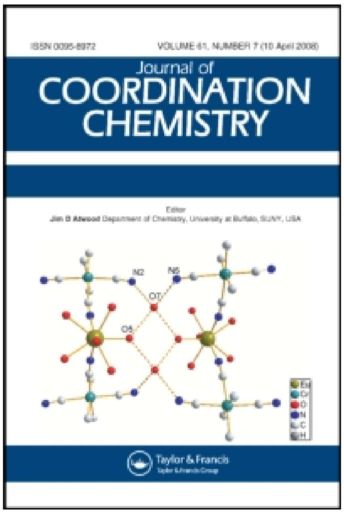

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COMPLEXES OF URAMILDIACETIC ACID

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COMPLEXES OF URAMILDIACETIC ACID

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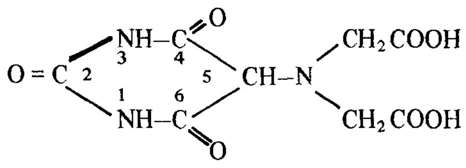
The stability constants of several transition metal complexes of uramildiacetic acid (H_3Ur) have been measured. In all cases the values of the 1:1 stability constants are the largest found for any derivative of iminodiacetic acid and are rationalized in terms of the structure of the ligand. The values of the 2:1 stability constants have also been obtained and are large only for metal ions having large ionic radii, as the bulkiness of the ligand would suggest.

INTRODUCTION

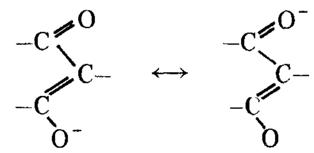
The stability constants of the complexes formed by uramildiacetic acid (H_3Ur) and several metal ions have been the subject of a number of publications.[1–5]



(H_3Ur)

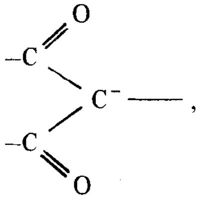
The first report by Schwarzenbach in 1946[1] included values for the 1:1 complexes with the divalent alkaline earth ions, and lithium and sodium ions. This work was extended in 1948[2] to include the 2:1 (ligand to metal) complexes of Ca^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Ce^{3+}, and La^{3+}. The values which were found are given in Table I.

The reported results were quite large, particularly those for the lithium and sodium ions, and led Irving and da Silva[3,4] to study the interactions in more detail. Their results are also given in Table I. In addition to repeating some of the previous work, they systematically added methyl groups to the 1 and 3 positions of the ring system in order to investigate the extent to which full resonance in this ring affected the stabilities of the complexes. The stabilities of the complexes with H_3Ur did not differ appreciably from those of the 1- and 1,3- substituted compounds which led to the conclusion that full resonance in the ring system is not a factor. Rather it seems more likely that the resonance that occurs is of the β-diketone type.[4]



In all these studies a remarkably large affinity for the alkali metals was found. More recently Gromova, Litvina, and Peshkova[5] measured the stability constants for the europium (II) and (III) complexes of this ligand and the results they reported are listed in Table I.

The magnitudes of the stability constants of the 1:1 complexes for the alkaline earth metals are greater even than the corresponding values for nitrilotriacetic acid (NTA). The implication is that in H_3Ur the ring system forms a "cage" which would bring the moiety,



as well as the iminodiacetate group into close proximity to the metal, thus increasing the stability.[4]

Since no values of the stabilities of the 1:1 complexes of H_3Ur with the transition elements had been reported, we measured them to see if this increase in stability over the complexes of NTA found by Irving and da Silva[4] for the alkali and alkaline earth metal ions also exists in the case of the transition elements. Moreover, the value reported for the 2:1 complex with lanthanum was only an approximate value and was extraordinarily large. Because of our interest in the lanthanides, we wished to obtain a better value for log K_2 and also to determine the value of the stability constant of the

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TABLE I
Stability constants of complexes with uramildiacetic acid

