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Complexation of the Uranyl Ion with the Aminomethylenediphosphonates MAMDP and AMDP

James. E. Bollinger and D. Max Roundhill*

Department of Chemistry, Tulane University,
New Orleans, Louisiana 70118

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Introduction

The use of uranium as a nuclear energy source has made it a valuable mineral resource over the past forty years. Processing uranium generally involves leaching the metal as the uranyl ion (UO_2^{2+}) from ore, followed by solvent extraction, precipitation or batch adsorption onto ion exchange-type resins. Uranium reserves exist also in the form of $UO_2(CO_3)_3^{4-}$ dissolved in seawater, and although these concentrations are very low they represent globally some 4.9×10^9 tons. In the interest of tapping this resource efforts toward developing more efficient and selective means of UO_2^{2+} ion sequestering have been underway for some time.[1]

More recently there has developed an environmental need to complex and extract uranyl ion from soils and storage solutions. This problem has arisen because temporary facilities have been used for extended periods of time for the deposition of waste fission products from nuclear reactors and weapons fabrication plants. As a result there is an increasing exigency to find permanent storage for these radioactive uranium wastes.

We have recently examined the complexation properties of aminomethylenebis(phosphonic acids) towards selected trivalent metal ions, and have found that they form highly stable complexes with these oxophilic metal centers.[1,2] These metal complexes were found resistant to metal ion dissociation in acidic media and present in aqueous solution as both 1:1 and 1:2 (metal ion:ligand, M:L) species. The uranyl ion, although structurally different from simple M^{3+} ions because of its linear geometry, possesses a similar +3 to +4 charge at the metal center due to participation of the uranium 5f atomic orbitals.[3] Because of the high positive charge on uranium in the ion UO_2^{2+}, and because of the potential capacity of the axial oxygens on this ion to form intramolecular hydrogen bonds with a proton on the ligand, there is a good possibility that the uranyl ion will form stable complexes having 1:1, 1:2 and 1:3 (M:L) stoichiometries with aminomethylenebis(phosphonates) as ligands. There is considerable precedent that a phosphonate group will form strong complexes with the UO_2^{2+} ion, and there is the additional possibility that the amino moiety on these ligands will provide further selectivity for complexation *via* hydrogen bonding.[4] Furthermore, these ligands are simple and inexpensive to synthesize, thus making them potentially useful for application in large scale batch separation processes.

To test these concepts, we have measured the stability and protonation constants of the different complexes formed in aqueous solution between the UO_2^{2+} ion and the compounds *N,N'*-dimethylaminomethylenebis(phosphonic acid) (MAMDP) and aminomethylenebis(phosphonic acid) (AMDP) (Figure 1). From these data we can evaluate the potential for compounds of this type to be useful as uranyl ion sequestering agents.

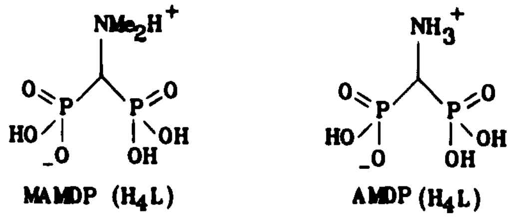

Figure 1. Structures of the aminomethylenediphosphonic acids MAMDP and AMDP.

Experimental Section

Uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (99+%), was obtained from Strem Chemical Co. Tetramethylammonium hydroxide, $[(CH_3)_4N]OH$, was obtained as a 1.0 M solution from Aldrich Chemicals. Perchloric acid was obtained from CMS, and tetramethylammonium nitrate, $[(CH_3)_4N]NO_3$, was obtained from Johnson Matthey. The tetramethylammonium nitrate was dried in a vacuum oven prior to use. Reagents used in the ligand syntheses were standard reagent grade, and were used without prior purification. Microanalyses were carried out by Galbraith Inc., Knoxville, TN. Melting points were determined on a hot stage apparatus. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker AC200 spectrometer as D_2O solutions. The compound MAMDP was synthesized by the Mannich-type reaction of dimethylformamide with phosphorus trichloride and phosphorous acid as reported in the literature.[2,5] Standard base solutions were kept free of carbonate as much as possible by diluting commercial solutions with degassed distilled water, followed by storage under nitrogen.

