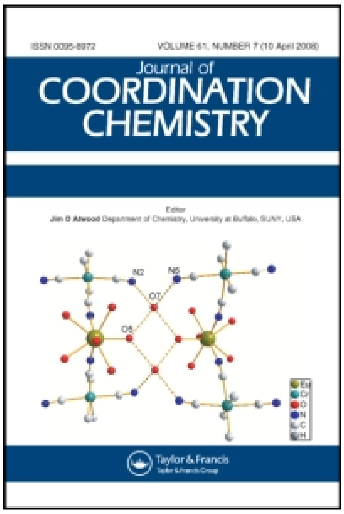

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INTERPRETATION OF STABILITY CONSTANTS OBTAINED FROM ELECTROMETRIC DATA FOR ZINC TRIAD CATION-ETHANEDIAMINE COMPLEXES IN AQUEOUS SOLUTION. THE PARADOX OF COMPLEX EQUIVALENCE, THEIR ACID PROPERTIES AND CHELATION EFFECTS

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INTERPRETATION OF STABILITY CONSTANTS OBTAINED FROM ELECTROMETRIC DATA FOR ZINC TRIAD CATION-ETHANEDIAMINE COMPLEXES IN AQUEOUS SOLUTION. THE PARADOX OF COMPLEX EQUIVALENCE, THEIR ACID PROPERTIES AND CHELATION EFFECTS

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Some basic elements have been developed for the interpretation of stability constants of metal-ion complexes obtained from electrometric data alone. Zinc triad cation-1,2-ethanediamine systems have been considered. The paradox of electrometric equivalence of complexes has been discussed. Relations for electrometric apparently indistinguishable complexes have been derived and acid properties of the protonated complexes and chelation effects have been estimated on the basis of Bjerrum's and Schwarzenbach's empirical relations. The precision of the basic electrometric methods (potentiometry with amalgam and Hg electrodes, DC and tast polarography) and its influence on the possibility of the selection of a statistically unique model for complexation equilibria has been evaluated. Models including complexation with the monoprotonated form of 1,2-ethanediamine have been refined. A definitive model for complexation equilibria of zinc family cations in acid and near neutral aqueous solutions of 1,2-ethanediamine has been proposed.

Keywords: Stability constants, zinc, cadmium, mercury, 1,2-ethanediamine, speciation, indistinguishable complexes

INTRODUCTION

The chelate complexation equilibria of 1,2-ethanediamine with metal cations have been well recognized, mainly due to Bjerrum's investigations.[1-8] However, results of studies on protonated non- and partly chelated 1,2-ethanediamine complexes not only vary in the values of the appropriate stability constants, but models of complexation equilibria show fundamental disagreement.[8-19]

The complexing 1,2-ethanediamine forms (enH^+, en) are a coupled acid-base pair. This evident fact is the decisive difference between protonated complexes of such chelating ligands and classical ternary complexes. Moreover, it makes the determination of the full set of the stability constants much more complicated and some consequences for the determination of a unique model of complexation equilibria are still not understood.

Analysis of the acid-base equilibria of 1,2-ethanediamine and of the complexation equilibria of the zinc triad cations with the complexing species of ethanediamine, which is reported here, reveals that for labile systems it is impossible to distinguish between two types of complexes (even for error-free data): (i) $M(en)_i(enH)_j$ and $M(en)_{(i-a)}(enH)_{(j+a)}(OH)_a$, upon the basis of static electrometric data alone, and (ii) $M(en)_i(enH)_j$ and $M(en)_{(i-a)}(enH)_{(j+2a)}$ or between $M(en)_i(enH)_j$ and $M(en)_{(i-a)}(OH)_{(j+2a)}$, upon the basis of electrometric measurements for a single series with constant total $enH_2(ClO_4)_2$ concentration. In the former case the undistinguishability of the appropriate pairs of complexes is electrometrically real, while that of the latter is apparent. It should be noted that for ammonia systems the potentiometric equivalence of the respective amide or hydroxide complexes was first recognized by Bjerrum (Ref. 1, p. 15). Watters and Mason have mentioned the potentiometric equivalence of chelate $Hg(en)^{2+}$ and mixed $Hg(enH)(OH)^{2+}$ species (Ref. 13, p. 29). The apparent undistinguishability of the respective complexes which may be formed in solutions has not been reported either in the original papers or in a recent critical review.[20]

Here both types of the undistinguishability are discussed in detail. The relations which disclose the apparent undistinguishability of complexes are given, and the precision of the main electrochemical methods and the possibility of obtaining a statistically unique model of complexation equilibria are estimated. Existing models of complexation equilibria have been verified. The acid properties of the protonated zinc triad cations—ethanediamine complexes have also been discussed. Since ethanediamine is the standard chelating ligand, the relations reported here have general character and can be applied to the interpretation of results for other systems.

