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THERMODYNAMICS OF CO-ORDINATION OF ALKALINE-EARTH CATIONS TO SOME C,C'-SUBSTITUTED EDTA DERIVATIVES

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Abstract – Heats of co-ordination of four EDTA derivatives with H^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{+2} have been determined. The ligands studied were: 1,2-diaminopropane-NNN'N'-tetraacetic acid (PDTA), 1,2-dimethyl-1,2-diaminoethane-NNN'N'-tetraacetic acid (DIMEDTA), 1,2-diaminocyclopentane-NNN'N'-tetraacetic acid (CPDTA), and 1,2-diamino-cyclohexane-NNN'N'-tetraacetic acid (CDTA). The measured reaction entropies are considered to be primarily determined by the replacement of hydrate water. The enthalpies of co-ordination cannot be interpreted in terms of simple electrostatic interactions between the central ion and ligand. A significant correlation between complex formation entropies and corresponding enthalpies has been observed.

INTRODUCTION

THERMOCHEMICAL data on the co-ordination of bipositive alkaline earth cations to the anions of aminopolycarboxylic acids have been reported [1–7], but they are still less numerous than the corresponding stability data. We report here the results of an investigation of the effects produced by aliphatic and alicyclic substitution in the ethylene chain of the EDTA molecule on chelating properties. The following ligands have been studied: 1,2-diaminopropane-NNN'N'-tetraacetic acid (PDTA), 1,2-dimethyl-1,2-diaminoethane-NNN'N'-tetraacetic acid (DIMEDTA), *trans*-1,2-diaminocyclopentane-NNN'N'-tetraacetic acid (CPDTA), and *trans*-1,2-diaminocyclohexane-NNN'N'-tetraacetic acid (CDTA).

EXPERIMENTAL

Materials. Standard metal salt solutions (*ca.* 1 M) were prepared from analytical reagent grade chlorides and were standardized by complexometric titration [8]. These solutions were also 1 M in KCl. Other common chemicals were of analytical reagent grade. Redistilled water was used throughout, CDTA was purchased from Koch-Light Laboratories, (±)-DIMEDTA [9] and CPDTA [10] were prepared according to published methods. The established method [11] for the preparation of (±)-

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1. R. A. Care and L. A. K. Staveley, *J. chem. Soc.* 4571 (1956).
2. L. A. K. Staveley and T. Randall, *Disc. Faraday Soc.* **26**, 157 (1958).
3. R. G. Charles, *J. Am. chem. Soc.* **76**, 5854 (1954).
4. F. F. Carini and A. E. Martell, *J. Am. chem. Soc.* **76**, 937 (1964).
5. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes, Chem. Soc. Spec. Publ.* No. 17. London (1964).
6. S. Boyd, A. Bryson, G. H. Nancollas and K. Torrance, *J. chem. Soc.* 7353 (1965).
7. G. H. Nancollas and A. C. Park, *Inorg. Chem.* **7**, 58 (1968).
8. G. Schwarzenback, *Complexometric Titrations*, p. 620. Methuen, London (1957).
9. H. Irving and O. A. Weber, *Unpublished results*, *cf.* [12, 16].
10. O. A. Weber, N. Paulić and Vl. Simeon, To be published.
11. F. P. Dwyer and F. L. Garvan, *J. Am. chem. Soc.* **81**, 2955 (1959).

PDTA could not be successfully applied. The procedure applied was essentially that recommended for optically active acids[11] but diferred from this in the separation of the final product. Ligand stock solutions (*ca.* 0·01 M) were standardized by potentiometric titration.

