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Adsorption of Inorganic and Organic Arsenic Compounds by Aluminium-loaded Coral Limestone

Akira Ohki,* Kaori Nakayachigo, Kensuke Naka, and Shigeru Maeda
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1–21–40 Korimoto, Kagoshima 890, Japan

Coral limestones were treated with an aqueous solution of aluminium sulfate and thereby aluminium-loaded coral limestones (Al-CL) were prepared. By use of Al-CL as an adsorbent, the adsorption of inorganic arsenic compounds (arsenate [As(V)] and arsenite [As(III)] and of organic arsenic compounds (methylarsonic acid, dimethylarsinic acid, and arsenobetaine) was examined. The adsorption ability of Al-CL is superior to that of iron(III)-loaded coral limestone (Fe-CL) for As(V), As(III), methylarsonic acid and dimethylarsinic acid. The adsorption of As(V) and As(III) is almost independent of the initial pH over a wide range (2 or 3 to 11). The addition of other anions, such as chloride, nitrate, sulfate and acetate, in the solution does not affect the adsorption of As(V) and As(III), whereas the addition of phosphate greatly interferes with the adsorption. Arsenic adsorption is effectively applied to a column-type operation and the adsorption capability for As(V) is 150 μg/g coral limestone.

Keywords: adsorption; aluminium-loaded coral limestone; arsenate; arsenite; methylarsonic acid; dimethylarsinic acid; arsenobetaine

INTRODUCTION

In Japan, the environmental standard for the level of arsenic in drinking water changed from 0.05 mg l^{-1} to 0.01 mg l^{-1} in 1993. Thus development of stricter water-treatment processes to remove arsenic from industrial water and natural water is urgently required.

The most common arsenic removal method is precipitation with lime and iron(III) salts followed by adsorption onto the resulting iron(III) hydroxide flocs.[1] However, the flocs produced in the co-precipitation process are usually fine and in colloidal form. Thus it is difficult to dewater the flocs by settling and filtration processes, which result in the production of a large volume of sludge.

Other arsenic removal methods include adsorption by activated alumina,[2,3] activated carbon,[4,5] metal-loaded activated carbon,[6,7] hematite,[8] manganese(IV) dioxide[9] and iron(III)-loaded chelating resin.[10] However, those methods have difficulties in respect of cost and/or adsorption ability.

We have developed a new arsenic adsorbent, iron(III) hydroxide-loaded coral limestone (Fe-CL),[11,12] which has a great advantage over the conventional methods in terms of solid–liquid separation and cost. However, the adsorption ability for arsenic is two orders of magnitude less than that of activated carbons.[4,5]

In the present work, we prepared an aluminium-loaded coral limestone (Al-CL) by treating a coral limestone with aluminium sulfate. By using this adsorbent, we examined the adsorption of inorganic arsenic compounds, namely arsenate [As(V)] and arsenite [As(III)]. Some organic arsenic compounds, such as methylarsonic acid and dimethylarsinic acid, are utilized as herbicides. We also investigated the adsorption of these two organic arsenic compounds and arsenobetaine by use of Al-CL.

EXPERIMENTAL

Materials

Sodium arsenate ($Na_2HAsO_4.7H_2O$), sodium arsenite ($NaAsO_2$), dimethylarsinic acids and

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* Author to whom correspondence should be addressed.

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aluminium sulfate [$Al_2(SO_4)_3$] were purchased from Wako Pure Chemical Industries (Osaka, Japan). Methylarsonic acid and arsenobetaine were obtained from Tri Chemical Laboratories Inc. (Kanagawa, Japan). The coral limestone used was of the 'Porelime' variety (Tokunoshima Coral Reef Co. Ltd, Tokyo, Japan).

Preparation of Al-CL

The particle size of the coral limestone was adjusted to a diameter of 1.0–2.5 nm by sieving. The coral limestone particles were rinsed with water several times and dried in an electric oven (105 °C). The resulting coral limestone particles (50 g) were soaked in an aqueous solution (200 ml) of aluminium sulfate (2 wt%) for 1 day. Then the aluminium-loaded coral limestone particles were separated, rinsed with water, dried (105 °C) and sieved on a 120-mesh screen to remove free hydroxide particles which had been generated as a by-product. The aluminium-loading treatment was repeated several times and thereby Al-CL was prepared.

