126 *Inorg. Chem.* **1997,** *36,* 126−128

^1H NMR Study of Aqueous Molybdomethylarsonates

A. Kobayashi and A. Yagasaki*

Department of Chemistry, Kwansei Gakuin University,
Uegahara, Nishinomiya 662, Japan

Received July 18, 1996

Introduction

In our previous potentiometric investigation of the aqueous molybdoarsonate system, we established that the $[(RAs)_2Mo_6O_{24}(OH_2)]^{6-}$ ($R = CH_3, C_6H_5$) anion is the predominant species in a wide range of *p*H and Mo/As ratio.[1] The data also showed that this well-known molybdoarsonate anion is not the only species that exists in solution. Our initial guess was that all these species had Mo/As ratios higher than 3. However, during the attempt to fully characterize the system by the combined emf−NMR method,[2] we found that one of these additional species formed in solutions of low (<3) Mo/As ratios. In addition, we discovered that the $[(CH_3As)_2Mo_6O_{24}(OH_2)]^{6-}$ species undergoes an exchange reaction with the free arsonate anion in these low Mo/As ratio solutions on the ^1H NMR time scale. Here we report the characterization of this new low ratio species together with the result of the kinetic study on the $[(CH_3As)_2Mo_6O_{24}(OH_2)]^{6-}$ anion.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: D_2O (Isotech), DCl (Aldrich), TSP-d_4 (Aldrich), $Na_2MoO_4{\cdot}2H_2O$ (Kishida). NaCl (Manack, JIS primary standard) was dried at 300 °C for 30 min before use. $CH_3AsO_3Na_2{\cdot}nH_2O$ was prepared according to the literature[3] and characterized by IR, NMR, and elemental analysis. The concentration of the aqueous $CH_3AsO_3Na_2$ stock solution was determined potentiometrically by using the formation constants reported earlier.[1] The Na^+ ion concentrations of all sample solutions were kept constant at 1.00 M by adding appropriate amounts of NaCl. The least-squares calculations were performed by using the program LAKE[4] on the data in the ranges $3.8 \leq pH \leq 10.3$, $19 < [As]_T/mM < 39$, and $1.3 \leq [Mo]_T/[As]_T \leq 2.6$, where $[Mo]_T$ and $[As]_T$ stand for total concentrations of Mo and As, respectively.

NMR Measurements. ^1H NMR spectra were recorded on a JEOL JNM-A400 (400 MHz) spectrometer and referenced externally to TSP-d_4 by the sample replacement method. Unless otherwise stated, all measurements were performed at 295 ± 1 K. The spin−lattice relaxation times (T_1) were evaluated by the inversion-recovery method. In order to obtain reliable quantitative data, 90° pulses and pulse repetition times larger than 5 times the longest T_1 were used. Kinetic measurements were performed using the polarization transfer method.[5]

Results and Discussion

Figure 1 shows the relative intensities of the peaks observed in the ^1H NMR spectra as a function of *p*H. In addition to the peak of free arsonate (peak A), two other peaks of significant intensities (peaks B and D) were observed.[6] This result clearly tells us that there exist two different molybdoarsonates in solution as major species even at a Mo/As ratio as low as 1.86. The intensity of peak B was always higher than that of peak D. While peak B accounted for as much as 80% of the total arsonate in some solutions, the intensity of peak D never exceeded 30% of the total arsonate. Since there is accumulating evidence that $[(RAs)_2Mo_6O_{24}(OH_2)]^{4-}$ [$R = CH_3, C_6H_5, OH$; (12, 6, 2) in *(p, q, r)* notation[1,7]] is the predominant species in acidic aqueous solution,[1,7−9] we assigned peak B to (12, 6, 2). The result of a “vertical titration”,[2a,b] where the Mo/As ratio was varied and *p*H was kept constant around 4.5, gave further support to this assignment (Figure 2). The relative intensity of peak B reached a maximum at Mo/As = 3.

