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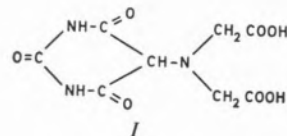


COMPLEXES OF TRANSITION METALS WITH URAMILDIACETIC ACID

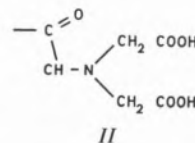
A competition method for determination of stability constants of metal complexes using a solid-state copper selective electrode is presented. The method is applied to the determination of the stability constants of the complexes of uramildiacetic acid with several transition metals, Zn, Cd and Pb. The results show that this ligand is particularly powerful among tetradentate complexones, but the fact that its alkali metals and Be complexes are more stable than the potentially hexadentate EDTA should rather be ascribed to the inability of this ligand to coordinate to very small ions or to those with little tendency to form covalent bonds due to their electronic configuration and reduced polarising power.

1 — INTRODUCTION

Uramildiacetic acid (I) was one of the first complexones synthesised by SCHWARZENBACH and col. who first noticed its unusual complexing properties towards alkali metals (1).



The study of this ligand was later on undertaken by H. IRVING and J. FRAÚSTO DA SILVA (2), who have improved the method of preparation and extended the determinations of stability constants to cover the series of alkali metals (Li^+ , Na^+ , K^+), thallium(I) and alkaline-earth metals (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}). It has been shown that the complexes of the alkali metals are stabilized by favourable enthalpy changes and that although the entropy changes are unfavorable they actually control the order of stabilities $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ (2). The facts remained unexplained that these complexes and that formed by beryllium are more stable than those of the same cations with ethylenediamine-tetracetic acid (EDTA), whereas the position is reversed for the alkaline earth ions. To investigate this point and to extend our knowledge of the complexing properties of the structural moiety (II) where $\text{C}=\text{O} \rightleftharpoons \text{C}-\text{OH}$ tautomerism is possible, some homologues of uramildiacetic acid were synthesised and studied (3) as well as several other compounds with closely related structures (4).



The results of these studies confirmed the abnormal behaviour of uramildiacetic acid and its homologues towards the alkali metals and beryllium, and the authors tentatively suggested that this might be due to a particularly favourable «cage» structure of the ligand, since the highest relative increases in stability were found for the smallest ions: Li^+ , Be^{2+} and, to a certain extent, Mg^{2+} .

Transition metal ions could not be conveniently studied, at that time, by similar techniques since

their complexes are so stable that the equilibria $M^{2+} + LH_3 \rightleftharpoons ML^- + 3H^+$ lies almost completely to the right. On the other hand, potentiometric methods currently used for very stable complexes, namely the method of SCHMID and REILLEY (5) could not be used because metallic mercury reduced the ligand. Other common techniques offered considerable experimental difficulties and were abandoned. The availability of reproducible solid-state selective copper electrodes in recent years prompted us to develop a competition method for the determination of formation constants of stable metal complexes similar to that proposed by SCHMID and REILLEY. The mathematical basis of this method (pCu method) is described in the present work, as well as its application to the determination of the stability constants of the transition metal complexes of uramildiacetic acid. Whenever possible (Mn^{2+} , Cd^{2+}) the pH titration method was also used, as a check for the series of results obtained by the pCu method.

2 — EXPERIMENTAL

2.1 — URAMILDIAACETIC ACID

The free acid was synthesised according to the instructions of H. IRVING and FRAÚSTO DA SILVA (1). The commercial Fluka product could also be used after repeated recrystallization from $HClO_4$ 2M. The aqueous solutions of the ligand decompose quite appreciably, so new solutions had to be prepared every day. This detail is important to obtain accurate and reproducible results.

2.2 — METAL SOLUTIONS

Metal nitrates of «Analar» grade were used and solutions were standardised by complexometric titrations or electrolytic deposition (copper).

2.3 — POTASSIUM HIDROXIDE AND NITRATE

Carbonate free solutions of potassium hidroxide were prepared according to SCHWARZENBACH and BIEDERMAN (6) and standardised against perchloric acid. Potassium nitrate was of «Analar» grade.