To determine the amount of aluminium loaded on the coral limestone, Al-CL (1.0 g) as prepared was completely dissolved in a 3 M hydrochloric acid solution (40 ml). A portion of the hydrochloric acid solution (30 ml) was taken and 3.0 ml of an aqueous solution containing 1.0 wt% 8-quinolinol and 2.7 wt% acetic acid was added. After adding a 2 M ammonium acetate solution to make the pH 5.0, the total volume of the solution was adjusted to 50 ml. Chloroform (10 ml) was added to the solution, which was then shaken vigorously for 1 min. After phase separation, the chloroform solution was analyzed using a Hitachi Model U-2000 spectrophotometer (390 nm).

Adsorption of arsenic compounds

An aqueous solution (20 ml) of the arsenic compound was shaken with Al-CL (1.0 g) at 24–25 °C for a definite period. After removal of the Al-CL, the concentration of arsenic remaining in the aqueous solution was determined by atomic absorption spectrophotometry using a Nippon Jarrel Ash AA-890 with an FLA-1000 flameless atomizer unit. Detailed conditions are given in the Figure captions.

Column operation

A glass tube (15 mm i.d.) was packed with Al-CL (50 g) to give a column 180 mm high. An aqueous solution of 5.0 mg l^{-1} As(V) was passed through the column at room temperature (22–25 °C) at a flow velocity of 120 ml l^{-1}. The effluent was collected in 7 ml fractions, and each was analyzed for arsenic.

RESULTS AND DISCUSSION

Adsorption of inorganic arsenic compounds [As(V) and As(III)] by Al-CL

An aqueous solution of As(V) or As(III) was shaken with Al-CL as prepared, and the concentration of arsenic in the aqueous solution was determined periodically by atomic absorption spectrophotometry. Figure 1 shows the plots of arsenic concentration in the aqueous solution against shaking time. The absorption reaches equilibrium after 8 h of shaking for As(V) and 17 h of shaking for As(III).

Coral limestone particles, for which the aluminium-loading treatment was carried out several times, were prepared. The amounts of aluminium loaded on the Al-CLs treated once, twice, three and four times were 2.1, 2.9, 3.3 and 3.7 mg l^{-1} coral limestone, respectively.

By use of the Al-CLs, adsorption isotherms for As(V) were examined (Fig. 2). These adsorption isotherms are almost linear. It appears that the adsorption mode is of a typical Freundlich isothermal nature. In Table 1 are recorded the Freundlich constants (log K and $1/n$) for the

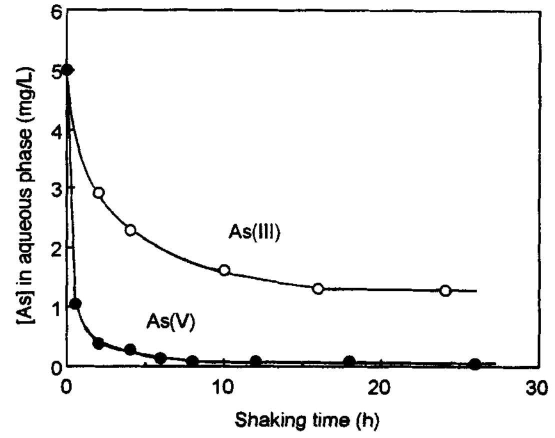

Figure 1 Adsorption of As(V) and As(III) by Al-CL. An aqueous solution (20 ml) of 5.0 mg As(V) or As(III) per liter was shaken with Al-CL (1.0 g).

adsorption of As(V) by the Al-CLs. These Al-CLs show about the same values of l/n (i.e. 0.32–0.34). The value of log K increases by 0.08–0.10 unit when the number of aluminium-loading treatments is raised. For Al-CLs which had been treated more than four times, the adsorption abilities for As(V) were similar to that of Al-CL treated four times. It is evident that treatment four times is the optimum for the preparation of an efficient arsenic adsorbent. Thus, Al-CL that had been treated four times was used in later experiments.