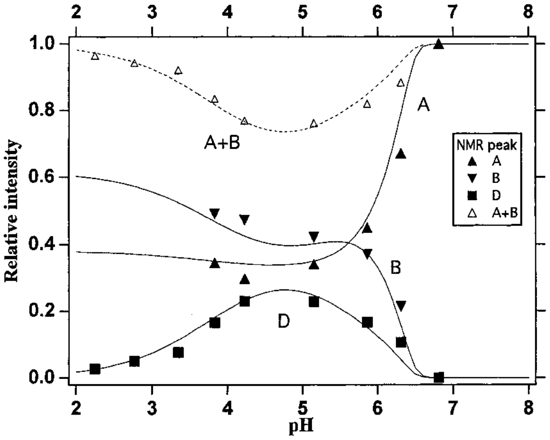


Figure 1. Relative intensities of different peaks as a function of *p*H. Total concentrations of molybdate and arsonate are 49.9 and 26.9 mM, respectively. Peak C, whose intensity never exceeded 3% of the total under these conditions, has been omitted for clarity. Solid lines show the distribution of free arsonate (peak A), Mo_6As_2 species (peak B), and Mo_5As_2 species (peak D) calculated by using the formation constants listed in Table 1. Although peaks A and B overlap at low *p*H and are observed as a single peak when $pH < 3.5$, the calculated sum of free arsonate and Mo_6As_2 species (dashed line) fits the observed data well.

The chemical shift of peak B exhibited two kinds of variation. One was observed between *p*H 6 and 5, and the variation of the shift was dependent only on *p*H. This indicates that (11, 6, 2), the deprotonated species of (12, 6, 2), coexists in solution. The other type of variation was observed in the range $pH < 4$ and dependent both on *p*H and the Mo/As ratio. This indicates that (12, 6, 2) is involved in some chemical exchange, which will be discussed later.

Figure 2 also tells us that the species that gives rise to peak D has a *q/r* ratio around 2. In order to determine the composition of this species, we performed a *pqr* search on the NMR intensity data using the general equilibrium analysis

---

[1] Yagasaki, A.; Takahama, H.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3925−3929.

[2] (a) Pettersson, L.; Andersson, I.; Öhman, L.-O. *Inorg. Chem.* **1986**, *25*, 4726−4733. (b) Yagasaki, A.; Andersson, I.; Pettersson, L. *Inorg. Chem.* **1987**, *26*, 3926−3933. (c) Ozeki, T.; Yagasaki, A.; Ichida, H.; Sasaki, Y. *Polyhedron* **1988**, *7*, 1131−1134.

[3] Quick, A. J.; Adams, R. *J. Am. Chem. Soc.* **1922**, *44*, 805−816.

[4] Ingri, N.; Andersson, I.; Pettersson, L.; Yagasaki, A.; Andersson, L.; Holmström, K. *Acta Chem. Scand.* **1996**, *50*, 717−734.

[5] Freeman, R. *A Handbook of Nuclear Magnetic Resonance*; Longman Scientific & Technical: Essen, England 1988; pp 98−202.

[6] Although one more peak (peak C) was observed in the spectra, it never accounted for more than 10% of the total arsonate when Mo/As < 3.4.

[7] (a) Pettersson, L. *Acta Chem. Scand.* **1975**, *A29*, 677−689. (b) Pettersson, L. *Acta Chem. Scand.* **1978**, *A29*, 681−688. (c) In a previous study[1] $CH_3AsO_3H^-$ was chosen as component. In this work $CH_3AsO_3^{2-}$ is used instead. The generalized equation we use in this work is $pH^+ + qMoO_4^{2-} + r\ CH_3AsO_3^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(CH_3AsO_3^{2-})_r$.

[8] Kwak, W.; Rajkovic, L. M.; Stalick, J. K.; Pope, M. T.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 2778−2783.