(±)-PDTA. NaOH (48 g) in ice cold water (100 ml) was added to chloroacetic acid (72 g) in water (30 ml). Precipitated sodium chloroacetate dissolved on the addition of redistilled (±)-1,2-diaminopropane (21 g). After one week standing at room temperature the solution was acidified with HCl (1 : 1) to a pH of 3·0 and evaporated to about half volume. The NaCl was filtered off and 400 ml of ethanol added. The resulting white, resin-like mass partly dissolved in 290 ml of glacial acetic acid. On the addition of benzene (200 ml) a white resin formed which could *not* be induced to crystallize. Therefore it was dissolved in a small volume of water and on acidification with HCl (1 : 1) white crystals of (±)-PDTA appeared. The product was recrystallized from water (1 : 250) and dried at 80°C. $C_{11}H_{18}N_2O_8$ (306·31) requires, C, 43·13%; H; 5·92%; N, 9·15%: found C, 42·97%; H, 6·08%; N; 9·07%. m.p. 235–6°C (*cf.* value of 236°C quoted by Irving and Conesa[12]).

Calorimetric measurements. The calorimeter has been described previously[13]. The desired reagent was contained in a thin-walled glass ampoule (*ca.* 3 ml volume) which could be instantaneously broken by the propeller of the stirrer. The heats of co-ordination have been determined by following procedure:

0·01 M solutions of the tetrapotassium salts (K_4Y) of the complexone were prepared by dissolution of the appropriate complexone (in H_4Y form) in an equivalent amount of carbonate-free KOH[14] followed by the addition of sufficient KCl to adjust the concentration of the latter to 1·00 M. These solutions were prepared and stored under a nitrogen atmosphere. 100·0 ± 0·1 ml of such a solution was pipetted (under nitrogen) into the reaction vessel of the calorimeter, which had been flushed with CO_2-free nitrogen gas (under a suitable cover) for 30 min. The ampoule was charged with 1·0 ± 0·002 ml of Molar metal salt stock solution (containing the same salt background) and the whole apparatus assembled and placed in a thermostat bath (21·0 ± 0·01°C). After 30 min equilibration the temperature of the calorimeter contents was adjusted to 20·0 ± 0·01°C and a calibration experiment was performed. The temperature was again adjusted to 20°C and the reaction followed. The details of the procedure for recording time-temperature curve are available elsewhere[13]. The pH of the solution was measured before and after each experiment because it dropped markedly on complex formation. The pH-meter (Radiometer pHM 4c, equipped with a glass electrode, G 202 B, for use in highly alkaline media) was standardized (in terms of hydrogen ion concentrations rather than activities) with the solutions of known H^+ concentration (0·5 mM $HClO_4$ and KOH solutions) so that the linearity of the electrode function was checked. The pH of K_4Y (whether or not containing the metal salt) was not very sensitive to exposure to atmospheric CO_2. Thus, in 10 min it changed by only 0·01–0·02 units.

The heats of protonation were measured in an analogous way (in this case the ampoule was charged with 1 M HCl standardized potentiometrically against potassium hydrogen phthalate). The quantity of HCl was chosen such that no appreciable quantity of the species H_2Y^{2-} was present after such an experiment.

No detectable heats of dilution could be observed.

Units and calculations. Energies are expressed in thermochemical calories (1 cal = 4·1840 abs. j), and the entropies in cal mole^{-1} deg^{-1}.

The corrected temperature changes were evaluated from the time-temperature curves by Dickinson's method[15].

It was assumed that the co-ordination reactions studied could be represented by the equation:

$$xY^{4-} + zHY^{3-} + (x+z)\,M^{2+} \rightleftharpoons (x+z)\,MY^{2-} + zH^{+} + q. \qquad (1)$$

This equilibrium was considered as quantitatively displaced to the right under the conditions employed. The composition of the solution before and after mixing could be calculated from the respective pH's and the formation constant of HY^{3-}. Total concentrations of metal salt and the complexone were equal. The measured heat, q, was corrected for the heat of dissociation of HY^{3-} and for the heat

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12. H. M. N. H. Irving and J. P. Conesa, *J. inorg. nucl. Chem.* **26**, 1945 (1964).
13. Vl. Simeon and M. Tkalčec, *Lab. Pract.* **17**, 1353 (1968)
14. G. Schwarzenbach and W. Biedermann, *Helv. chim. Acta* **31**, 331 (1948).
15. J. M. Sturtevant, Calorimetry, In *Physical Methods of Organic Chemistry* (Edited by A. Weissberger), p. 732. Interscience, New York (1949).

of formation of water in order to obtain the net heat of complex formation. This was recalculated to 1 mole of the complex and the sign changed in order to obtain the molar enthalpy change.