Metal ion	log K_1†	log K_2†	μ	t(°C)	Ref.
Li^+	5.40		0	20	1
	4.90 ± 0.02		0.1	20	4
Na^+	3.32		0	20	1
	2.72 ± 0.01		0.1	20	4
K^+	1.23 ± 0.03		0.1	20	4
Tl^+	5.99 ± 0.02		0.1	20	4
Be^{2+}	10.36 ± 0.02		0.1	20	4
Mg^{2+}	8.85	3.1	0	20	1, 2
	8.19 ± 0.02	3.62 ± 0.05	0.1	20	3
Ca^{2+}	8.77	5.2	0	20	1, 2
	8.31 ± 0.01	5.27 ± 0.02	0.1	20	3
Sr^{2+}	7.65		0	20	1
	6.93 ± 0.02	4.06 ± 0.1	0.1	20	3
Ba^{2+}	6.78		0	20	1
	6.13 ± 0.02	3.68 ± 0.1	0.1	20	3
Cd^{2+}		6.7	0	20	2
Co^{2+}		3.2	0	20	2
Mn^{2+}		4.0	0	20	2
Ni^{2+}		3.3	0	20	2
Zn^{2+}		3.2	0	20	2
La^{3+}		~10	0	20	2
Ce^{3+}		~10	0	20	2
Eu^{3+}	10.84 ± 0.04	10.72 ± 0.04	0.1	20	5
Eu^{2+}	11.56 ± 0.09	10.62 ± 0.09	0.1	20	5

†$K_1 = \dfrac{[MUr]}{[M][Ur]}$, $K_2 = \dfrac{[MUr_2]}{[MUr][Ur]}$

(In these, and subsequent definitions, the charges on the ions will be omitted except when needed for clarity.)

1:1 lanthanum complex. The expectation that these values would also be among the largest ever found for ligands of this basic structure was fulfilled.

EXPERIMENTAL

Materials and Solutions

The uramildiacetic acid was obtained from Eastman Organic Chemicals and recrystallized twice from dilute perchloric acid.

Anal. Calcd. for $C_8H_9O_7N_3$: C, 37.1; H, 3.5; N, 16.2; Found: C, 36.8; H, 3.5; N, 16.2. Carbonate-free tetramethylammonium hydroxide (TMAOH) solution was prepared from Eastman Organic Chemicals 10% solution by a standard ion exchange procedure,[6] diluted to 0.1 *M*, and standardized against potassium hydrogen phthalate. Tetramethylammonium nitrate was prepared from the TMAOH by neutralizing with nitric acid, evaporating the resulting solution to dryness, and recrystallizing twice from 80% enthanol-water. The remaining solutions were prepared as described previously.[7]

Experimental Procedure

The potentiometric titration procedure which was utilized has been described previously.[7] The direct titration method was used to determine the acid dissociation constants of H_3Ur and the formation constants of the 1:1 complexes of the alkaline earths and the 2:1 complexes of the alkaline earths and transition metals. In all cases the temperature was 25°C, the ionic strength was maintained at 0.1 *M* with $TMANO_3$, the metal ion concentration was 0.001 *M*, and the concentration of H_3Ur was either 0.001 *M* or 0.002 *M*.

For the determination of the formation constants of the 1:1 complexes of the transition metals and the 2:1 complex of lanthanum it was necessary to use the tren method.[8] The compositions of the solutions which were used are given in Table II.

Calculations

The electrode system was calibrated in terms of $-\log [H^+]$ ($[H^+]$ = hydrogen ion concentration) by measurements on solutions of 10^{-3} to 10^{-4} *M* nitric acid in 0.1 *M* $TMANO_3$. This procedure gave a correction factor of −0.062 ± 0.002 which was then applied to all readings taken from the pH meter. The value of pK_w was determined as described in the literature[9] and was found to equal 13.79 ± 0.01 for 0.1 *M* $TMANO_3$ at 25°C.

TABLE II
Composition of solutions for tren method (*M*)
$t = 25°C$, $\mu = 0.1$ ($TMANO_3$)

Metal ion	Auxiliary metal ion	TREN[a]	H_3Ur
Mn^{2+}(0.01)	Zn^{2+}(0.001)	0.001	0.001
Cd^{2+}(0.001)	Cu^{2+}(0.001)	0.001	0.001
Ni^{2+}(0.001)	Ca^{2+}(0.001)	0.001	0.001
Cu^{2+}(0.001)	Ca^{2+}(0.001)	0.001	0.001
Zn^{2+}(0.001)	Ca^{2+}(0.001)	0.001	0.001
La^{3+}(0.001)	Cu^{2+}(0.001)	0.001	0.001
La^{3+}(0.001)	Cu^{2+}(0.001)	0.001	0.002

[a]TREN = 2,2′,2″-triaminotriethylamine

The computations of the acid dissociation constants and the formation constants determined by the direct method were carried out on an IBM 1620 computer using Gauss G.[10] A computer program was also written to carry out the usual calculations involved in the tren method.