EXPERIMENTAL

Potentiometric measurements were performed by means of an Orion Digital Ionanalyser (Research Model 701A) using glass electrodes (Radiometer G 202C), Kawai-type (J-shape) Zn(Hg), Cd(Hg) and Hg electrodes, and a Kawai (Ag/AgCl) reference half cell, as described previously.[14,19] DC polarographic measurements were performed by means of a Radelkis OH-105 polarograph and a Laboratorni Pristroje Polarographic Analyser (PA-2, PA-3 and PA-4). Tast polarograms were measured with a Princeton Applied Research potentiostat/galvanostat (Model 273A) equipped with an IBM PS/2 computer which recorded the waves and, separately, the respective supporting electrolyte background currents. The polarographic waves (after a numerical subtraction of background currents) were elaborated by means of a logarithmic analysis using a weighted least-squares computer procedure.

All other potentiometric, polarographic and other equipment, chemicals and computer programmes used have been described previously.[14–17,19]

RESULTS AND DISCUSSION

The Nature of the Complexation of Zinc Triad Cations in Aqueous 1,2-ethanediamine Solutions

Two acid-base forms of 1,2-ethanediamine, en, enH^+, can be involved in complexation with metal cations in aqueous solutions with $pH < \log(k_1^H k_{12}^H)^{1/2}$ and $C_M \ll C_{enH_2(ClO_4)_2}$ (Figure 1); k_1^H, k_{12}^H are the successive protonation constants of

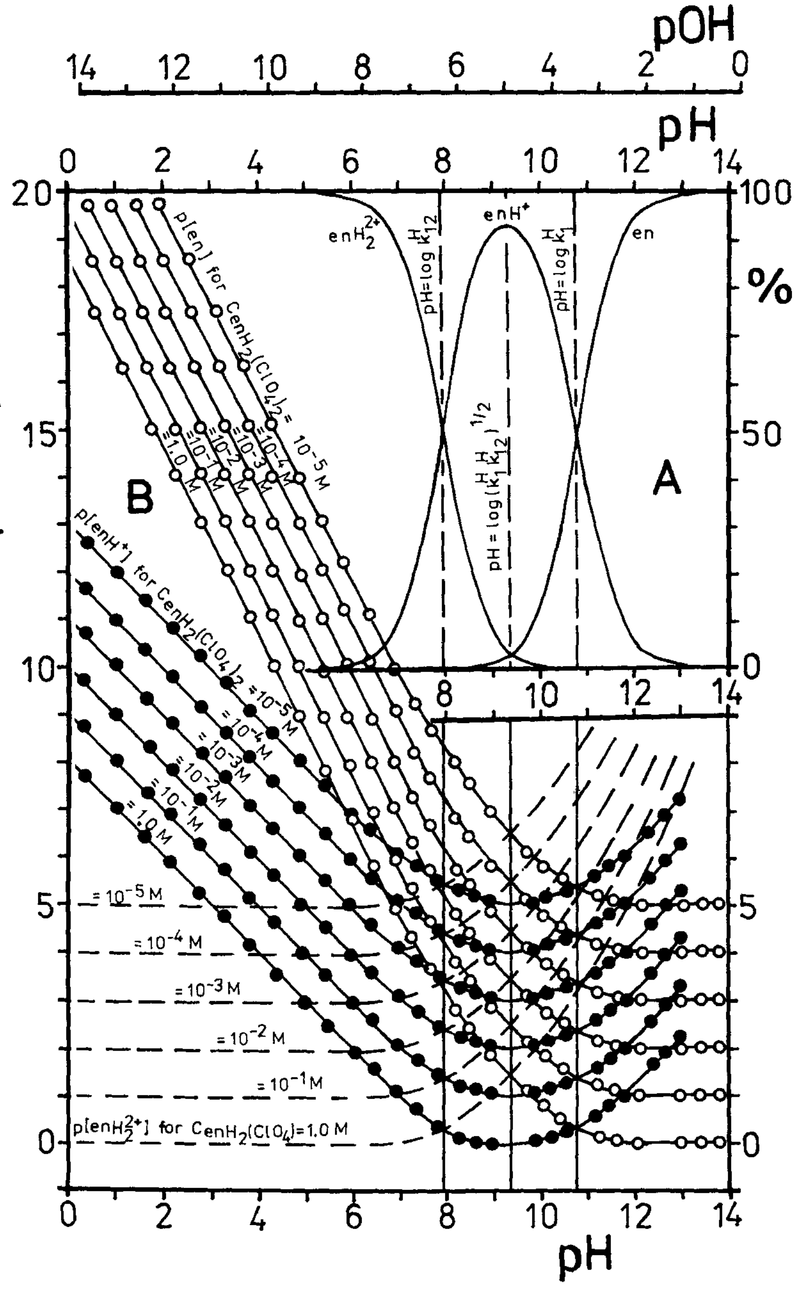

FIGURE 1 (A): Percentage distribution of enH_2^{2+}, enH^+ and en as a function of pH; (B): negative logarithm of equilibrium 1,2-ethanediamine concentration, p[en], negative logarithm of equilibrium 2-aminoethyl ammonium concentration, $p[enH^+]$, negative logarithm of equilibrium 1,2-ethanediammonium concentration, $p[enH_2^{2+}]$, plotted as a function of pH; curves calculated with: $k_1^H = 10^{10.81}$, $k_{12}^H = 10^{7.93}$ (Ref. 16).