Ligand Synthesis. Aminomethylenediphosphonic acid (AMDP), $^+H_3NCH(PO_3H_2)(PO_3H^-)$. Using formamide in place of dimethylformamide as solvent, AMDP was synthesized in a similar manner to MAMDP. One difference was that after the water had been added to the reaction mixture, the solution was refluxed for 5 h. After completion of the reaction, a colorless precipitate appeared. The solvent was then partially removed on a rotary evaporator, and the residue triturated completely with the addition of 95% ethanol. Filtration and recrystallization of this solid material in dilute hydrochloric acid yielded the product as colorless microcrystals. Yield: 60%. Anal. Calcd for $CH_7NO_6P_2$: C, 6.32; H, 3.72. Found: C, 6.98; H, 4.02. ^1H NMR: δ 3.60 t ($^2J(PH)$ = 18 Hz). $^{31}P\{^1H\}$ NMR: δ 9.49 s. Mp: 290 °C dec.

Potentiometric Methods. Potentiometric titrations were carried out in an airtight 150 mL vessel fitted with a nitrogen inlet/outlet, a Ross combination electrode, an automatic temperature compensating probe, and a magnetic stirrer.[6] Readings were taken using an Orion 720A digital pH/ISE meter, and acid/base aliquots were delivered through a 10 mL buret accurate to 0.01 mL. The system was single-point calibrated by measuring the p[H] of an accurately known strong acid solution. All titrations were carried out at μ = 0.10 M with tetramethylammonium nitrate as supporting electrolyte. The pK_w of this solution was measured as 13.88. All solutions used were degassed prior to titration. Standardized solutions of 0.1 M tetramethylammonium hydroxide and perchloric acid were used as the base and acid, respectively. Metal and ligand solutions were gravimetrically standardized at concentrations of 0.01 M. Both ligands were titrated in the forward direction (acid to base) to determine the pK_a's. The stability constant determination was achieved by back titrating, first by adding the volume of base necessary to bring the p[H] >11.5, then titrating with acid generally until a precipitate formed. Triplicate titrations were carried out at each of the 1:1, 1:2, and 1:3 metal to ligand concentration ratios, with metal concentrations at ca. 1−2 mM and solution volume of 60−70 mL. Data from each titration were analyzed separately using the iterative least-squares fit programs PKAS and BEST, none to a σ fit (standard deviation) of $>5 \times 10^{-2}$. The stability and protonation

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(1) *Uranium Extraction Technology*; Joint Report by the OECD Nuclear Energy Agency and the IAEA, Paris, 1983.

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Table 1. Logarithms of the Protonation Constants for the Ligands AMDP and MAMDP[a]

		MAMDP	AMDP
log K_1	$L^{4-} + H \rightleftharpoons HL^{3-}$	13.4(0.1)	11.72(0.04)
log K_2	$HL^{3-} + H^+ \rightleftharpoons H_2L^{2-}$	9.18(0.02)	8.42(0.02)
log K_3	$H_2L^{2-} + H^+ \rightleftharpoons H_3L^-$	5.01(0.02)	5.42(0.02)
log K_4	$H_3L^- + H^+ \rightleftharpoons H_4L$	1.3(0.1)	1.4(0.1)

[a] Numbers in parentheses are mean standard deviations.

constant values were determined through averaging the individual constants obtained over successive titrations. The error values are represented by their respective mean standard deviations. All titration data were used in this error analysis. Values for metal hydrolysis were obtained from the literature.[7]

PKAS is a computer program for the calculation of protonation constants from potentiometric data. It is an interactive program which refines the protonation constants to the titration parameters. The program BEST minimizes the standard deviation of fit between the observed and calculated pH values of the entire titration curve. This minimization is accomplished through either manual or automatic variation of selected stability constants.[6]