[9] (a) Kwak, W.; Rajkovic, L. M.; Pope, M. T.; Quicksall, C. O.; Matsumoto, K. Y.; Sasaki, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6463−6464. (b) Matsumoto, K. Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 492−498.

S0020-1669(96)00852-X CCC: $14.00

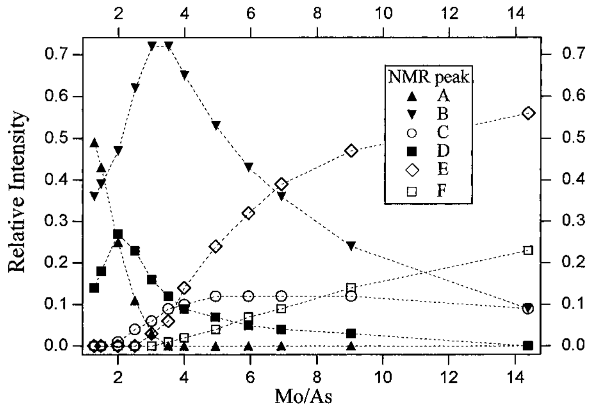


Figure 2. Relative intensities of different peaks as a function of the Mo/As ratio at pH = 4.5. Total molybdate concentration was kept constant at 50 mM. The dashed curves that connect experimental points are drawn in order to make it easier to follow the change of each peak.

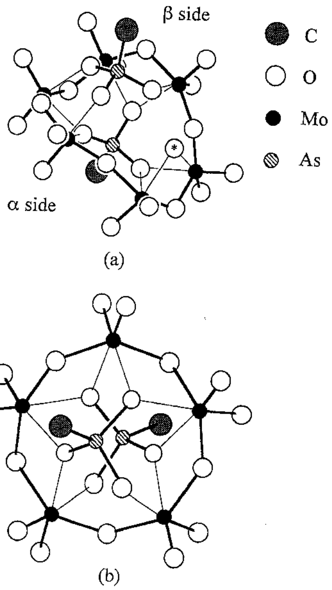
Table 1. Results of the Final Least-Squares Calculation

(p, q, r)	proposed formula	log $\beta_{p,q,r}$[a]	chemical shift/ppm[a]
(11, 6, 2)	$[(CH_3As)_2Mo_6O_{24}(OH)]^{5-}$	83.4(4)	2.26(1)
(12, 6, 2)	$[(CH_3As)_2Mo_6O_{24}(OH_2)]^{4-}$	88.3(5)	2.32(1)
(10, 5, 2)	$[(CH_3As)_2Mo_5O_{21}]^{4-}$	75.2(4)	2.40(1)
(0, 0, 1)	$CH_3AsO_3^{2-}$		1.56(1)
(1, 0, 1)	$CH_3AsO_3H^-$	8.57(4)	1.90(1)
(2, 0, 1)	$CH_3AsO_3H_2$	12.46(5)	2.29(1)

[a] The figures in parentheses are the estimated standard deviations for the least significant digits.

program LAKE[4] (Figure 3).[10] The result established that the species responsible for peak D is (10, 5, 2). All the other species tested gave unacceptably high residuals in the least-squares calculations. The result of the final least-squares calculation is summarized in Table 1. The proton consumption factor, $p/(q + r)$, of (10, 5, 2) is 1.43. This is consistent with the result of the previous potentiometric study,[1] where it was clearly shown that the proton consumption factors of the species formed in low (< 3) Mo/As ratio solutions should be between 1.37 and 1.50.