Metal chelate stability constants and acid dissociation constants have been determined in 0·1 M KCl[9, 10, 17]. Since the sensitivity of the calorimeter (about 0·25 cal/mm galvanometer deflection) did not permit work at concentrations lower than about 0·01 M, an ionic medium of high ionic strength (1 M KCl) has been used to keep the activity coefficients constant. The equilibrium constants have been recalculated by applying Harned's rule[19].

RESULTS AND DISCUSSION

The determined molar reaction enthalpies were considered to be approximately equal to the respective standard quantities because no heats of dilution could be observed. The standard state is a hypothetical ideal molar solution in the 1 M KCl solvent. The measured ΔH° values, together with appropriate free energies and entropies, are shown in Table 1.

Table 1. Thermodynamic quantities for co-ordination reactions of PDTA, DIMEDTA, CPDTA, and CDTA (molar scale, 20°C, solvent 1 M aqueous KCl)

Complexone	Cation	$-\Delta G°$ (kcal.mole^{-1})	$\Delta H°$ (kcal.mole^{-1})	$\Delta S°$ (kcal.mole^{-1}deg.$^{-1}$)
PDTA	H^+	14·03*	−6·1	27·1
	Mg^{2+}	12·88*	+1·00	47·3
	Ca^{2+}	15·09*	−3·02	41·2
	Sr^{2+}	12·39*	−0·55	40·4
	Ba^{2+}	11·04*	−1·94	31·0
DIMEDTA	H^+	14·41*	−5·6	30·1
	Mg^{2+}	11·35*	+3·80	51·7
	Ca^{2+}	12·34*	−3·54	30·0
	Sr^{2+}	9·67*	+0·37	31·7
	Ba^{2+}	8·09*	−1·83	21·4
CPDTA	H^+	13·68†	−6·44	24·7
	Mg^{2+}	12·54†	+4·37	57·7
	Ca^{2+}	15·25†	−4·87	35·4
	Sr^{2+}	12·78†	−0·32	42·5
	Ba^{2+}	11·64†	−2·63	30·7
CDTA	H^+	15·84‡	−6·65§	31·3
	Mg^{2+}	13·96‡	+1·89	54·1
	Ca^{2+}	17·05‡	−5·55	39·2
	Sr^{2+}	14·11‡	−0·56	46·2
	Ba^{2+}	10·88‡	−0·91	34·0

*Ref.[9], cf. [12, 16].
†Ref.[10].
‡Ref.[17].
§Ref.[18].

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16. R. D. Gillard and H. M. Irving, *Chem. Rev.* **65**, 603 (1958).
17. G. Schwarzenbach and H. Ackermann, *Helv. chim. Acta* **32**, 1682 (1949).
18. G. Anderegg, *Helv. chim. Acta* **46**, 1833 (1963).

Molar enthalpies of reaction were reproducible to between ±0·05 and ±0·1 kcal mole^{-1}. Since the uncertainty of the free energy data[9, 10, 17] is claimed to be only slightly more than 0·01 kcal mole^{-1}, this can be neglected and, consequently, the entropies of reaction (calculated from the Gibbs–Helmholtz equation) should be reliable to ± 0·5 *cal mole*$^{-1}$ deg^{-1}.