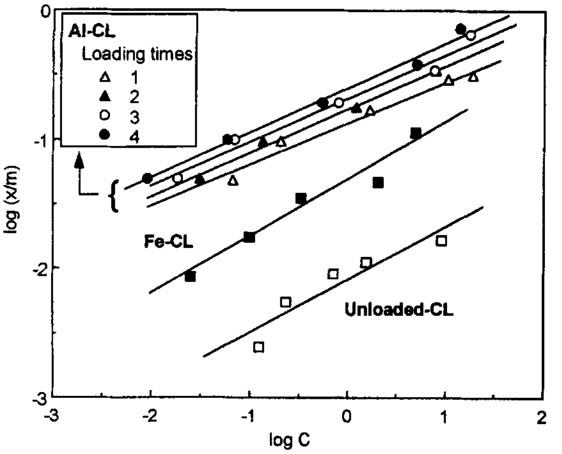

Figure 2 Adsorption isotherms for As(V) by use of Al-CLs treated by aluminium-loading several times. Aqueous solutions (20 ml) of 2.5–50 mg As(V) l^{-1} were shaken with Al-CL (1.0 g) for 10 h. Symbols C and x/m denote the equilibrium concentration of arsenic in the aqueous solution (mg l^{-1}) and the amount of arsenic adsorbed on the adsorbent (mg per g coral limestone), respectively. Data for Fe-CL (four times loaded) and unloaded-CL are from Ref. 11.

Evidently, as the number of the aluminium-loading treatments is raised, the amount of aluminium loaded on the coral limestone particle becomes larger and thus the adsorption of As(V) increases. This result suggests that the As(V) adsorption mostly occurs at active sites on aluminium species deposited on the coral limestone surface.

When the coral limestone particles are soaked in an aqueous solution of aluminium sulfate, the reaction represented by Eqn [1] is proposed to take place on the coral limestone surface.

$$2Al^{3+}+3CaCO_3 \text{ (coral limestone)} \\ +3H_2O \rightarrow 2Al(OH)_3 \\ +3Ca^{2+}+3CO_2p+3CO_2 \qquad [1]$$

Acidic aquo–aluminium complexes may react with the calcium carbonate of the coral limestone, resulting in the formation of colloidal aluminium hydroxide with evolution of carbon dioxide gas. The colloid produced is tightly

Table 1. Freundlich constants log K and l/n

Adsorbent	Loading times (No.)	Arsenic species	log K	l/n
Al-CL	1	As(V)	−0.87	0.32
Al-CL	2	As(V)	−0.77	0.34
Al-CL	3	As(V)	−0.67	0.34
Al-CL	4	As(V)	−0.59	0.34
Fe-CL	4	As(V)	−1.32[a]	0.44[a]
Unloaded-CL	—	As(V)	−2.08[a]	0.41[a]
Al-CL	4	As(III)	−1.09	0.32
Fe-CL	4	As(III)	−1.56[b]	0.59[b]
Unloaded-CL	—	As(III)	−2.33[b]	0.38[b]
Al-CL	4	Methylarsonic acid	−1.28	0.64
Fe-CL	4	Methylarsonic acid	−1.74	1.2
Unloaded-CL	—	Methylarsonic acid	−2.00	1.6
Al-CL	4	Dimethylarsinic acid	−1.34	0.75
Fe-CL	4	Dimethylarsinic acid	−1.72	0.92
Unloaded-CL	—	Dimethylarsinic acid	−2.30	0.97
Al-CL	4	Arsenobetaine	−0.92	1.4
Fe-CL	4	Arsenobetaine	−0.97	1.4
Unloaded-CL	—	Arsenobetaine	−1.10	1.5

[a] Data from Ref. 11

[b] Data from Ref. 12.

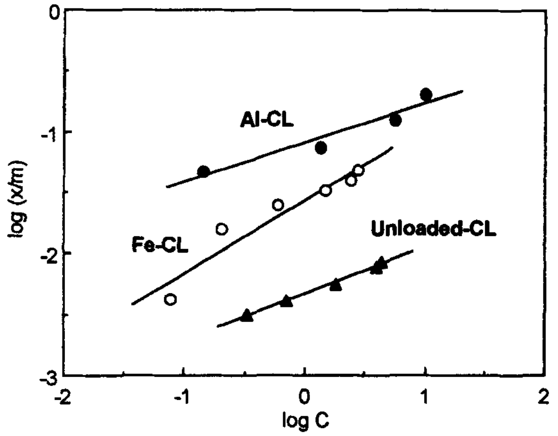

Figure 3 Adsorption isotherms for As(III) by use of Al-CL. Aqueous solutions (20 ml) of 2.5–50 mg As(III) l^{-1} were shaken with Al-CL (1.0 g) for 20 h. The meanings of C and x/m are the same as those in Fig. 2. Data for Fe-CL and unloaded-CL are from Ref. 12.