Results

Protonation Constants. Protonation constants for the diphosphonic acids MAMDP and AMDP were determined quantitatively under the same experimental conditions that were used for the stability constant determinations.[8] The potentiometric curves obtained from these data were fitted using four protonation parameters. The protonation constants obtained from the titration of each of these diphosphonic acids with base are shown in Table 1. In each case the highest valued constant (log K_1) was assumed to involve protonation at the amine site. This first protonation is followed by protonations at three of the phosphonate sites (log K_2, K_3 and K_4). The unusually high values for log K_1 reflect the electrostatic stablizing effect of protonation on the small tetraanion, and, in the case of MAMDP, the significant electron donating properties of the methyl groups. The low values found for log K_4 show the high potential of these compounds to act as bidentate ligands at very high acid concentrations. Indeed, studies on bis-phosphonate metal complexes have shown that this class of ligand display far more affinity for polyvalent metal ions at high acid concentrations than do most carboxylate analog ligands.[9-12]

Stability Constants. Uranyl complexes with MAMDP and AMDP both share a characteristic insolubility at low solution pH. The titrations used to obtain the stability constant values have therefore been carried out in the reverse (base to acid) direction than those that were carried out to obtain the protonation constants. Dissolution to give a homogeneous solution is achieved by adding base to an aqueous solution of the diphosphonate and the UO_2^{2+} ion until a p[H] value of greater than 10 is obtained. In all cases bright yellow clear solutions are formed. The complexes remain soluble in aqueous solution, depending on the M:L ratio, down to a solution pH of 2.5–5. The AMDP/uranyl combination shows a somewhat lower solubility in aqueous media than does the MAMDP/uranyl combination.

Acceptable fitting[13] of a chemical model to the titration data requires the presence of both 1:1 and 1:2 (M:L) complexes in solution, with protonations occurring successively up to MLH_2 and $ML_2H_4^{2-}$ species. Also required is the inclusion of both the mono- and the bis-hydroxylated derivatives of the mono-ligated complexes, $ML(OH)^{3-}$ and $ML(OH)_2^{4-}$. These species are present in solution at high p[H]. The stability constant data are obtained from titrations performed at M:L concentration ratios of both 1:1 and 1:2, which provided well-fit refinements based on this chemical model. Titrations of solutions containing a M:L ratio of 1:3 were also carried out, but attempts to include more complicated (ML_3) species and their respective protonated forms in the refinements lead to ambiguous results. The inclusion of polynuclear complexes in the model failed as well to give lower standard deviations. Uncomplexed uranyl ion and hydroxy uranyl species are estimated from the data fitting to be present at concentrations of less than 1 ppm throughout the p[H] range of the titration. For $ML_2H_n^{n-6}$ complexes the overall results do not preclude the existence of protonated species beyond $n = 4$, the presence of which cannot be detected given the solubility constraints at the lower end of the pH range. The continued addition of strong acid to the solution after precipitation occurs does not noticeably dissolve any of the precipitate. The results of the iterative stability constant calculations for solutions containing the UO_2^{2+} ion and either MAMDP or AMDP are given in Table 2. The species distribution plots obtained from these data are shown in Figure 2. The 1:1 (M:L) species distribution plots (Figure 2) show that in the p[H] range of 5.5–8 the major solution species is MHL^-, with ML^{2-} and $M(OH)L^{3-}$ among others being formed at higher p[H] values. In the low p[H] range a precipitate forms. From the species distribution curves, the predominant complex present under these experimental conditions is MH_2L, although the precipitate has not been positively identified as having this stoichiometry. The major feature of the 1:2 plots is the predominance of the complex $MH_2L_2^{4-}$ over a wide p[H] range.