2.4 — DE-IONISED WATER

Laboratory distilled water was passed through a mixed-bed ion exchange resin.

2.5 — INSTRUMENTS

For pH measurements and titrations a Radiometer PHM 4 was used, fitted with a Radiometer glass electrode type G 2025 B and a Radiometer saturated calomel reference.

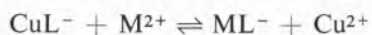
For the measurements of E_{Cu} an expanded scale Coleman model 38A potentiometer was used, with a Coleman specific copper electrode type 3-804 and a Coleman calomel reference type 3-711.

All the measurements were carried out in double-walled cells thermostatically controlled at $25.0 \pm 0.1^\circ C$ by circulating water through the jacket. The glass electrode was calibrated by titrating a sample of perchloric acid in 0.1M KNO_3 . The copper electrode was calibrated using a series of copper nitrate and copper buffer solutions (NITA, EDTA) in 0.1M KNO_3 at pH ~ 3 .

The slope of the calibration line was, in every case, close to the theoretical value.

2.6 — TECHNIQUE

For the determination of the stability constant of the copper complex of uramildiacetic acid 1 : 1 mixtures of the metal and the ligand (in slight excess) were used over a range of concentrations $4 \times 10^{-4} M$ to $2.5 \times 10^{-3} M$. For the determination of the stability constants of the complexes of the other metals 1 : 1 mixtures of copper and ligand were used and variable amounts of the second metal were added to ensure sufficient displacement of copper ion according to the reaction



The least favourable case was that of Mn^{2+} when the concentration of this metal varied from 7 to 16 times the concentration of copper.

Formation of protonated complexes was taken into account but it was found that the difference between $\log K_{MHL}$ and $\log K_{ML}$ was sufficiently high to allow the independent determination of $\log K_{ML}$.

at pH values of the order of 3, the difference in $\log K_{ML}$ values being less than 0.1 log units when MHL was taken into consideration and when it was not. Furthermore, when CuHL was not considered, $\log K_{ML}$ values were practically identical in both cases due to compensation of errors.

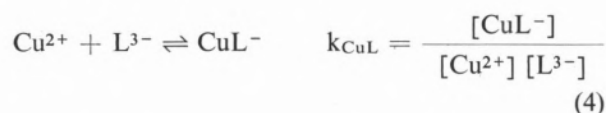
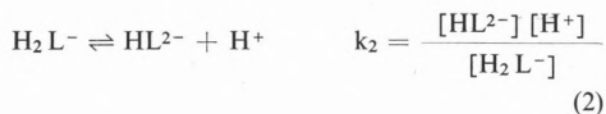
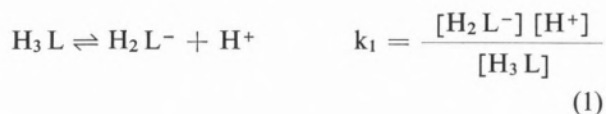
The method used for the determination of stability constants by pH titrations has been described in previous works (2).

3 — CALCULATIONS. THE *pCu* METHOD

3.1 — THE STABILITY CONSTANT OF THE COPPER COMPLEX

3.1.1 — Only *CuL* is formed

The following equilibria have to be considered



The mass balances for the ligand and the metal are as follows, where charges are omitted for the sake of simplicity

$$C_L = [H_3L] + [H_2L] + [HL] + [L] + [CuL] \quad (5)$$

$$C_{Cu} = [Cu] + [CuL] \quad (6)$$

by taking into account equations 1 to 3

$$C_L \equiv [CuL] + [L] \left(\frac{[H]^3}{k_1 k_2 k_3} + \frac{[H]^2}{k_2 k_3} + \frac{[H]}{k_3} + 1 \right) \quad (7)$$

or

$$C_L = [CuL] + \alpha_H [L] \quad (8)$$

Combining equations 6 and 8

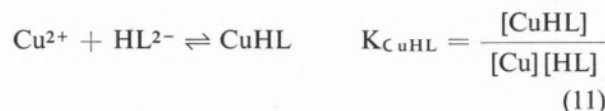
$$[L] = \frac{C_L - (C_{Cu} - [Cu])}{\alpha_H} \quad (9)$$

and finally

$$K_{CuL} = \frac{(C_{Cu} - [Cu]) \cdot \alpha_H}{[Cu] \{C_L - (C_{Cu} - [Cu])\}} \quad (10)$$