The heats of formation of alkaline-earth complexes with CDTA have been determined previously by others[18, 20, 21]. It can be seen from the data in Table 2 that there is little agreement between published results. It is, however, evident that the values determined indirectly from the temperature dependence of the stability constants[21] deviate appreciably from the others. The values obtained during this work fall in most cases between those quoted by Anderegg [18] and Reilley *et al.* [20] being, except for strontium, closer to those of the latter authors. A rigorous comparison is difficult because of the different experimental conditions used by different workers.

Table 2. Enthalpy changes for co-ordination reactions of CDTA

Cation	Temp. °C	Medium	$\Delta H°$	Ref.	Method
Mg^{2+}	20	0·1(KNO_3)	+3·80	[18]	calorim.
	25	0·1(KNO_3)	−1·5	[21]	temp. coeff.
	25	0·1(KNO_3)	+1·6	[20]	calorim.
	20	1·0(KCl)	+1·89	this work	calorim.
Ca^{2+}	20	0·1(KNO_3)	−3·70	[18]	calorim.
	25	0·1(KNO_3)	−11	[21]	temp. coeff.
	25	0·1(KNO_3)	−6·2	[20]	calorim.
	20	1·0(KCl)	−5·55	this work	calorim.
Sr^{2+}	20	0·1(KNO_3)	−0·74	[18]	calorim.
	25	0·1(KNO_3)	−6·7	[21]	temp. coeff.
	25	0·1(KNO_3)	−3·6	[20]	calorim.
	20	1·0(KCl)	−0·56	this work	calorim.
Ba^{2+}	20	0·1(KNO_3)	+0·33	[18]	calorim.
	25	0·1(KNO_3)	−2·2	[20]	calorim.
	20	1·0(KCl)	−0·91	this work	calorim.

Staveley and co-workers[1, 2] have reported that the entropies of formation of EDTA complexes with alkaline earths can be correlated with the respective Pauling's[22] ionic radii and have explained their results using the "iceberg concept" of Evans and Frank[23]. A quantitative semi-empirical approach has been developed by Yatsimirskii[24]:

19. G. N. Lewis and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer, 2nd Edn., p. 568, ff. 643. McGraw-Hill, New York 1961.
20. D. L. Wright, J. H. Holloway and C. N. Reilley, *Analt. Chem.* 37, 884 (1965).
21. T. A. Bohigian and A. E. Martell, *Unpublished results, cf.* [5], p. 690.
22. L. Pauling, *Nature of the Chemical Bond*, 2nd Edn, p. 505. Cornell Univ. Press, Ithaca (1960).
23. M. Evans and H. Frank, *J. chem. Phys.* 13, 507 (1945).
24. K. B. Yatsimirskii, *Usp. Khim.* 22, 410 (1953).

$$\Delta S = 0{\cdot}1\,L + A, \qquad (2)$$

L denotes the heat of hydration of the metal ion and A is a constant. Others have evaluated the heats of hydration of a number of metal ions[25] and proposed a modified form of the above equation[26]:

$$\Delta S = 66{\cdot}2/(r + 0{\cdot}62) + A. \qquad (3)$$

Here r stands for the ionic radius of the metal ion. By subtracting the hydration-heat term from the experimental value of ΔS we have calculated the value of A for each metal-ligand pair. Values of A calculated by means of Equation (2) conformed approximately to a Student's distribution with a mean of $+2{\cdot}8$ and 99 per cent confidence limits of $\pm 4{\cdot}3$. Analogously, Equation (3) yielded values of $-1{\cdot}2 \pm 2{\cdot}3$. Thus, in both cases A is not significantly different from zero. Both equations are correct but somewhat crude approximations. They do, however, fail to predict the order of entropies of formation of the complexes which has been found to be, almost invariably, Mg > Sr ≥ Ca > Ba. As could be expected, the entropies of chelation are primarily determined by the water displacement which takes place during complex formation.

Considering the entropies of reaction for any metal with the four ligands studied and for EDTA[1] it will be observed that their order is CDTA > CPDTA ≥ PDTA > DIMEDTA > EDTA. With the exception of DIMEDTA this is the order of decreasing substitution. The ligand molecules become more rigid with increasing substitution so that the loss of conformational entropy (which takes place on complex formation) gradually decreases and the entropies of formation consequently increase.