The results show exceptionally high values for 1:1 stability constants, with log K_{101} being 25.9 and 24.8 for complexation with AMDP and MAMDP respectively. This high stability is in agreement with other studies of phosphonate complexes of the uranyl ion, where it has been shown that these complexes are unusually stable in comparison to isostructural carboxylate complexes.[11] This high stability has been attributed to differences in the electrostatic net charge between carboxylate and phosphonate type ligands,[10] as well as to a small entropic effect of phosphonate ligands having more potentially binding oxygen atoms than do carboxylates. In addition, bis-phosphonate ligands with a planar configuration possess more favorable coordination properties toward the restrictive geometry of the uranyl cation than do "wrap around" type ligands such as EDTA.

The values of our stability and successive protonation constants for AMDP and MAMDP with the uranyl ion are very consistent. Differences between the ligands are reflected in slightly higher stability constants for the combination of MAMDP and UO_2^{2+}, and, except for log K_{142}, slightly more

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(7) Baes, C. F.; Mesmer R. E. *The Hydrolysis of Cations*; R. E. Krieger Publishing Co.: Malabar, FL, 1986.

(8) It is noted that the protonation constants are somewhat shifted in comparison to those previously reported[2] because of a change in ionic media.

(9) Nash, K. L. *Eur J. Solid State Inorg. Chem.* **1991**, *28*, 389.

(10) Nash, K. L. *Radiochim. Acta* **1993**, in press.

(11) Rizkalla, E. N. *Rev. Inorg. Chem.* **1983**, *5*, 223.

(12) The pK_a values for MAMDP were measured previously using 0.2 M acid and base titrant solutions.[2] In this present work we have measured the pK_a values for both MAMDP and AMDP at acid and base titrant concentrations of 0.1 M. Comparable pK_a values for MAMDP are obtained for both titrant solutions. The titrations have been carried out over a pH range 2.1–11.9 for the 0.1 M solutions and over a pH range of 1.8–12.0 for the 0.2 M solutions. The Ross electrode used for these titrations is specified to have acceptable reliability over this pH range provided that Na^+ ions are absent; therefore, we have used tetramethylammonium nitrate as the supporting electrolyte. The titration data have been fitted using the program PKAS to obtain approximate values, and then further refined using the program BEST to obtain the final values. The high errors placed on log K_1 and log K_4 reflect the uncertainties in the reported values.

(13) A curve fitting was generally considered acceptable if its σ fit (standard deviation) was less than 3×10^{-2}.

Table 2. Logarithms of the Protonation and Stability Constants for the Complexation of AMDP and MAMDP with UO_2^{2+} [a]

		AMDP	MAMDP
$\frac{[ML^{2-}]}{[M^{2+}][L^{4-}]}$	log K_{101}[b]	25.9(0.4)	24.8(0.6)
$\frac{[M(OH)L^{3-}][H^+]}{[ML^{2-}]}$	log K_{1-11}[c]	−10.4(0.2)	−10.7(0.1)
$\frac{[M(OH)_2L^{4-}][H^+]}{[M(OH)L^{3-}]}$	log K_{1-21}	−11.3(0.2)	−12.0(0.3)
$\frac{[MHL^-]}{[ML^{2-}][H^+]}$	log K_{111}	6.7(1.2)	9.8(0.1)
$\frac{[MH_2L]}{[MHL^-][H^+]}$	log K_{121}	6.0(1.0)	5.3(1.1)
$\frac{[ML_2^{6-}]}{[M^{2+}][L^{4-}]^2}$	log K_{102}	30.5(0.3)	32.4(0.5)
$\frac{[MHL_2^{5-}]}{[ML_2^{6-}][H^+]}$	log K_{112}	11.0(0.3)	21.8(0.5)[d]
$\frac{[MH_2L_2^{4-}]}{[MHL_2^{5-}][H^+]}$	log K_{122}	10.3(0.2)	
$\frac{[MH_3L_2^{3-}]}{[MH_2L_2^{4-}][H^+]}$	log K_{132}	6.6(0.1)	7.4(0.1)
$\frac{[MH_4L_2^{2-}]}{[MH_3L_2^{3-}][H^+]}$	log K_{142}	5.0(0.4)	5.0(0.1)

