METAL COMPLEXES OF THIOPOLYCARBOXYLIC ACIDS. VIII.*

EQUILIBRIA IN SOLUTIONS OF THE COMPLEXES OF DIVALENT METALS WITH ETHYLIDENETETRATHIOTETRAACETIC ACID

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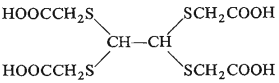
Equilibria in systems containing divalent cations (Mn, Fe, Co, Ni, Cu) and ethylidenetetrathiotetraacetic acid were studied by measuring the pH at 25°C and $I = 0{\cdot}1$. It was found that mononuclear (protonated) and binuclear complexes are formed and their stability constants were calculated. Several conclusions about the structure of these complexes were made.

In a previous work[1], we found that in solutions containing a divalent cation of a transition metal and ethylidenetetrathiotetraacetic acid complicated equilibria are formed among mixed and polynuclear complexes. Solutions of the ligand alone and of its copper and nickel complexes were studied by Saini and coworkers[2] and by Geary and Malcolm[3]. Equilibria in the system Cu^{2+}–H_4E were determined by the method of trial and error, from which even an approximate estimate of the magnitude of the error in the stability constants could not be obtained. The conditions, under which Geary and Malcolm worked, ensured that only the NiE^{2-} and $NiHE^-$ complexes were present in solution. The association of protons in solutions of the ligand alone is considerably simpler and the corresponding acid dissociation constants are known with sufficient accuracy[2,3].



$= H_4E$

This work is concerned with a detailed study of the system Me^{2+} (Mn, Fe, Co, Ni, Cu)–H_4E and provides stability constants for the complexes produced calculated employing statistical treatment of the potentiometric titration curves.

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EXPERIMENTAL

Reagents and apparatus. The preparation of the ligand and the metal perchlorates, as well as the instruments used, are given in the works[1,4]. Calculations were made on the IBM 7040 computer.

Measuring method. Series of potentiometric titrations were carried out at 25 ± 0·1°C and $I = 0{\cdot}1$ ($NaClO_4$) in an atmosphere of pure nitrogen, using solutions from which dissolved oxygen and carbon dioxide were removed. In all cases, 50 ml of $5 \,.\, 10^{-3}$M solution of H_4E containing subsequently 0; $2{\cdot}5 \,.\, 10^{-3}$; $5 \,.\, 10^{-3}$; $1 \,.\, 10^{-2}$; $2{\cdot}5 \,.\, 10^{-2}$ mol/l $Me(ClO_4)_2$ were titrated with 0·1000M-NaOH (free of carbonates), in 0·2 ml increments, to pH 11 or to initiation of precipitation of $Me(OH)_2$. The titrations were repeated at least twice with a precision of ±0·01 pH and ±0·002 ml. The details of the apparatus used have already been published[4].

Calculations. Average pH values were recalculated to $-\log [H^+]$ using tabulated activity coefficient values for hydrogen ions under these conditions[5]. The $-\log [H^+]$ values were then handled in the following manner: *1*) From the titrations in the absence of Me^{2+} were calculated the protonization curve of the ligand, $\bar{n}_H$ *vs* $-\log [H^+]$, and approximate dissociation constant values using the programme described by Romary, Donelly and Andrews[6]. *2*) The dissociation constants were refined by the non-linear least squares method using the SGOCS programme[7]. *3*) Using the refined dissociation constants, the formal $\bar{n}$ *vs* $-\log [E^{4-}]$ curves were calculated from titrations in the presence of Me^{2+}.

Since the shape of the $\bar{n}$ *vs* $-\log [E^{4-}]$ curves indicates the formation of polynuclear and mixed complexes (Fig. 1), the titration data were directly processed by the SCOGS programme. Simultaneously, the formation of various groups of complex particles was assumed, which were changed by the method of trial and error until the computing iteration converged to a minimum residual[7,8]. As initial trial constant estimates, the values obtained in the work[1] were used.