RESULTS AND DISCUSSION

The usual procedure in studies of this kind is to prepare a standard solution of the ligand and withdraw aliquots for dilution. However, it was noted that 0.005 *M* solutions of H_3Ur became pink after standing for several days and upon restandardization it was found that the concentration had changed. In order to avoid this decomposition a fresh solution was prepared each day. The solution was standardized at the beginning and end of each day and pH data were taken for the calculation of pK_3. In this way there were 41 different determinations of pK_3 using a total of approximately 500 data points. All 41 values of pK_3 lay between 9.696 and 9.734 with an average value of 9.71 ± 0.02 at the 95% confidence level. In all cases the pk_3 values at the beginning and end of the day's measurements were in good agreement. The values are also in good agreement with those found by Irving and da Silva[3] when account is taken of the difference in temperature. The values of the acid dissociation constants for H_3Ur are summarized in Table III.

In order to utilize the tren method it was necessary to determine the formation constants of the appropriate metal–tren complexes in the 0.1 *M* $TMANO_3$ medium used in this work. These values are collected in Table IV and they are in satisfactory agreement with the values previously determined in 0.1 *M* KCl.

TABLE III
Acid dissociation constants of H_3Ur†

t, °C	25‡	20[1]	20[3]
μ	0.1 ($TMANO_3$)	→0	pk_1 and pk_2, 0.1 (KNO_3) pk_3, 0.1 ($TMANO_3$)
pk_1	2	2.86	1.7 ± 0.3
pk_2	2.76 ± 0.04	3.76	2.67 ± 0.03
pk_3	9.71 ± 0.02	10.44	9.63 ± 0.03

† $k_1 = \dfrac{[H][H_2Ur]}{[H_3Ur]}$; $k_2 = \dfrac{[H][HUr]}{[H_2Ur]}$; $k_3 = \dfrac{[H][Ur]}{[HUr]}$

‡This work.

TABLE IV
Logarithms of the formation constants for metal 1:1 tren complexes and pk values for the acid dissociation constants†

t, °C	25‡	25
μ	0.1 ($TMANO_3$)	0.1 (KCl)
Mn^{2+}	5.77 ± 0.06	5.76 ± 0.05[11]
Co^{2+}	12.42 ± 0.02	–
Ni^{2+}	14.44 ± 0.02	14.61 ± 0.05[11]
Cu^{2+}	18.77 ± 0.02	18.55 ± 0.07[11]
Zn^{2+}	14.40 ± 0.01	14.48 ± 0.05[11]
Cd^{2+}	11.72 ± 0.01	–
H^+	pk_1 = 8.383 ± 0.003	8.42[12]
	pk_2 = 9.453 ± 0.002	9.44[12]
	pk_3 = 10.123 ± 0.001	10.13[12]

† $K = \dfrac{[M\,tren]}{[M][tren]}$, $k_1 = \dfrac{[H][H_2tren]}{[H_3tren]}$, $k_2 = \dfrac{[H][Htren]}{[H_2tren]}$,

$k_3 = \dfrac{[H][tren]}{[H\,tren]}$

‡This work.

The final values of the stability constants for the various H_3Ur complexes are given in Table V. The error limits given on these numbers are the 95% confidence limits. For those values determined by the tren method, however, these do not contain the uncertainties in the auxiliary constants used in the calculations.

Where it is possible to compary results with those of Irving and da Silva,[3,4] the comparison found to be satisfactory when account is taken of the slightly different experimental conditions. The internal consistency of our results was checked in the case of cadmium by carrying out a second measurement using zinc as the auxiliary ion rather than copper. The value obtained for log K_1, 11.63, is in excellent agreement with that given in Table V. The values of

TABLE V
Formation constants for H_3Ur complexes
(μ = 0.1 *M* $TMANO_3$, t = 25°C)

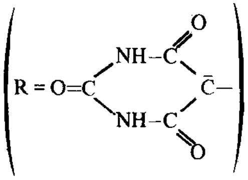
Metal ion	log K_1	log K_2
Mg^{2+}	8.35 ± 0.01	–
Ca^{2+}	8.40 ± 0.01	5.50 ± 0.05
Sr^{2+}	7.02 ± 0.01	–
Ba^{2+}	6.16 ± 0.01	–
Mn^{2+}	10.28 ± 0.01	3.76 ± 0.03
Ni^{2+}	14.19 ± 0.03	3.1 ± 0.1
Cu^{2+}	15.54 ± 0.02	3.9 ± 0.1
Zn^{2+}	13.39 ± 0.02	3.3 ± 0.1
Cd^{2+}	11.64 ± 0.01	6.64 ± 0.04
Pb^{2+}	–	3.74 ± 0.04
La^{3+}	12.82 ± 0.01	9.82 ± 0.02

log K_1 for Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and La^{3+} and log K_2 or Cu^{2+}, and Pb^{2+} have not been reported previously.