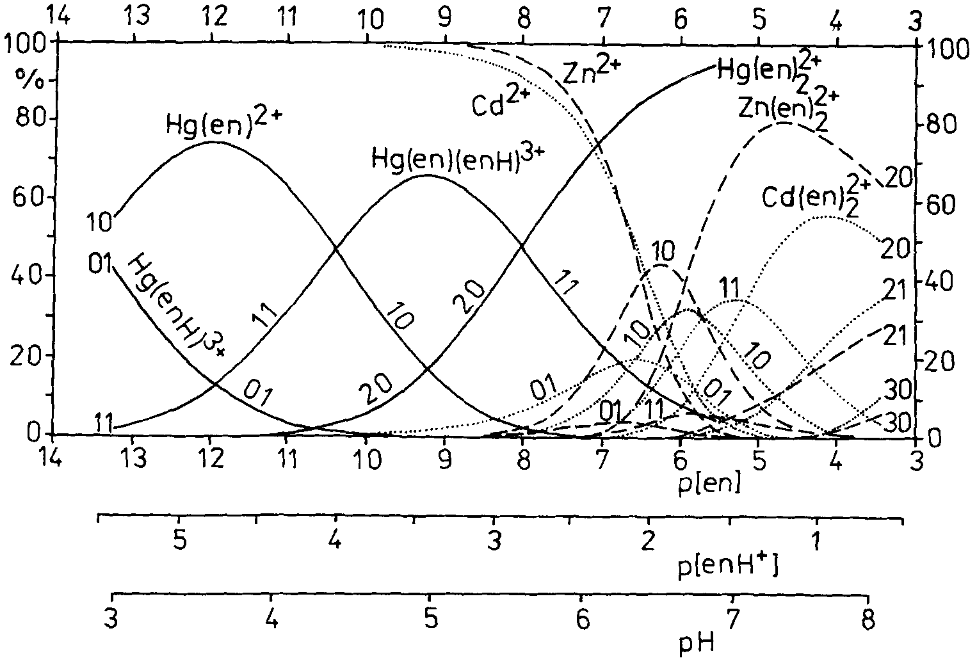

FIGURE 2 Percentage distribution of $Hg(en)_i(enH)_j^{(2+j)+}$ (———), $Cd(en)_i(enH)_j^{(2+j)+}$ (∘∘∘∘∘), and $Zn(en)_i(enH)_j^{(2+j)+}$ complexes (– – –) as a function of p[en] for $C_{enH_2(ClO_4)_2} = 0.3333$ M. The abscissa also shows the corresponding values of p[enH^+] and pH. The curves are calculated with $\beta_{01} = 10^{8.21}$, $\beta_{10} = 10^{16.749}$, $\beta_{11} = 10^{20.751}$, $\beta_{20} = 10^{25.970}$ (for Hg(II) complexes),[14] $\beta_{01} = 10^{1.70}$, $\beta_{10} = 10^{6.21}$, $\beta_{11} = 10^{7.88}$, $\beta_{20} = 10^{11.64}$, $\beta_{21} = 10^{12.23}$, $\beta_{30} = 10^{14.38}$ (for Cd(II) complexes),[16] $\beta_{01} = 10^{1.03}$, $\beta_{10} = 10^{6.49}$, $\beta_{11} = 10^{7.47}$, $\beta_{20} = 10^{12.44}$, $\beta_{21} = 10^{12.81}$, $\beta_{30} = 10^{14.88}$ (for Zn(II) complexes).[19]

1,2-ethanediamine. The basic properties of ethanediamine require consideration of metal cation complexation with hydroxyl ion ($\sum \beta_{00k}[OH^-]^k + \sum\sum \beta_{i0k}[en]^i[OH^-]^k$). The contribution of complexation with hydroxyl ion in the total complexation function, F_{000}, increases with an increase of total metal cation concentration and may cause (*e.g.*, for $C_{Zn} \geqslant C_{en}$) the precipitation of hydroxocomplexes (for $\bar{n} < 1.9$ in perchlorate medium).[19] Therefore, the determination of lower chelate stability constants alone (β_{10}, β_{20}) may be impossible (for Zn(II)-en-3M(Na, H)ClO_4 system).[19] On the other hand (for $C_M \ll C_{enH_2(ClO_4)_2}$), pure non-chelate complexation (with 2-aminoethylammonium cation only, $\sum \beta_{0j}[enH^+]^j$), cannot be determined experimentally, because of simultaneous overlap with chelate and part-chelate complexation ($\sum \beta_{i0}[en]^i + \sum\sum \beta_{ij}[en]^i[enH^+]^j$), *c.f.*, Figure 2. In the general case, the full set of stability constants for all complexes coexisting under labile equilibrium should be determined simultaneously from the total complexation function, $F_{000} = C_M/[M^{2+}]$, this being the sum of all partial complexation functions mentioned above. That is the reason why additional measuring requirements (precision of measurements) are important and some complications in the interpretation of the obtained set of stability constants for $M(en)_i(enH)_j(OH)_k$ complexes arise.