As mentioned earlier, behavior of peak B suggested the existence of a chemical exchange involving (p, 6, 2), the Mo_6-As_2 species. This was confirmed by variable-temperature NMR measurements. Both peaks A and B became broader as the pH of the solution was lowered, and they were observed as a single broad peak around 2.3 ppm at pH = 3.8. When the temperature was lowered, however, this broad peak split to give two distinct peaks. The result clearly showed that there is an intermolecular exchange between (p, 6, 2) and the free arsonate in solution. Spin saturation transfer (SST) experiments revealed that (p, 6, 2) exchanged with free arsonate anion even at pH 5.2, where both peaks A and B were relatively narrow (half-height widths 2.6 and 3.7 Hz, respectively) and the chemical shift of peak B was independent of the Mo/As ratio (Figure 4).[10] An interesting thing to note here is that, unlike (p, 6, 2), (10, 5, 2) (peak D) showed no sign of exchange in both variable temperature and SST experiments. The width of peak D was virtually invariant with the temperature. Saturation of peak A or B did not affect the intensity of peak D, and saturating peak D had no effects on peaks A and B, either. The result of a series of quantitative polarization transfer experiments at pH 5.2 gave activation parameters $\Delta H^‡ = 63 \pm 4$ kJ mol^{-1} and $\Delta S^‡ = -19 \pm 14$ JK^{-1} mol^{-1} for this process.[11]



(a)

(b)

Figure 5. Probable structures for (12, 6, 2) (a) and (10, 5, 2) (b). The oxygen atom of the water molecule is marked with an asterisk.

The probable structures for (12, 6, 2) and (10, 5, 2) are presented in Figure 5. Although an X-ray crystallographic study confirmed that the hexamolybdobis(methylarsonate) ion conformed to a more symmetrical structure in sodium–tetramethylammonium double salt crystals,[8] it has been later revealed that hexamolybdobis(arsonates) take up a water molecule into its framework in aqueous solution and assume the bent Matsumoto-type structure depicted in Figure 5a.[9] Dissociation of a proton from this water molecule gives a structure for (11, 6, 2). The composition and hence the charge of (10, 5, 2) are consistent with the Strandberg-type structure[12] shown in Figure 5b. Strandberg-type molybdopropyl- and molybdoallylarsonates have been structurally characterized recently,[13] although a molybdomethylarsonate of this structure has not been isolated so far.

The Matsumoto- and Strandberg-type anions shown in Figure 5 have a common structural feature. Both consist of a $(MoO_3)_x$ ring and two arsonate groups, which are bound to the ring by relatively weak Mo–O bonds.[14] As can be seen from the figure, each arsonate unit in (10, 5, 2) is bound to the ring by five weak Mo–O bonds. The arsonate unit on one side of (12, 6, 2), labeled α in Figure 5a, is bound to the ring by six weak Mo–O bonds, but that on the other side, labeled β, is bound by only four Mo–O bonds. This indicates that the latter arsonate unit is anchored to the ring less strongly than the other one and those in (10, 5, 2).

Bond order calculations give further support to this argument. Bond orders of those weak Mo–O bonds that hold the arsonate units on the ring can be calculated from the length of these bonds following Brown's method.[15] Two molybdoarsonates of Strandberg-type structure, $[(C_3H_7As)_2Mo_5O_{21}]^{4-}$ and [(CH$_2$CH-

---

(10) See paragraph at end of paper regarding Supporting Information.

(11) Small entropic term ($T\Delta S^‡ \approx -6$ kJ mol^{-1} at 295 K) tells us that the exchange process is enthalpy-controlled. This is not inconsistent with the discussion given later in the current note. Large experimental errors, especially that of $\Delta S^‡$, make further discussion on the activation parameters difficult.

(12) Strandberg, R. *Acta Chem. Scand.* **1973**, *27*, 1004–1018.

(13) (a) Liu, B; Ku, Y.; Wang, M.; Zheng. P. *Inorg. Chem.* **1988**, *27*, 3868–3871. (b) Wang, M.; Zeng, P.; Liu, B.; Gu, Y. *Acta Crystallogr. Sect. C* **1988**, *44*, 1503–1505. (c) Liu, B.; Ku, Y.; Wang, X. *Inorg. Chim. Acta* **1989**, *161*, 233–237.