It is evident that H_3Ur forms 1:1 complexes of greater stability with these metal ions than does NTA,[13] in keeping with the results found for the alkaline earths. For each of the ions the difference in log K_1 values is between 2.0 and 3.0. (For the alkaline earths this difference is between 1.4 and 3.0.) It is also apparent that the previous suggestion that H_3Ur is particularly suited to form strong complexes with small cations or cations that form tetrahedral complexes[3] is only partly true since both cadmium and lanthanum, which are very large ions, are also greatly stabilized with respect to NTA.

Although NTA and H_3Ur are dissimilar ligands in some respects, they can both be derived formally from iminodiacetic acid and can be considered as N-substituted iminodiacetic acids, $R\text{-}N(CH_2COOH)_2$. For NTA, R– is an acetic acid function and for H_3Ur, R– is the pyrimidinetrione function. With this in mind it is then possible to compare the affinity of the two R– groups for a given metal ion by utilizing a procedure first developed by Schwarzenbach.[14] In this method a standard curve is constructed by plotting log K_1 for the metal ion in question *versus* pk_3 for a series of N-substituted iminodiacetate ligands $(R\text{–}N(CH_2COO^-)_2$ in which R– is an alkyl or aryl group. Complexes of ligands which have potential coordinating groups contained in R– will then lie above the standard curve when the log K_1 values are plotted against the corresponding pk_3 values. This deviation will be related to the relative affinity of the fourth coordinating group for the particular metal ion. The results for this type of correlation for NTA and H_3Ur are given in Table VI. In all cases the enhanced stability conferred on the complex by the ring system exceeds that conferred by the acetato group. Moreover, an examination of the existing data[14,15] shows that with the exception of the enhancement found for the $-CH_2CH_2-S^-$ group with ions such as Zn^{2+} and Cd^{2+}, the largest effect is found when R is the ring system in H_3Ur.

TABLE VI
Effect of fourth coordinating group in $R\text{–}N(CH_2COOH)_2$ in units of Δ log K_1

Metal ion	$\Delta(R = -CH_2COO^-)$	Δ 
Mg^{2+}	2.0	5.0
Ca^{2+}	2.8	4.6
Sr^{2+}	2.1	4.1
Ba^{2+}	2.2	3.8
Mn^{2+}	2.1	4.9
Ni^{2+}	2.9	5.5
Cu^{2+}	1.8	4.4
Zn^{2+}	3.0	5.7
Cd^{2+}	3.0	4.8
La^{3+}	4.1	6.6

Of these ions, the only ones which form 2:1 complexes of moderate stability are the two largest ions, cadmium and lanthanum. This is certainly a reflection of the fact that the ligand is quite bulky and that a second ligand could only be bound tightly by those metal ions which are large. The value of log K_2 for the cadmium–H_3Ur complex is only slightly larger than that of the corresponding NTA complex, whereas for lanthanum the 2:1 H_3Ur complex is more stable than the NTA complex by 2.5 log K_2 units. This is most likely due to the combination of the large size of the lanthanum ion, the enhanced affinity of H_3Ur for metal ions, and the tendency of lanthanum to form complexes of high coordination number.

The result reported for the stability of the 1:1 europium (III) complex with uramildiacetic acid[5] does not appear to be reasonable. First of all, the reported values give a difference between log K_1 and log K_2 that is much smaller than for any other polydentate ligand. In addition, the value of log K_1 is about 2 units less than the value for the corresponding lanthanum complex. The log K_2 value seems reasonable, however, when compared to the lanthanum value, and we conclude that most likely it is the log K_1 value for the europium (III) complex that is in error.

Of all the ligands derived formally from iminodiacetic acid, H_3Ur forms the strongest complexes with all the metals which have been investigated up to this time. As mentioned previously, this is somewhat unexpected since NTA would probably be expected to form the strongest complexes with these metals. It would seem that the source of this enhanced stability lies in the conformation of the ring system which effectively forms a cage about the metal ion. In this conformation, molecular models show that although the two carbonyl oxygen atoms do not point at the metal ion, they would be close enough that they could be coordinated. This, coupled with the likelihood that there is a negative charge which is distributed over this system, could account for the enhanced stability. Although there is no way that the two carbonyl oxygen atoms could both point toward the metal, it has been shown that in systems with equivalent atoms held closer together than they would be if independent of one another, there is a tendency for both atoms to interact with the metal such that the mean position of the pair of atoms lies on a vertex of a usual coordination polyhedron.[16]

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