The Electrometric Equivalence of Complexes

(*i*) *Basic relations for electrometric indistinguishable complexes*

For labile systems, the chelated, $M(en)_i^{2+}$, and protonated, $M(en)_i(enH)_j^{(2+j)+}$, complexes are electrometrically equivalent to the appropriate mixed $M(en)_{(i-a)}(enH)_{(j+a)}(OH)_a^{(2+j)+}$ complexes formed in (*1*),

$$M(en)_i(enH)_j^{(2+j)+} + a\,H_2O = M(en)_{(i-a)}(enH)_{(j+a)}(OH)_a^{(2+j)+} \qquad (1)$$

where $1 \leqslant i \leqslant (N = 3)$, $(2i + j) \leqslant 2N$, $N \geqslant a \geqslant 1$. Between their stability constants, the following equivalence exists;

$$\beta_{(i-a)(j+a)(a)} = \beta_{ij0}/(k_{B_1})^a \qquad (2)$$

where

$$k_{B_1} = [enH^+][OH^-]/[en] = k_1^H K_{H_2O} = 10^{-3.41} \qquad (3)$$

k_{B_1} is the first successive basic dissociation constant, $K_{H_2O} = 10^{-14.22}$ (for 3 M $NaClO_4$, Ref. 21).

Therefore, analysis of the electrometric data alone leads to an interesting paradox since it implies that the chelate complexes are equivalent to mixed (2-aminoethylammonium-hydroxide) species. For example, $M(en)^{2+}$ and $M(enH)(OH)^+$ or $M(en)_2^{2+}$ and $M(en)(enH)(OH)^{2+}$ and $M(enH)_2(OH)_2^{2+}$ ($\beta_{200} = \beta_{111}k_{B_1} = \beta_{022}(k_{B_1})^2$), are electrometrically indistinguishable.

It should be noted that the complexes containing chelate ligand, $M(en)_i(enH)_j^{(2+j)+}$, are electrometrically equivalent to the mixed (2-aminoethylammonium, 2-aminoethylamide) species

$$M(en)_i(enH)_j^{(2+j)+} \Leftrightarrow M(enH)_{(j+a)}(en^-)_a^{(2+j)+} \qquad (4)$$

where $i = 2a$, $en^- = NH_2CH_2CH_2NH^-$.

$$\beta_{(j+a)a} = \beta_{ij}/K_{en} \qquad (5)$$

$$K_{en} = [enH^+][en^-]/[en]^2 \qquad (6)$$

The equilibrium constant, K_{en}, has not been determined experimentally. However, by comparison with that for ammonia,[22] $[en^-]$ should be regarded as being negligibly small in aqueous ethanediamine solutions (especially for $pH < \log(k_1^H k_{12}^H)^{1/2}$). The formation of imido complexes, still less probable in aqueous solution, is also neglected here.

(*ii*) *Basic relations for apparently indistinguishable complexes*

The complexes, which cannot be distinguished on the basis of calculations for single measurement series (with $C_{enH_2(ClO_4)_2} = \text{const.}$) but can be distinguished on the basis of two or more series (with different $C_{enH_2(ClO_4)_2} = \text{const.}$), are called here apparently indistinguishable complexes. Under $C_{enH_2(ClO_4)_2} = \text{constant}$ conditions, the following complexes are indistinguishable (see also Table I).

(i) $M(en)_i(enH)_j^{(2+j)}$ and $M(en)_{(i-a)}(enH)_{(j+2a)}^{(2(1+a)+j)+}$ (*7*)

$$\beta_{(i-a)(j+2a)0} = \beta_{ij0}/(\gamma C_{enH_2(ClO_4)_2})^a, \qquad (7a)$$

where: $0 \leqslant {}^{i} \leqslant (N \leqslant 3)$, $(2i + j) \leqslant 2N$, $0 \leqslant a \leqslant i$.

$$\gamma = [enH^+]^2/([en]C_{enH_2(ClO_4)_2}), \qquad (7b)$$

TABLE I

Electrometric apparently indistinguishable complexes. Relation between stability constants for complexes B and A.