3.1.2 — *CuL* and *CuHL* are formed

A further system has to be considered



The mass balances become

$$C_L = [CuHL] + [CuL] + \alpha_H \cdot [L] \quad (12)$$

$$C_{Cu} = [CuHL] + [CuL] + [Cu] \quad (13)$$

Equation 11 can be written in the form

$$K_{CuHL} = \frac{[CuHL]}{[Cu][L]} \cdot \frac{k_3}{[H]} \quad (14)$$

from which $[CuHL]$ is obtained. The value of $[CuL]$ can then be derived from equation 13

whereas the value of $[L]$ is obtained from equations 11 and 12.

Hence, by substituting $[ML]$ in the expression of K_{CuL} :

$$\frac{C_{Cu} - [Cu]}{[Cu][L]} = K_{CuL} + \frac{[H]}{k_3} \cdot K_{CuHL} \quad (15)$$

where

$$[L] = \{C_L - (C_{Cu} - [Cu])\} / \alpha_H \quad (16)$$

K_{CuL} and K_{CuHL} can then be obtained from a plot of $\frac{C_{Cu} - [Cu]}{[Cu][L]}$ against $\frac{[H]}{k_3}$. Since the first term is identical with the expression for K_{CuL} when $CuHL$ is absent, the presence of this species is easily detected when the calculated $K_{CuL}^{calc.}$ values are not constant and increase linearly with $\frac{[H]}{k_3}$.

3.2—THE STABILITY CONSTANTS OF METAL COMPLEXES OTHER THAN Cu^{2+} BY A COMPETITION METHOD

3.2.1—Only ML and CuL are formed

Besides equilibria 1, 2, 3 and 4, the reaction of metal M with L has now to be included



The mass balances for the ligand and each of the two metals, take the form

$$C_L = \alpha_H[L] + [CuL] + [ML] \quad (18)$$

The final expressions are

$$K_{ML} = \frac{\left\{ K_{CuL} + \frac{K_{CuHL}}{k_3} \times [H] \right\} \times \{C_L - C_{Cu} - [Cu] - \alpha_H[L]\} \times [Cu]}{(C_{Cu} - [Cu])\{C_M - [C_L - (C_{Cu} - [Cu]) - \alpha_H[L]]\}} \quad (25)$$

$$C_M = [M] + [ML] \quad (19)$$

$$C_{Cu} = [Cu] + [CuL] \quad (20)$$

Replacing $[CuL]$ from 20 in the expression for K_{CuL} one obtains

$$[L] = \frac{C_{Cu} - [Cu]}{[Cu] \cdot K_{CuL}} \quad (21)$$

And combining 18 and 20

$$[ML] = C_L - (C_{Cu} - [Cu]) - \alpha_H \cdot [L] \quad (22)$$

From 19 and 22, $[M]$ can be obtained

$$[M] = C_M - \{C_L - (C_{Cu} - [Cu]) - \alpha_H[L]\} \quad (23)$$

Hence

$$K_{ML} = K_{CuL} \times \frac{[Cu] \times \{C_L - (C_{Cu} - [Cu]) - \alpha_H \cdot [L]\}}{(C_{Cu} - [Cu])\{C_M - [C_L - (C_{Cu} - [Cu]) - \alpha_H[L]]\}} \quad (24)$$

where $[L]$ is given by 21.