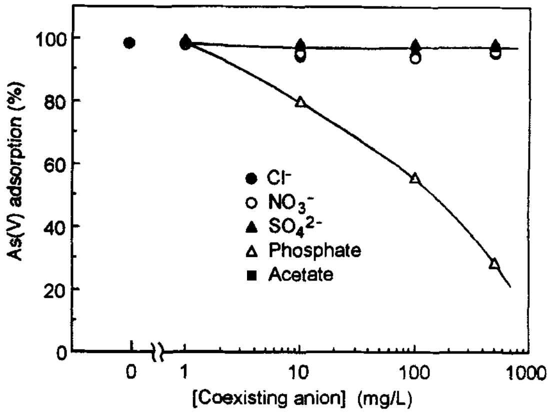

Figure 5 Influence of adding coexisting anions upon the adsorption efficiency of As(V). Aqueous solutions (20 ml) of 5.0 mg As(V) l^{-1} and sodium salts of the anions were shaken with Al-CL (1.0 g) for 10 h.

deposited on the porous coral limestone surface, which leads to the preparation of aluminium hydroxide-loaded coral limestone (Al-CL).

In the As(V) adsorption by Fe-CL, we have proposed that hexacoordinate iron(III) ions on the Fe-CL surface undergo a ligand-exchange reaction between H_2O or OH and arsenate ligands.[11] It is anticipated that the present As(V) adsorption by Al-CL occurs via a similar mechanism.

Compared with Fe-CL,[11] the log K value for Al-CL is more positive by 0.73 unit, while the l/*n* value for Al-CL is smaller by 0.10 (see Table 1). This result suggests that Al-CL has a higher adsorption ability than does Fe-CL, especially when aqueous As(V) solutions of low concentrations are concerned.

Figure 3 indicates the adsorption isotherms for As(III) by use of Al-CL, Fe-CL and unloaded coral limestone (unloaded-CL); while the Freundlich constants (log *K* and l/*n*) are also recorded in Table 1. When Al-CL is used, the log *K* value for As(III) is more negative by 0.50 unit than that for As(V). The fact that the adsorption efficiency of As(V) is better than that of As(III) is general for other arsenic adsorbents.[1] Also, for the

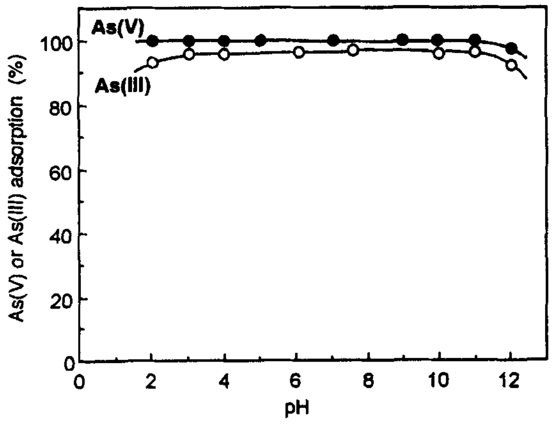

Figure 4 Dependence of adsorption efficiencies for As(V) and As(III) upon pH in aqueous solution. Aqueous solutions (20 ml) of 5.0 mg As(V) l^{-1} or 1.0 mg As(III) l^{-1}, in which pH was initially adjusted by use of 0.10 M hydrochloric acid and 0.10 M aqueous sodium hydroxide, were shaken with Al-CL (1.0 g) for 10 h [As(V)] or 20 h [As(III)].