$\gamma = [enH^+]^2/[en]C = [enH^+]k_{B_1}C/[OH^-] = [en](k_{B_1})^2C/[OH^-]^2$

$C = C_{enH_2}(ClO_4)_2$

Complex A	Complex B	Relation between stability constants
$M(enH)^{3+}$	$M(OH)^+$	$\beta_{001} = \beta_{010}\gamma C/k_{B_1}$
$M(en)^{2+}$	$M(enH)_2^{3+}$	$\beta_{020} = \beta_{100}/\gamma C$
$M(en)^{2+}$	$M(OH)_2$	$\beta_{002} = \beta_{100}\gamma C/(k_{B_1})^2$
$M(en)(enH)^{3+}$	$M(enH)_3^{5+}$	$\beta_{030} = \beta_{110}/\gamma C$
$M(en)(enH)^{3+}$	$M(en)(OH)^+$	$\beta_{101} = \beta_{110}\gamma C/k_{B_1}$
$M(en)(enH)^{3+}$	$M(OH)_3^-$	$\beta_{003} = \beta_{110}(\gamma C)^2/(k_{B_1})^3$
$M(en)_2^{2+}$	$M(en)(enH)_2^{4+}$	$\beta_{120} = \beta_{200}/\gamma C$
$M(en)_2^{2+}$	$M(enH)_4^{6+}$	$\beta_{040} = \beta_{200}/(\gamma C)^2$
$M(en)_2^{2+}$	$M(en)(OH)_2$	$\beta_{102} = \beta_{200}\gamma C/(k_{B_1})^2$
$M(en)_2^{2+}$	$M(OH)_4^{2-}$	$\beta_{004} = \beta_{200}(\gamma C/(k_{B_1})^2)^2$
$M(en)_2(enH)^{3+}$	$M(en)(enH)_3^{5+}$	$\beta_{130} = \beta_{210}/\gamma C$
$M(en)_2(enH)^{3+}$	$M(enH)_5^{7+}$	$\beta_{050} = \beta_{210}/(\gamma C)^2$
$M(en)_2(enH)^{3+}$	$M(en)_2(OH)^+$	$\beta_{210} = \beta_{210}\gamma C/k_{B_1}$
$M(en)_2(enH)^{3+}$	$M(en)(OH)_3^-$	$\beta_{103} = \beta_{210}(\gamma C)^2/(k_{B_1})^3$
$M(en)_2(enH)^{3+}$	$M(OH)_5^{3-}$	$\beta_{005} = \beta_{210}(\gamma C)^3/(k_{B_1})^5$
$M(en)_3^{2+}$	$M(en)_2(enH)_2^{4+}$	$\beta_{220} = \beta_{300}/\gamma C$
$M(en)_3^{2+}$	$M(en)(enH)_4^{6+}$	$\beta_{140} = \beta_{300}/(\gamma C)^2$
$M(en)_3^{2+}$	$M(enH)_6^{8+}$	$\beta_{060} = \beta_{300}/(\gamma C)^3$
$M(en)_3^{2+}$	$M(en)_2(OH)_2$	$\beta_{202} = \beta_{300}\gamma C/(k_{B_1})^2$
$M(en)_3^{2+}$	$M(en)(OH)_4^{2-}$	$\beta_{104} = \beta_{300}(\gamma C/(k_{B_1})^2)^2$
$M(en)_3^{2+}$	$M(OH)_6^{4-}$	$\beta_{006} = \beta_{300}(\gamma C/(k_{B_1})^2)^3$

$$\text{(ii)}\ M(en)_i(enH)_j^{(2+j)+} \quad \text{and} \quad M(en)_{(i-a)}(OH)_{(j+2a)}^{(2(1-a)-j)} \tag{8}$$

$$\beta_{(i-a)0(j+2a)} = \beta_{ij0}(\gamma C_{enH_2(ClO_4)_2})^{(j+a)}/(k_{B_1})^{(j+2a)} \tag{8a}$$

where: $0 \leqslant i \leqslant (N \leqslant 3)$, $(2i+j) \leqslant 2N$, $0 \leqslant a \leqslant i$,

$$\gamma = [enH^+]k_{B_1}C_{enH_2(ClO_4)_2}/[OH^-] \tag{8b}$$

$$\gamma = [en](k_{B_1})^2C_{enH_2(ClO_4)_2}/[OH^-]^2, \tag{8c}$$

The quantities $\beta_{(1-a)(j+2a)0}$ and $\beta_{(1-a)0(j+2a)}$ depend on $C_{enH_2(ClO_4)_2}$ and in this sense they have the character of apparent stability constants (Table I). However, they are neither apparent, nor conditional or effective stability constants in the meaning of Schwarzenbach,[23] Ringbom[24] or Reilley,[25] respectively. Generally the γ value is pH dependent (Figure 3) and can be calculated from (*7b*), (*8b*), (*8c*) or (*9*).