[a] The numbers in parentheses indicate standard errors. [b] The designation uses MHL as 111. [c] The designation uses M(OH)L as 1−11. [d] The composite value of log K_{112} + log K_{122}.

acidic ancillary protonation sites for the AMDP and UO_2^{2+}. These numbers appear to reflect macroscopically the trends of the uncomplexed ligand acid dissociation constants, yet they cannot unambiguously be assigned to the amine or to any particular phosphonate oxygen site. It is difficult therefore to ascertain the degree of hydrogen bonding between the protonated amine and the "yl" oxygens on UO_2^{2+}, although it is reasonable to assume that such an interaction would bestow added stability to these complexes at solutions of moderate to low p[H]. At higher p[H], deprotonation of the amino moiety should lessen this effect considerably for AMDP and, lacking any further potentially hydrogen-bonding hydrogens, eliminate it entirely in the case of MAMDP. Because the stability constant for AMDP is only slightly greater for the 1:1 complexes than those for MAMDP, a strong hydrogen bond interaction to the axial oxygen atoms of the uranyl ion is likely non-existent for both series of complexes.

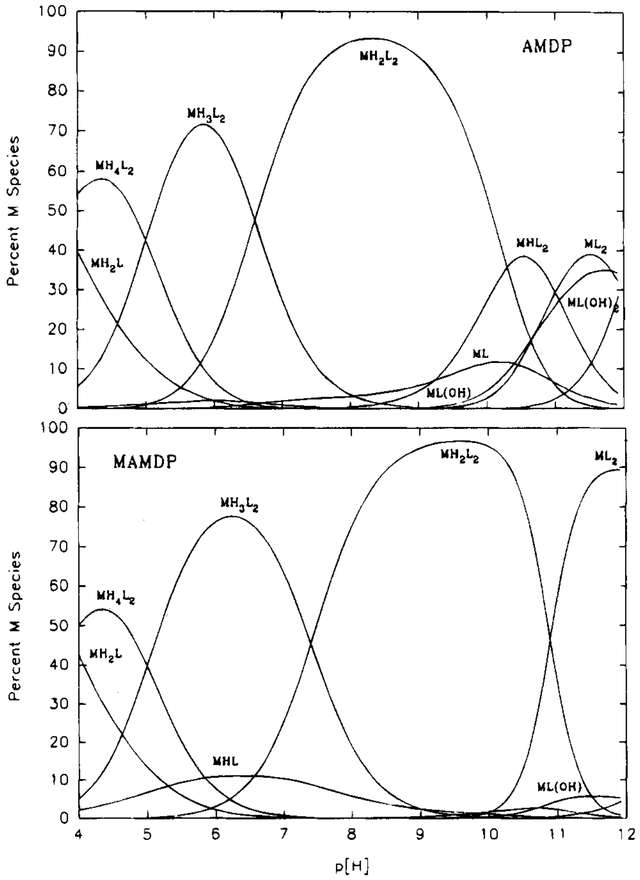

Figure 2. Species distribution plot for an aqueous solution containing UO_2^{2+} and AMDP or MAMDP at a 1:2 metal:ligand (M:L) ratio; $[UO_2^{2+}]$ = 4.0 mM. The % on the ordinate is the percent of metal species.