While the entropies of formation can be roughly predicted on the ground of relatively simple electrostatic considerations this is not so for the corresponding enthalpies. One would expect, provided the ligands are always co-ordinated in a similar way, that the complex formation would become more exothermic with decreasing ionic radius and with increasing cation charge.

If the electrostatic metal-ligand interactions were virtually decisive the order of exothermicity of complex formation should be Mg > Ca > Sr > Ba. The actual order for the ligands studied, as well as for EDTA[1] is invariably Ca > Ba > Sr > Mg, i.e. nearly reversed.

It is interesting to note that there is a rough but highly significant ($P = 0{\cdot}001$) correlation between the observed ΔH and ΔS values. This correlation, together with the regression line and 95 per cent confidence limits, is shown in Fig. 1. The regression equation is

$$\Delta S = 2{\cdot}29\,\Delta H + 42. \qquad (4)$$

A correlation of this kind has been observed by others[27, 28] for the heats and entropies of vaporization and solution of a number of organic compounds. Care

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25. V. P. Vasil'ev, E. K. Zolotarev, A. F. Kapustinskii, K. P. Mishchenko, E. A. Podgornaya and K. B. Yatsimirskii, *Zh. fiz. Khim.* **34**, 1763 (1960).
26. V. P. Vasil'ev, *Zh. neorg. Khim.* **3**, 2060 (1958).
27. J. A. V. Butler, *Trans. Faraday Soc.* **33**, 229 (1937).
28. I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.* **34**, 1445 (1938).

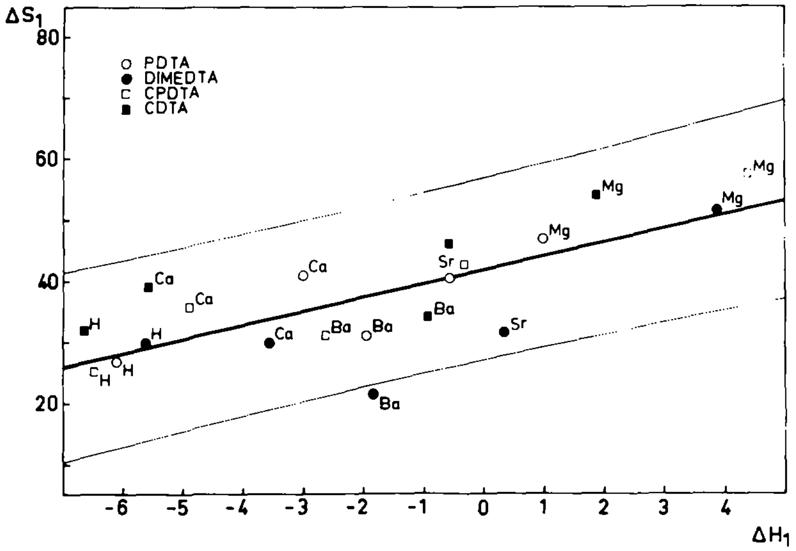

Fig. 1. Correlation between complex formation enthalpies and entropies (95 per cent confidence limits are shown.)

and Staveley[1] have also observed that for EDTA chelate the higher reaction entropies of reaction are in some way associated with less exothermic heats of reaction. Although the number of points is not very large, so that the correlation given by Equation (4) may be purely fortuitous, it is to be noted that this equation gives a nearly correct order for the exothermicity of alkaline earth complex formation with the ligands studied.

It has been reported[18, 20] that the formation of CDTA complexes is more endothermic than that of the corresponding EDTA complexes and it is proposed that this "endothermic effect" should increase with the size of the cation. This confirmed with CDTA, but only partly with the other ligands, where the order of "endothermic effect" is Mg < Ca < Sr > Ba.