$$\gamma = [enH_2^{2+}]k_1^H/(C_{enH_2(ClO_4)_2}k_{12}^H) \tag{9}$$

For pH ≪ log k_{12}^H the γ value is constant and is approximately equal to the relation (*10*).

$$\gamma \simeq k_1^H/k_{12}^H \tag{10}$$

For 3 M $NaClO_4$ as a medium, and $pH \leqslant 5.5$, $p[en] \leqslant (7.74 - \log C)$, $p[enH^+] \leqslant (2.4 - \log C)$, γ is equal to $10^{2.882 \pm 0.002}$ (estimated with k_1^H, k_{12}^H data

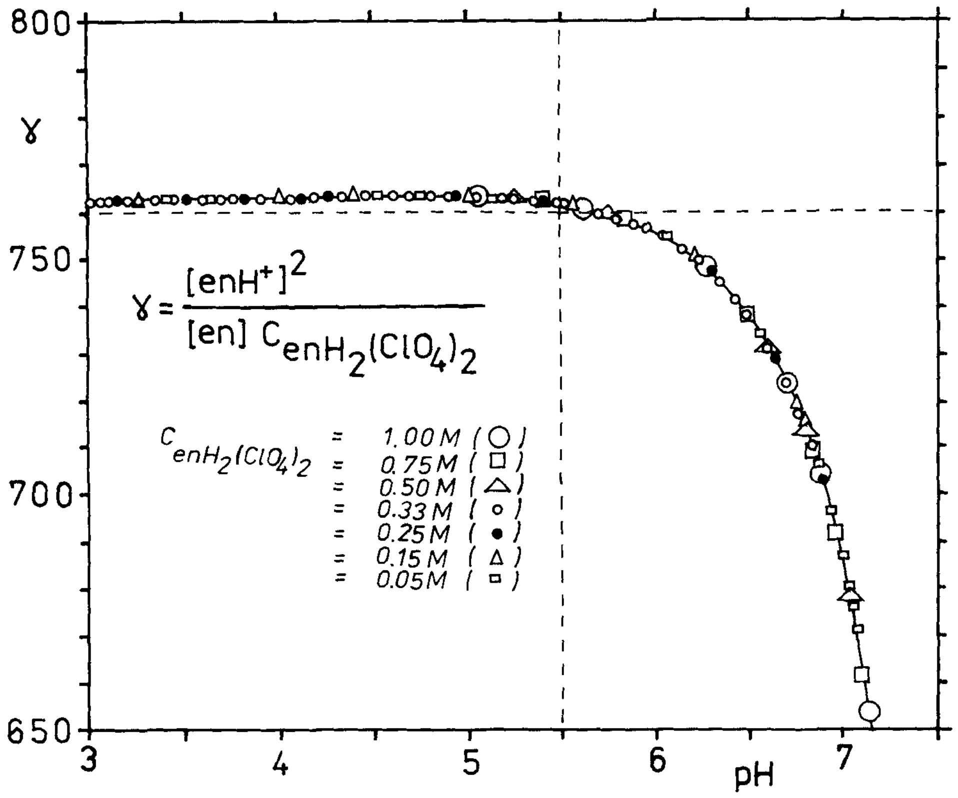

FIGURE 3 Dependence of γ upon pH for constant values of $C_{enH_2(ClO_4)_2}$ (= 1.0, 0.75, 0.50, 0.33, 0.25, 0.15, 0.05 M) in 3 M (Na, H)ClO_4.

from Ref. 14); $C = C_{enH_2(ClO_4)_2}$. For 1.3 M KNO_3 and pH = 5.5–6.3, γ is equal to $10^{2.675 \pm 0.006}$ (estimated with k_1^H, k_{12}^H from Ref. 8).

From equations (*11*) and (*12*),

$$\log(\beta^{c_1}_{(i-a)(j+2a)0}/\beta^{c_2}_{(i-a)(j+2a)0}) = a \log(c_1/c_2), \qquad (11)$$

$$\log(\beta^{c_1}_{(i-a)0(j+2a)}/\beta^{c_2}_{(i-a)0(j+2a)}) = (a + j) \log(c_1/c_2), \qquad (12)$$

it follows that for two measuring series with $C_{enH_2(ClO_4)_2} = C_1, C_2$ ($= 1/2C_1$), the calculated difference in logarithms of the apparent stability constants is equal to 0.3a or 0.3(a + j), respectively. Therefore, for precise measurements ($\sigma_{\log \beta_{ijk}} \ll 0.15$) these differences are sufficient for evaluation if the (β_{ijk}) parameters are $C_{enH_2(ClO_4)_2}$-dependent. Thus, these differences are sufficient for correct selection of a unique model of complexation equilibria.