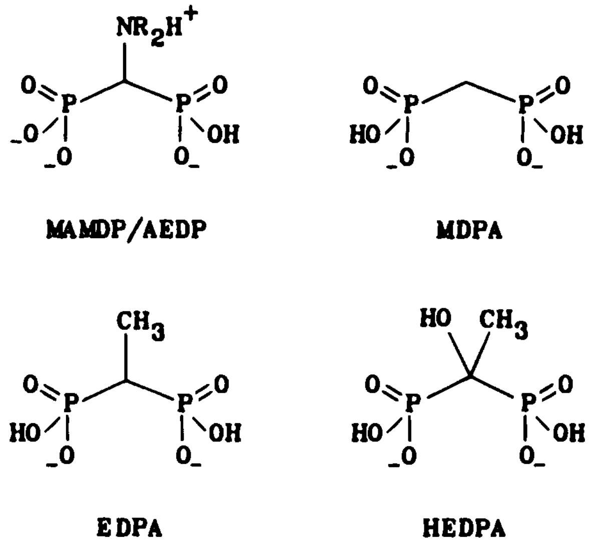

Figure 3. Structures of the H_2L^{2-} forms of the methylenediphosphonic acids MAMDP/AMDP, MDPA, EDPA and HEDPA.

Recently the stability constants for the complexation of UO_2^{2+} with the diphosphonates, methanediphosphonic acid (MDPA), 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) and ethane-1,1-diphosphonic acid (EDPA) have been measured. The structures of these ligands are shown in their doubly deprotonated forms (H_2L^{2-}) in Figure 3. The respective log Q_{101} and log Q_{102} values for H_2L^{2-} as the ligand are 5.34 and 8.31 for EDPA.[10] The log Q_{102} values for H_2L^{2-} are 11.67 and 11.76 for MDPA and HEDPA respectively. By comparison these respective log Q_{101} and log Q_{102} values, where Q is an equilibrium expression of the type $[MH_2L]/[M^{2+}][H_2L^{2-}]$,[14] are 18.5 and 23.1 for AMDP, and 17.4 and 21.6 for MAMDP. These values reflect the higher basicity of these two ligands. Thus AMDP and MAMDP have significantly higher stability constants (Table 3). MDPA, EDPA and HEDPA differ from AMDP and MAMDP in that they do not have an appended

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(14) These log Q values are obtained from equilibrium calculations with Q designated as $Q_{101} = [MH_2L]/[M][H_2L]$ and $Q_{102} = [MH_4L_2]/[M][H_2L]^2$ with log Q_{101} = log β_{121} − log β_{021} and log Q_{102} = log β_{142} − 2 log β_{021}.

Table 3. Comparative Stability Data for Binding of Phosphonate Ligands to UO_2^{2+}.

ligand	log Q_{101}	log Q_{102}
AMDP	18.5	23.1
MAMDP	17.4	21.6
EDPA	5.34	8.31
MDPA		11.67
HEDPA		11.76

amino group. The presence of this group leads to the formation of zwitterions, which results in the H_2L^{2-} forms of AMDP and MAMDP being phosphonate trianions rather than dianions.

One approach to comparing ligating abilities relates stability constants to ligand total basicities. A linear regression fit based upon stability constants of a variety of carboxylate ligands proposed by Nash[10] relates log K_{101} to the total free energy of ligand protonation represented by the sum of the ligand protonation constants, given by log $K = 0.22\ (\pm 0.27) + [0.68\ (\pm 0.03)]\Sigma pK_a$. Application of this formula to MAMDP and AMDP gives calculated log K_{101} values of 19.8 (±1.1) and 18.6 (±1.1) for MAMDP and AMDP respectively. The difference of $10^{3.9-8.4}$ between the regression line and the experimental data represents substantially enhanced stability as compared to carboxylate ligands. Several other geminal bis(phosphonates) likewise possess increased stability, showing differences in the range of $10^{1-4.3}$, somewhat lower than the differences for the structurally similar MAMDP and AMDP ligands. This correlation suggests that some added stability is conferred through the presence of the amino groups. This added stability may be the result of delocalization of the lone electron pair of the aminomethylenediphosphonate into the complex, or it may be due to more subtle factors.

Our data show that the compounds MAMDP and AMDP have extremely high binding constants for the UO_2^{2+} ion, and that the complexes remain in solution over a wide pH range. Under highly acidic conditions, however, the combination of a high stability constant coupled with a low solubility of the uranyl complexes makes these ligands good candidates for use as uranyl ion precipitating agents.

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