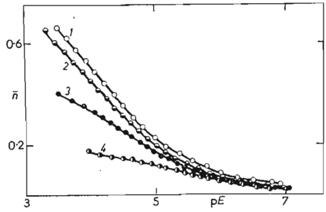

FIG. 1

The Shape of the Function $\bar{n}$ *vs* $-\log [E^{4-}] = pE$ for the Nickel Complexes

H_4E: $5 \,.\, 10^{-3}$M, $Ni(ClO_4)_2$: *1* $2{\cdot}5 \,.\, 10^{-2}$M, *2* $1 \,.\, 10^{-2}$M, *3* $5 \,.\, 10^{-3}$M, *4* $2{\cdot}5 \,.\, 10^{-3}$M.

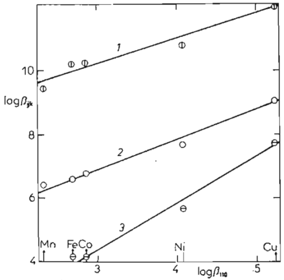

FIG. 2

The Dependence of $\log \beta_{ijk}$ on $\log \beta_{110}$ for Individual Metals

1 β_{210}, *2* β_{111}, *3* β_{112}.

RESULTS

The titration data are given in Table I. As was determined from calculations, the optimal characterization of this data is a set of four simultaneously formed complexes independent of the type of metal (the overall stability constant symbols are given in brackets):

MeE^{2-}	(β_{110})	
Me_2E	(β_{210})	undetectable with Mn
$HMeE^-$	(β_{111})	
H_2MeE	(β_{112})	

The final constant values are gathered in Table II, together with the stability constants of the protonated complexes $H_iE^{(4-i)-}$ (β_{01i}).

DISCUSSION

The trend of the stability constants in the Mn–Cu series is consistent with the Irving–Williams series, within experimental error. The absolute constant values are approximately the same as with simple thiopolycarboxylic acids[4,9,10] and reflect a relatively weak interaction between the transition metals of the first series and sulphidic sulphur, as well as the tendency of the ethylidenetetrathiotetraacetate ion against hexa-coordination.

Comparison of the stability constants with the values so far given in the literature indicates relatively good agreement within the slightly differing experimental conditions, especially where the data were statistically treated[3]. Our previous results[1], based on the assumption that only the MeE^{2-} complex is formed in the presence of excess ligand, are also comparable with the results of this work, as long as it was not necessary to use too extensive extrapolation of the corresponding straight lines during graphical treatment (especially with Mn). It is obvious that, in cases where several complexes of limited stability coexist in the system, the best method of solving the equilibria is by statistical treatment of large amounts of data covering a wide range of reagent ratios.

In Fig. 2, values of the logarithms of the constants of binuclear and mixed complexes are plotted *versus* $\log \beta_{110}$ for individual metals. The dependences of $\log \beta_{210}$, β_{111}, and β_{112} on $\log \beta_{110}$ are linear, from which it follows that the bonding type of the second metal ion and of both protons on the MeE^{2-} complex is analogous for all the metals studied. By extrapolation of the straight line for β_{210}, the value of the consecutive stability constant of the Mn_2E complex can be estimated, giving $K_2 = 10^{0.9}$. Thus the concentration of the given complex was so low in the studied solutions that it was not possible to identify it at all during processing of the titration curves.

TABLE I

pH Values During the Titration of H_4E and $H_4E + Me(ClO_4)_2$ Mixtures

$H_4E = 5 \,.\, 10^{-3}$M; NaOH = 0·1000M; $Me(ClO_4)_2 = 2{\cdot}5 \,.\, 10^{-3}$M (A), $5 \,.\, 10^{-3}$M (B), $1 \,.\, 10^{-2}$M (C), $2{\cdot}5 \,.\, 10^{-2}$M (D).