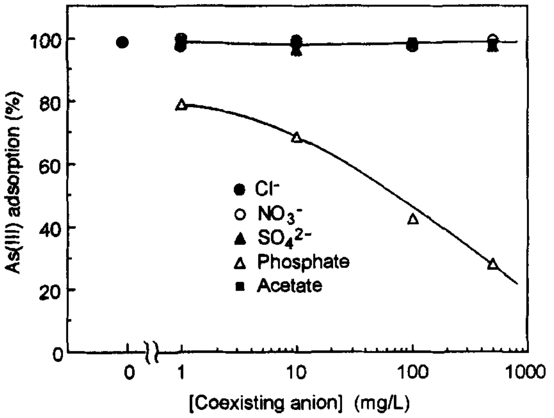

Figure 6 Influence of adding coexisting anions upon the adsorption efficiency of As(III). Aqueous solutions (20 ml) of 1.0 mg As(III) l^{-1} and sodium salts of the anions were shaken with Al-CL (1.0 g) for 20 h.

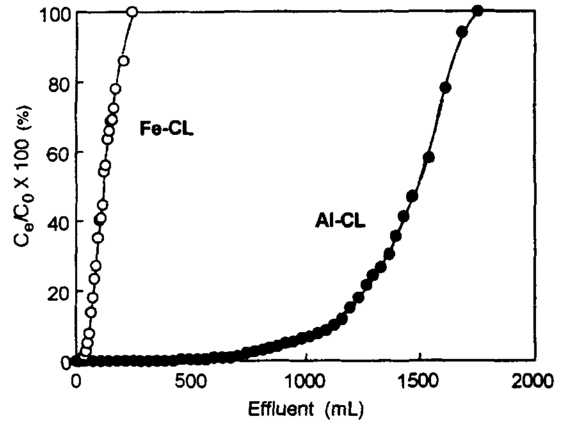

Figure 7 Breakthrough curve of As(V) on column operations by use of Al-CL and Fe-CL. Symbols C_0 and C_3 denote the intiial concentration of As(V) and the concentration in each effluent fraction, respectively. Conditions are described in the text.

adsorption of As(III), Al-CL is superior to Fe-CL.

Effects of pH and adding other anions

The adsorption of As(V) and As(III) by Al-CL was carried out when the initial pH of the aqueous solutions was adjusted by use of 0.10 M hydrochloric acid and 0.10 M sodium hydroxide (Fig. 4). The adsorption by Al-CL is almost independent of the initial pH in the range 2–11 for As(V) and the range 3–11 for As(III). For arsenic adsorption methods so far reported, in which activated carbon[4,6] and activated alumina[2] are used, the pH of the sample solution greatly affects the efficiency of the adsorption.

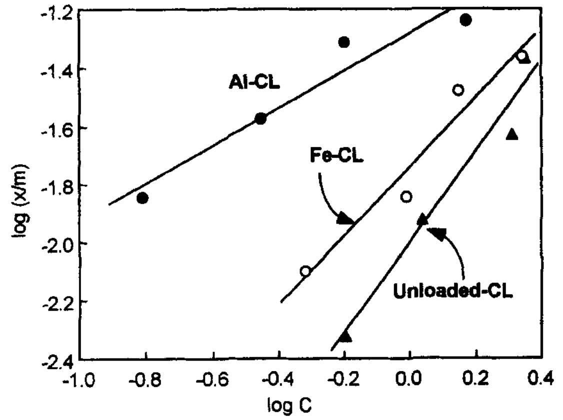

Figure 8 Adsorption isotherms for methylarsonic acid. Aqueous solutions (20 ml) of methylarsonic acid (0.50–5.0 mg l^{-1} as arsenic) were shaken with Al-CL (1.0 g), Fe-CL (1.0 g) or unloaded-CL (1.0 g) for 20 h. The meanings of *C* and *x/m* are the same as those in Fig. 2.

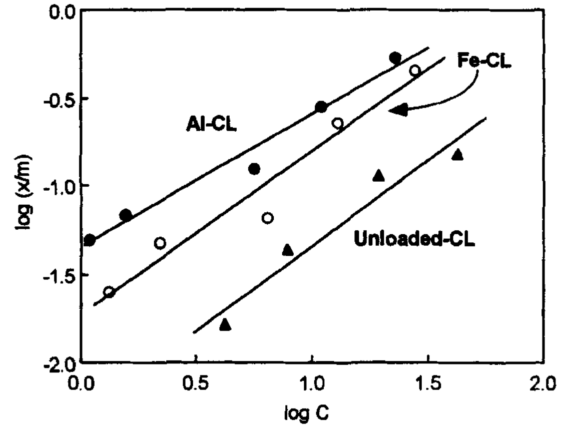

Figure 9 Adsorption isotherms for dimethylarsinic acid. Aqueous solutions (20 ml) of dimethylarsinic acid (2.5–50 mg l^{-1} as arsenic) were shaken with Al-CL (1.0 g), Fe-CL (1.0 g) or unloaded-CL (1.0 g) for 20 h. The meanings of *C* and *x/m* are the same as those in Fig. 2.