Final Model of Complexation Equilibria

(*i*) *Electrometric indistinguishable complexes*

An X-ray diffraction study of bis(ethanediamine)mercury(II) diperchlorate revealed that both 1,2-ethanediamine molecules are bidentate ligands (bonded in *gauche* conformation) and that the $Hg(en)_2^{2+}$ complex cation has a distorted tetrahedral structure.[26] On the other hand, from an X-ray diffraction study of bis(ethanediamine)triiododimercury(II) triiodomercurate(II) crystals it was shown that in the trigonal planar $[Hg(en)I]^+$ complex cation the mercury cation is also coordinated by two nitrogen atoms of 1,2-ethanediamine.[27] Moreover, analysis of X-ray scattering data (and Raman spectra) of $Cd(en)_2^{2+}$ and $Cd(en)_3^{2+}$ as well as $Zn(en)_2^{2+}$ and $Zn(en)_3^{2+}$ nitrate solutions show that $Cd(en)_2^{2+}$ and $Zn(en)_2^{2+}$ complex cations have tetrahedral structures,[28,29] while $Cd(en)_3^{2+}$ and $Zn(en)_3^{2+}$ are regular octahedral complex cations in aqueous solution.[28,29] Therefore, although the results of calculations of the sum of the weighted squares of residuals (and standard deviations of stability constants) for the following models: (i) $Hg(enH)^{3+}$, $Hg(en)^{2+}$, $Hg(en)(enH)^{3+}$ and $Hg(en)_2^{2+}$; (ii) $Hg(enH)^{3+}$, $Hg(enH)(OH)^{2+}$, $Hg(enH)_2(OH)^{3+}$ and $Hg(en)(enH)(OH)^{2+}$; (iii) $Hg(enH)^{3+}$, $Hg(enH)(OH)^{2+}$, $Hg(enH)_2(OH)^{3+}$, $Hg(enH)_2(OH)_2^{2+}$, are the same and $C_{enH_2(ClO_4)_2}$-independent, only the first model, in which the mixed (2-aminoethylammonium-hydroxo) complexes are absent, can be X-ray justified.[26–29] For that reason, model (i) could be regarded as the final one (Table II). Naturally, these experimental facts do not exclude the formation of such species as $M(en^*)^{2+}$ and/or $M(enH)(OH)^{2+}$ in the chelate ring formation process at the moment of mixing of $M(ClO_4)_2$ and $enH_2(ClO_4)_2$ solutions (Figure 4); en* denotes $NH_2CH_2CH_2NH_2$ attached as a monodentate ligand (*c.f.*, Ref. 8, pp. 30–35). It is noteworthy that in $Hg(ClO_4)_2$ solution with pH = 3, the $[Hg^{2+}]/[Hg(OH)^+]$ concentration ratio is equal to 3.55. In an $enH_2(ClO_4)_2$ solution with pH = 3, the $[enH^+]/[en]$ concentration ratio is equal to 6.5×10^7 (and $[enH_2^{2+}]/[enH^+] = 841$). For such labile systems kinetic data are not available. Therefore, the experimental values of stability constants for probable intermediate ($Hg(enH)(OH)^{2+}$, $Hg(en^*)_i^{2+}$)

TABLE II
Final model of complexation equilibria for Zn(II), Cd(II), and Hg(II)-1,2-ethanediamine-3 M (Na, H)ClO_4 systems and comparison of stability constants of ethanediamine and ammonia complexes

Zn(II), Cd(II) or Hg(II), en, enH^+, 3 M, 25°C	Zn(II), Cd(II) or Hg(II), NH_3 2 M, 25°C	Found
Zn(II), log β_{01} = 1.03 ± 0.06[a]	Zn(II), log K_1 = 2.41[b]	Zn(II), log(K_1/β_{01}) = 1.38
Cd(II), = 1.70 ± 0.03[c]	Cd(II), = 2.69[b]	Cd(II), = 0.99
Hg(II), = 8.82 ± 0.02[d]	Hg(II), = 8.8[b]	Hg(II), ≅ 0
Zn(II), logβ_{10} = 6.49 ± 0.01[a]	Zn(II), log K_2 = 2.48[b]	
Cd(II), = 6.21 ± 0.02[c]	Cd(II), = 2.14[b]	
Hg(II), = 16.750 ± 0.006[d]	Hg(II), = 8.7[b]	
Zn(II), log β_{11} = 7.47 ± 0.13[a]	Zn(II), log K_3 = 2.54[b]	Zn(II), log(β_{11}/β_{10}) = 0.98
Cd(II), = 7.88 ± 0.03[c]	Cd(II), = 1.48[b]	Cd(II), = 1.67
Hg(II), = 20.751 ± 0.007[d]	Hg(II), = 1.0[b]	Hg(II), = 4.00
Zn(II), log β_{20} = 12.44 ± 0.01[a]	Zn(II), log K_4 = 2.19[b]	
Cd(II), = 11.64 ± 0.02[c]	Cd(II), = 0.97[b]	
Hg(II), = 25.970 ± 0.003[d]	Hg(II), = 0.78[b]	
Zn(II), log β_{21} = 12.81 ± 0.03[a]		Zn(II), log(β_{21}/β_{20}) = 0.37
Cd(II), = 12.230 ± 0.005[c]	Cd(II), log K_5 = −0.32[b]	Cd(II), = 0.59
Zn(II), log β_{30} = 14.88 ± 0.12[a]		
Cd(II), = 14.38 ± 0.02[c]	Cd(II), log K_6 = −1.66[b]	