NaOH	Mn				Fe				Co				Ni				Cu				0
ml	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	
0·0	2·70	2·68	2·70	2·72	2·67	2·68	2·66	2·65	2·68	2·66	2·66	2·64	2·66	2·65	2·63	2·56	2·56	2·49	2·40	2·30	2·70
0·2	2·74	2·72	2·74	2·76	2·71	2·72	2·71	2·69	2·72	2·70	2·70	2·67	2·70	2·68	2·66	2·59	2·59	2·51	2·42	2·32	2·74
0·4	2·79	2·77	2·78	2·80	2·76	2·76	2·75	2·73	2·76	2·75	2·74	2·71	2·74	2·72	2·69	2·62	2·62	2·54	2·44	2·34	2·78
0·6	2·83	2·81	2·82	2·83	2·80	2·81	2·79	2·76	2·81	2·79	2·79	2·75	2·78	2·76	2·72	2·64	2·65	2·56	2·46	2·35	2·83
0·8	2·87	2·85	2·86	2·87	2·84	2·84	2·83	2·80	2·85	2·84	2·83	2·79	2·82	2·80	2·75	2·67	2·68	2·58	2·48	2·37	2·88
1·0	2·92	2·90	2·91	2·91	2·89	2·89	2·87	2·84	2·90	2·88	2·87	2·83	2·86	2·83	2·77	2·69	2·70	2·61	2·50	2·39	2·92
1·2	2·96	2·94	2·95	2·95	2·94	2·94	2·91	2·88	2·94	2·92	2·91	2·86	2·90	2·87	2·82	2·72	2·73	2·63	2·52	2·40	2·97
1·4	3·01	2·99	2·99	2·98	2·98	2·98	2·96	2·92	2·99	2·97	2·95	2·90	2·94	2·90	2·85	2·74	2·76	2·66	2·54	2·42	3·01
1·6	3·05	3·03	3·03	3·02	3·02	3·02	3·00	2·95	3·03	3·01	3·00	2·94	2·97	2·93	2·87	2·77	2·79	2·68	2·57	2·44	3·06
1·8	3·10	3·07	3·07	3·06	3·07	3·07	3·04	2·99	3·07	3·05	3·04	2·98	3·01	2·97	2·90	2·79	2·82	2·70	2·58	2·45	3·11
2·0	3·15	3·12	3·11	3·10	3·11	3·11	3·08	3·03	3·13	3·10	3·08	3·01	3·04	3·00	2·93	2·82	2·85	2·73	2·60	2·47	3·16
2·2	3·19	3·16	3·16	3·13	3·16	3·16	3·12	3·06	3·17	3·14	3·11	3·05	3·08	3·03	2·96	2·84	2·88	2·75	2·62	2·49	3·20
2·4	3·23	3·21	3·20	3·17	3·21	3·20	3·17	3·10	3·21	3·17	3·16	3·07	3·11	3·06	2·99	2·86	2·92	2·78	2·64	2·51	3·24
2·6	3·28	3·25	3·24	3·21	3·25	3·24	3·21	3·13	3·26	3·22	3·20	3·11	3·15	3·09	3·01	2·88	2·95	2·80	2·66	2·53	3·29
2·8	3·32	3·29	3·28	3·24	3·30	3·28	3·25	3·17	3·30	3·27	3·23	3·15	3·19	3·12	3·04	2·90	2·98	2·83	2·68	2·54	3·33
3·0	3·36	3·34	3·32	3·28	3·34	3·32	3·29	3·21	3·34	3·31	3·27	3·19	3·22	3·16	3·06	2·93	3·01	2·85	2·70	2·56	3·38
3·2	3·40	3·37	3·36	3·32	3·38	3·36	3·32	3·24	3·37	3·34	3·31	3·22	3·26	3·18	3·09	2·95	3·05	2·88	2·72	2·58	3·42
3·4	3·44	3·41	3·40	3·35	3·42	3·40	3·36	3·28	3·41	3·38	3·34	3·26	3·29	3·21	3·12	2·97	3·08	2·90	2·75	2·60	3·46
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4·4	3·64	3·60	3·58	3·51	3·61	3·59	3·54	3·43	3·60	3·56	3·51	3·40	3·45	3·35	3·25	3·08	3·27	3·04	2·86	2·70	3·66
4·6	3·68	3·64	3·61	3·55	3·65	3·62	3·57	3·46	3·64	3·60	3·54	3·43	3·48	3·38	3·27	3·10	3·31	3·07	2·88	2·72	3·71
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5·0	3·76	3·72	3·69	3·61	3·73	3·70	3·64	3·52	3·72	3·67	3·61	3·49	3·55	3·43	3·32	3·14	3·39	3·12	2·93	2·77	3·79
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5·6	3·88	3·83	3·80	3·72	3·84	3·81	3·74	3·62	3·83	3·77	3·70	3·58	3·65	3·52	3·39	3·22	3·52	3·23	3·02	2·85	3·91
5·8	3·92	3·87	3·84	3·75	3·89	3·84	3·78	3·64	3·87	3·81	3·74	3·61	3·69	3·55	3·42	3·25	3·56	3·26	3·05	2·87	3·96
6·0	3·96	3·91	3·88	3·78	3·93	3·88	3·81	3·68	3·91	3·85	3·77	3·64	3·72	3·58	3·45	3·28	3·61	3·30	3·08	2·90	4·00
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6·4	4·04	4·00	3·96	3·86	4·01	3·96	3·88	3·74	4·00	3·93	3·84	3·70	3·80	3·65	3·50	3·33	3·71	3·37	3·14	2·96	4·09
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8·4	4·59	4·54	4·48	4·34	4·55	4·48	4·37	4·16	4·55	4·44	4·31	4·12	4·36	4·08	3·89	3·70	4·35	3·87	3·61	3·41	4·65
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9·2	4·95	4·90	4·82	4·68	4·91	4·82	4·70	4·45	4·94	4·81	4·65	4·47	4·76	4·44	4·20	4·02	4·77	4·25	3·96	3·74	5·03
9·4	5·09	5·04	4·95	4·81	5·03	4·96	4·82	4·56	5·10	4·96	4·79	4·62	4·91	4·58	4·34	4·14	4·93	4·41	4·10	3·88	5·19