In all runs in Fig. 4 except those for pH > 10, the pH of the aqueous solutions after equilibrium became 8.0–8.5. As previously mentioned,[11] the calcium carbonate of the coral limestone, which dissolves slightly into aqueous solution, works as a buffer to keep the pH of the solution constant (8.0–8.5). Consequently the pH independence of the efficiency of arsenic adsorption by Al-CL should be of great advantage compared with

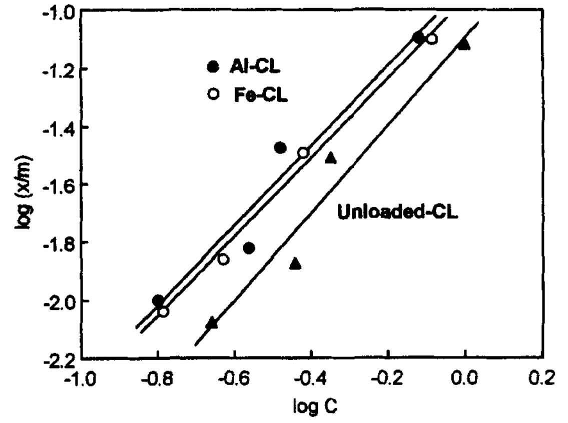

Figure 10 Adsorption isotherms for arsenobetaine. Aqueous solutions (20 ml) of arsenobetaine (0.50–5.0 mg l^{-1} as arsenic) were shaken with Al-CL (1.0 g), Fe-CL (1.0 g) or unloaded-CL (1.0 g) for 20 h. The meanings of *C* and *x/m* are the same as those in Fig. 2.

other adsorption methods.[2,4,6]

Adsorption of As(V) and As(III) was performed when other anions were added in the aqueous solutions. Figures 5 and 6 show the results for As(V) and As(III), respectively. For both of these species, the addition of chloride, nitrate, sulfate and acetate hardly affects the adsorption, whereas the adsorption of arsenic species is greatly influenced by the addition of phosphate.

Column operation

Columns packed with Al-CL and Fe-CL in glass tubes were prepared. When an aqueous solution of As(V) was passed through the columns, the arsenic concentration in the effluent was measured. Figure 7 shows breakthrough curves for As(V) by use of those columns. The absorption capacities (μg of adsorbed arsenic per g of dry coral limestone) for the Al-CL and Fe-CL columns were calculated from the breakthrough curves to be 150 $\mu g\ g^{-1}$ and 15 $\mu g\ g^{-1}$, respectively.

Adsorption of organic arsenic compounds

The adsorption of organic arsenic compounds such as methylarsonic acid, dimethylarsinic acid and arsenobetaine, was carried out. When Al-CL, Fe-CL and unloaded-CL were used, adsorption equilibrium was reached within 20 h. Adsorption isotherms for methylarsonic acid, dimethylarsinic acid and arsenobetaine are indicated in Figs 8–10, respectively; while the Freundlich constants (log K and $1/n$) are also recorded in Table 1. For acidic arsenic compounds, such as methylarsonic acid and dimethylarsinic acid, adsorption ability decreases in the order Al-CL>Fe-CL>unloaded-CL, which parallels the order for the adsorption of inorganic arsenic compounds.

However, for neutral arsenobetaine, the adsorption abilities of Al-CL, Fe-CL and unloaded-CL are quite similar to each other. It is believed that metal hydroxides on the coral limestone surface do not work favorably as adsorption sites for arsenobetaine. These results support the mechanism mentioned above, that the adsorption of anionic arsenic species on Al-CL and Fe-CL occurs via a ligand-exchange reaction between the H_2O or OH ligand of the aquo-complexes and the anionic arsenic ligands.

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