behavior of boric and arsenous acids in their reactions with vicinal diols can be explained based on simple acid–base considerations: while boric acid is a relatively strong antibase or Lewis acid, the arsenous acid behaves like a weak Brønsted acid, and arsenic(III) seldom achieves coordination numbers larger than three. However, in aqueous solution, the weak binding of a second ligand is also suggested in the presence of an excess of the ligands. To discover the binding mode in this complex further crystallization experiments are going to be undertaken.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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