3.2.2— ML , CuL and $CuHL$ are formed

The equations are derived by a similar procedure from the mass balances and definition of the relevant constants.

where

$$[L] = \frac{C_{Cu} - [Cu]}{[Cu] \cdot \left\{ K_{CuL} + \frac{K_{CuHL}}{k_3} \cdot [H] \right\}} \quad (26)$$

3.2.3 — ML , MHL , CuL and $CuHL$ are formed

The calculations may proceed following the lines of case 1b, that is, K_{ML} can be calculated by using expression 25 and related to the real K_{ML} and K_{MHL} by

$$K_{ML}^{calc.} = K_{ML}^{real} + \frac{[H]}{k_3} \cdot K_{MHL}^{real} \quad (27)$$

In all cases, only $[Cu]$ and $[H]$ have to be measured experimentally, since C_L , C_{Cu} , C_M and the ionization constants k_1 , k_2 and k_3 of the ligand LH_3 are known in advance. K_{CuL} and K_{CuHL} must be determined in the first place for they are necessary in the calculation of K_{ML} and K_{MHL} . The method can, of course, be adapted to any reference metal provided that the appropriate specific electrode is

Table I

Stability constants of complexes of uramildiacetic acid with alkali and alkaline-earth metals (2)

$T = 20,0^\circ C$ $\mu = 0.1$ ($Me_4N.NO_3$)

Ion	log K_{MHL}	log K_{ML}
Li^+	—	4.90
Na^+	—	2.72
K^+	—	1.23
Be^{2+}	3.44	10.36
Mg^{2+}	—	8.19
Ca^{2+}	—	8.31
Sr^{2+}	—	6.93
Ba^{2+}	—	6.13

Table II

Stability constants of complexes of uramildiacetic acid with dispositive transition metals, zinc, cadmium and lead (present work)

$T = 25,0^\circ C$ $\mu = 0.1$ $M(KNO_3)$

Ion	Method	log K_{MHL}	log K_{ML}
Mn^{2+}	A	—	10.03
	B	3.48	9.87
Fe^{2+}	B	—	10.56
Co^{2+}	A	—	11.84
Ni^{2+}	A	—	13.12
Cu^{2+}	A	7.04	14.10
Zn^{2+}	A	—	12.21
	B	4.19	10.79
Cd^{2+}	A	—	10.83
	B	4.19	10.79
Pb^{2+}	A	—	12.73

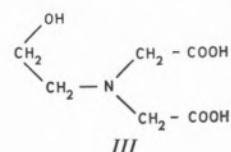
A — pCu method. B — pH titration.

available for the determination of its free concentration in the presence of other metals; copper is, however, ideally suitable for most purposes since it forms quite stable complexes and the copper electrode is remarkably selective.

4 — RESULTS AND DISCUSSION

The stability constants of the complexes of uramildiacetic acid with several metals are summarized in Tables I and II.

The values obtained in the present and previous works show clearly the strong complexing properties of this ligand, even towards potassium and beryllium ions. For the transition and other metals studied, uramildiacetic also behaves as a strong complexing agent, more so than common tetradentate complexones, such as nitrilotriacetic acid or the closely related N-hydroxyethyliminodiacetic acid (III), as compared with (II)



For the alkali and alkaline-earth metals the order of stabilities is



e. g., the order of the ionic potentials Z/r , as it is to be expected for Schwarzenbach's group A metals. The inversion in the pair Mg^{2+} , Ca^{2+} is quite common and usually ascribed to steric effects due to the small size of the Mg^{2+} ion, which appears to be in a critical range, since for Be^{2+} a remarkable increase in stability is verified.

For the transition metals the Irving-Williams' order of stabilities is verified, e. g.:



as it happens with most other analogous ligands. Figs. 1 and 2 show the correlations of the stability constants of the complexes formed by uramildiacetic acid (UDA) with those of the complexes formed by nitrilotriacetic acid (NITA) and N-hydroxyethyliminodiacetic acid (HEIDA) with the same metals. Both are linear and the slope of the straight lines obtained are close to 1.