(14) Day, V. W.; Klemperer, W. G. *Science*, **1985**, *228*, 532–541.

$CH_2As)_2Mo_5O_{21}]^{4-}$, have been structurally characterized.[11] The bond order sums for the five Mo−O bonds that anchor each arsonate unit are 1.9 in both cases. The structure has a 2-fold symmetry, and the arsonate unit on one side of the $(MoO_3)_5$ ring is bound to the ring as strongly as the one on the other. The sums for the arsonate units in a Matsumoto-type molybdoarsonate are, however, significantly different. The sum for the arsonate unit on the α side of structurally characterized $[(C_6H_5As)_2Mo_6O_{24}(OH_2)]^{4-}$ [11] is 2.1, and the sum for the other is 1.6. Thus the arsonate unit that has only four Mo−O bonds is bound to the $(MoO_3)_x$ ring more weakly than that on the α side and those in (10, 5, 2).

This difference of the total strength of the bonds that anchor the arsonate units can explain different dynamic behaviors of (10, 5, 2) and (12, 6, 2) mentioned above. The cumulative strength of the Mo−O bonds that hold arsonate units to the $(MoO_3)_5$ ring of (10, 5, 2) is relatively strong and makes this species nonlabile on the ^{1}H NMR time scale. The arsonate unit on the α side of (12, 6, 2) is bound to the $(MoO_3)_6$ ring even more strongly, but the one on the β side is held less tightly and is vulnerable to intermolecular exchange. If we make a rough assumption that the activation enthalpy for the exchange reaction between the Mo_6As_2 species and free methylarsonate corresponds to the energy needed to break the four Mo−O bonds that hold the arsonate unit to the ring, the average bond energy for these bonds can be estimated to be 16 kJ mol^{-1}.

Acknowledgment. This work was supported in parts by a Grant-in-Aid for Scientific Research Nos. 08232276 and 08874084 from the Ministry of Education, Science and Culture of Japan (Monbusho).

Supporting Information Available: Figures 3 and 4, showing results of the *pqr* search and spin saturation transfer experiments (2 pages). Ordering information is given on any current masthead page.

IC960852T

---

[15] Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect. B* **1985**, *B41*, 244−247.

Additions and Corrections

Volume 35, 1996

I. Antes, S. Dapprich, G. Frenking, and P. Schwerdtfeger*: Stability of Group 11 Carbonyl Complexes Cl−M−CO (M = Cu, Ag, Au).

Pages 2089−2096. In the original paper we presented ab initio calculations on group 11 carbonyl complexes Cl−M−CO (M = Cu, Ag, Au). While ClAuCO is a well-characterized compound and ClAgCO is unknown, we overlooked two important papers on ClCuCO by Jagner et al.[1,2] In their first paper,[1] Håkansson and Jagner characterized ClCuCO as a white solid with chloride-bridged layers with significant deviation from linearity. Hence it may be difficult to compare their experimental work with our theoretical work. Nevertheless, the experimental Cu−C distance of 1.86 Å is somehow larger than our calculated MP2 value of 1.73 Å for the free species. The Cu−Cl distance of 2.35−2.37 Å is significantly larger compared to that of the free ClCuCO species (2.03 Å at the MP2 level), probably due to the bridging behavior of the chlorine ligand. In a subsequent paper Jagner et al. studied the infrared spectrum of solid ClCuCO.[2] Their CO stretching frequency is in good agreement with our calculated value.

Acknowledgment. We thank Prof. Susan Jagner for pointing out the experimental work on ClCuCO performed in her group.

---

[1] Håkansson, M.; Jagner, S. *Inorg. Chem.* **1990**, *29*, 5241.
[2] Håkansson, M.; Jagner, S.; Kettle, S. F. *Spectrochim. Acta, A* **1992**, *48*, 1149.

IC9612414