TABLE II

Values of the Logarithms of the Stability Constants

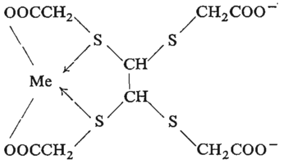
The errors given represent three times the standard deviation.

Constant	Mn	Fe	Co	Ni	Cu
β_{110}	2·32 ± 0·02	2·68 ± 0·03	2·86 ± 0·03	4·08 ± 0·01	5·35 ± 0·02
β_{210}	—	4·18 ± 0·06	4·12 ± 0·13	5·65 ± 0·05	7·75 ± 0·03
β_{111}	6·41 ± 0·03	6·59 ± 0·04	6·77 ± 0·03	7·71 ± 0·02	9·07 ± 0·02
β_{112}	9·48 ± 0·19	10·22 ± 0·05	10·23 ± 0·06	10·81 ± 0·03	12·02 ± 0·03
Residual, ml	0·048	0·050	0·054	0·042	0·070

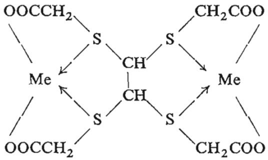
β_{011} 4·62 ± 0·01; β_{012} 8·59 ± 0·01; β_{013} 12·15 ± 0·01; β_{014} 15·05 ± 0·01; residual 0·015 ml.

Overall constant of the species log β_{ijk}	Reference (ref.[2]) (20°C)	(ref.[3]) (25°C)	This work (25°C)
HE^{3-}	4·93	4·57	4·62
H_2E^{2-}	8·92	8·53	8·59
H_3E^-	12·48	12·07	12·15
H_4E	15·72	14·96	15·05
NiE^{2-}	—	4·17	4·08
$HNiE^-$	—	7·45	7·71
CuE^{2-}	5·00	5·72	5·35
Cu_2E	7·33	—	7·75
$HCuE^-$	9·03	—	9·07
H_2CuE	12·16	—	12·02

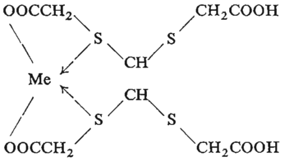
The ratio of the Me_2E and MeE^{2-} stability constants is considerably lower than that corresponding to the rule of stability consecutiveness based on purely statistical concepts. Similarly, both protons in the mixed H_2MeE complexes are acidified very little compared to H_4E. The probable explanation is that the second transition metal ion, or both protons, are bonded to the opposite end of the ligand molecule than the first metal ion, so that they affect each other very little:



(MeE^{2-})



(Me$_2$E)



(H$_2$MeE)

This structural concept agrees with the previous preparation results, as well as with the position of the ligand in the spectrochemical series[1].

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