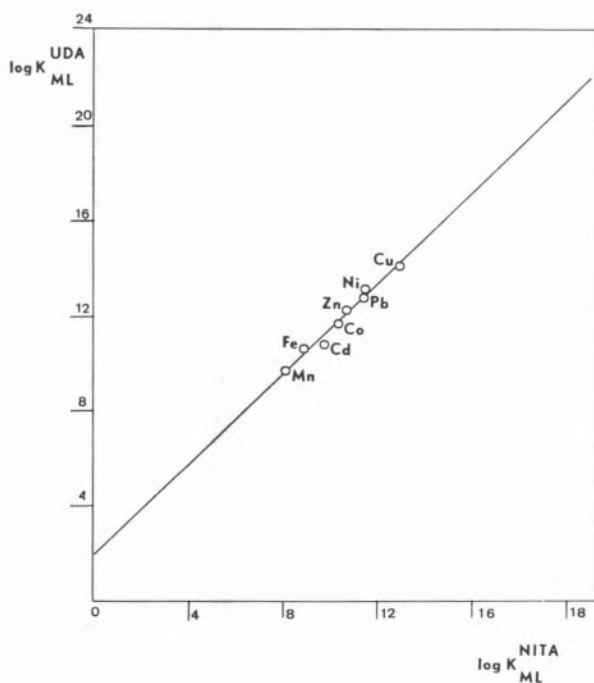


Fig. 1

Correlation of $\log K_{ML}$ for the complexes of uramildiacetic acid (UDA) with $\log K_{ML}$ for the corresponding complexes of nitrilotriacetic acid (NITA)

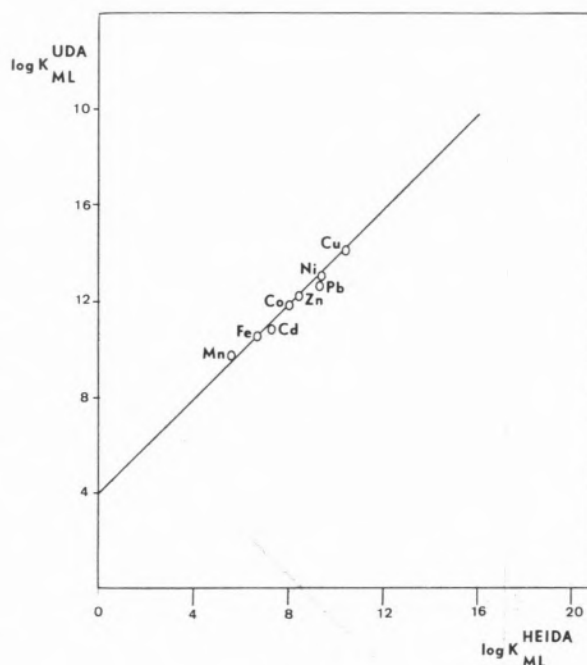
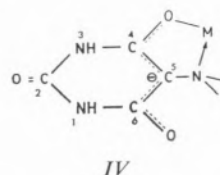


Fig. 2

Correlation of $\log K_{ML}$ for the complexes of uramildiacetic acid (UDA) with $\log K_{ML}$ for the corresponding complexes of hydroxyethyliminodiacetic acid (HEIDA).

Hence, no abnormality is apparent in the behaviour of uramildiacetic acid towards transition and related metals, except in the fact that its complexes are more stable by about 2.5 kcal/mole in the case of NITA and 5 kcal/mole in the case of HEIDA (ΔG° values).

This could correspond to the formation of a further chelation ring but resonance considerations and study of scale models show that it is impossible for this ligand to coordinate simultaneously its oxygen atoms in ring positions 4 and 6, to become pentadentate (see IV).



Hence, the increase in stability for the complexes of uramildiacetic acid is probably associated with the higher basicity of the coordinating oxygen atoms in position 4 or 6, as compared with oxygen atoms in carboxylate or alcohol groups, although other effects, related to a particularly

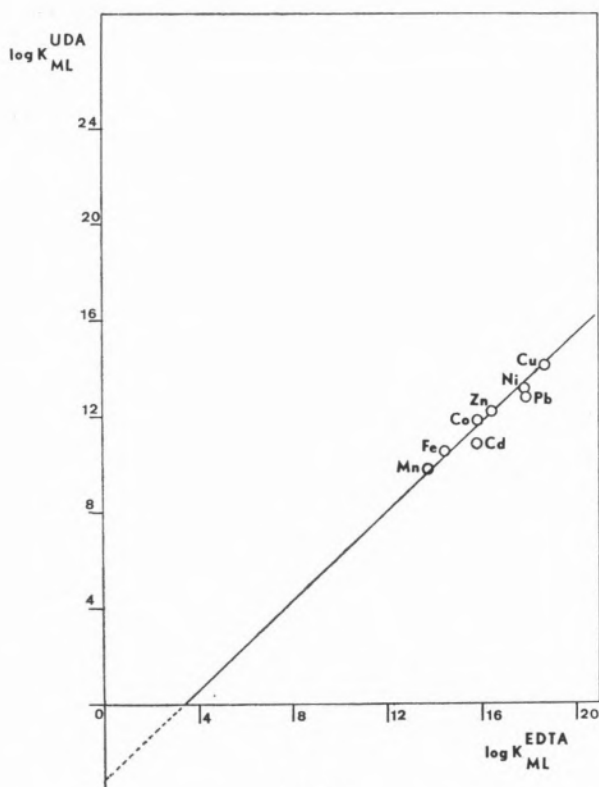


Fig. 3

Correlation of $\log K_{ML}$ for the complexes of uramildiacetic acid (UDA) with $\log K_{ML}$ for the corresponding complexes of ethylenediamine tetracetic acid (EDTA).

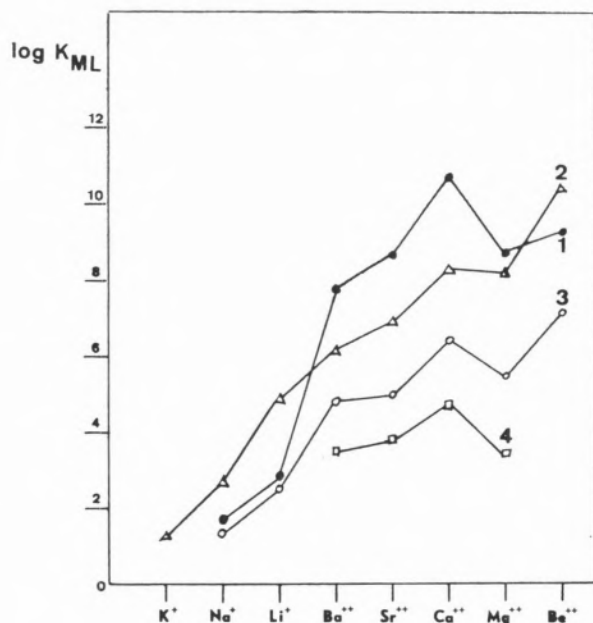


Fig. 4

Comparison of the stability constants ($\log K_{ML}$) of the complexes of ethylenediaminetetracetic acid (1), uramildiacetic acid (2), nitrilotriacetic acid (3) and hydroxyethyliminodiacetic acid (4) with alkali and alkaline-earth metals.

favourable conformation of the ligand, should also be taken into consideration. These effects may be quite important since they include the possibility of:

- more favourable metal-donors distances;
- more complete dehydration of metal ions;
- smaller loss in degrees of freedom when the translational vibrational and rotational energies of the ligand are converted into the corresponding energies of the complex species;
- saturation of the dielectric constant of water in the coordination sphere of the metals.

The comparison with ethylenediamine tetracetic-acid (EDTA), a more powerful ligand, also offers some interesting results — fig. 3.

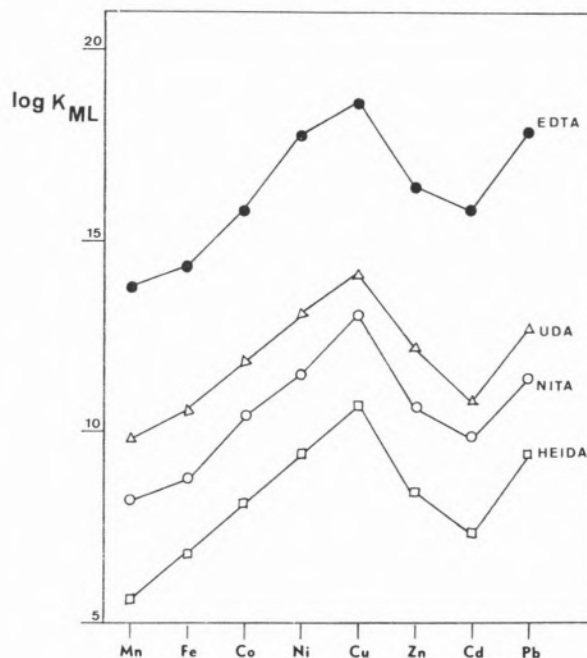


Fig. 5

Comparison of the stability constants ($\log K_{ML}$) of the complexes of ethylenediaminetetracetic acid (1), uramildiacetic acid (2), nitrilotriacetic acid (3) and hydroxyethyliminodiacetic acid (4) with transition metals, zinc, cadmium and lead.

The correlation is again a straight line but now a negative intercept is obtained showing that the EDTA complexes with the transition metals are indeed more stable, which is not the case when alkali and alkaline-earth metals are considered; figs. 4 and 5 summarize the situation and it is apparent that uramildiacetic acid behaves quite normally when compared with the other ligands.

The fact that the EDTA complexes of K^+ , Na^+ , Li^+ and Be^{2+} are less stable than the corresponding complexes of uramildiacetic acid, contrarily to what happens with the remaining metals, should only be ascribed to the inability of EDTA to fully use its coordinating capacity towards small ions such as Li^+ , Be^{2+} and also Mg^{2+} , or towards very weak acceptors like the other monovalent alkali metals. In both cases the reaction heat effects are insufficient to compensate the considerable entropy losses due to conformational stress in the complex species.

A compared thermodynamic study of the complexation reactions of the four representative ligands with certain selected metals will certainly help to clear up the problem and may lend support to this views. It may also throw some light on the factors responsible for the higher stabilities of the complexes of uramildiacetic acid, when compared with other tetradentate ligands, although in no way can these now be taken as rather mysterious or can the ligand be considered abnormal, as the comparison with EDTA restricted to alkali and alkaline-earth metals did indeed suggest.

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REFERENCES

1. Schwarzenbach, G., Kampitsch, E. and Steiner, R., *Helv. Chim. Acta*, **29**, 364 (1946).
2. Irving, H. and Silva, J. J. R. F., *J. Chem. Soc.*, 448 (1963).
3. Irving, H. and Silva, J. J. R. F., *J. Chem. Soc.*, 458 (1963).
4. Irving, H. and Silva, J. J. R. F., *J. Chem. Soc.*, 3308 (1963).
5. Schmid, R. and Reilley, C. N., *J. Am. Chem. Soc.*, **78**, 5513 (1956).
6. Schwarzenbach, G. and Biedermann, W., *Helv. Chim. Acta*, **31**, 456 (1948).

RESUMO

Apresenta-se um método de composição para determinar constantes de estabilidade de complexos utilizando um eléctrodo selectivo de cobre. O método é aplicado à determinação das constantes de estabilidade dos complexos do ácido uramildiacético com vários metais de transição, Zn, Cd, e Pb. Os resultados mostram que este ligando é particularmente poderoso entre os seus congêneres tetradentados, mas as anomalias verificadas relativamente aos metais alcalinos e ao Be, devem atribuir-se à incapacidade de adaptação do EDTA a iões de reduzidas dimensões ou com reduzida tendência para formar ligações covalentes, em resultado da sua configuração electrónica e baixo poder polarizante.