[a,c,d] 3 M $NaClO_4$, 25°C. [a] Ref. 19. [c] Ref. 16. [d] Ref. 14. [b] 2 M NH_4NO_3, 22°C, Ref. 1.

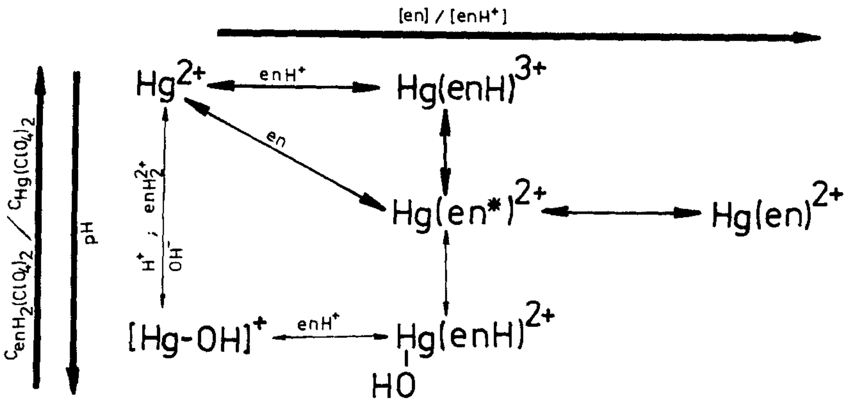

FIGURE 4 Mechanistic consideration of the possible intermediate steps in chelate ring formation of the first chelate, $Hg(en)^{2+}$, complex.

monodentate complexes still cannot be determined. However, the stability constant for the $Hg(en^*)^{2+}$ intermediate complex and the equilibrium constant (K_T) for tautomeric equilibrium

$$Hg(en^*)^{2+} \Leftrightarrow Hg(en)^{2+} \qquad (13)$$

can be roughly estimated from empirical relations given by Schwarzenbach[36] and Bjerrum,[8]

$$\log K_{Hg(en^*)} = q(\log k_1^H - \log 2) + \log 2 = 9.02 \qquad (14)$$

$$\log K_T = \log(K_{Hg(en)}/\log K_{Hg(en^*)}) = 7.73 \qquad (15)$$

$$\log k_T \simeq \log(K_{Hg(en)}/K_{Hg(NH_3)}) = 7.95 \qquad (16)$$

where

$$q = \log K_{Hg(RNH_2)}/\log k_1^H(RNH_2) = 0.83 \qquad (17)$$

On the other hand, the amount of the mixed (2-aminoethylammonium, 2-aminoethylamide) complexes, $M(enH)_a(en^-)_a^{2+}$, formed in aqueous solutions can be regarded as negligibly small (particularly for $pH \leq 7$). It should be noted that complexation of Cd(II) and Hg(II) with en^- has not been found even in non-aqueous ethanediamine solutions.[38] However, evidence for the formation of such amide complexes has been reported for Ir(III), Au(III), Pd(II), Pt(II), Os(IV) and Os(V).[39]

(*ii*) *Apparently indistinguishable complexes*

Analysis of our data for the Hg^{2+}-en-3 M $NaClO_4$ system[14] reveals that for one measurement series (with $C_{enH_2(ClO_4)_2}$ = const.) even such extreme models as: (i), $Hg(enH)^{3+}$, $Hg(en)^{2+}$, $Hg(en)(enH)^{3+}$, $Hg(en)_2^{2+}$; (ii), $Hg(enH)_j^{(2+j)+}$, $j = 1, \ldots, 4$; (iii), $Hg(OH)_k^{(2-k)}$, $k = 1, \ldots, 4$; are statistically equivalent because the sum of the weighted squares of residuals for all three models are practically equal ($SSR(i) \cong SSR(ii) \cong SSR(iii)$). Especially paradoxical is the model which postulates the interpretation of the results in terms of hydroxocomplexes despite the fact that contributions of two of them ($HgOH^+$ and $Hg(OH)_2$) were subtracted from the experimental function of total complexation.[14] Only for the first model are the calculated $\{\beta_{ij}\}$ parameters $C_{enH_2(ClO_4)_2}$-independent and thus they have the character of stability constants, whereas parameters for second $\{\beta_j\}$ and third models $\{\beta_k\}$ are apparent stability constants. That is the reason why models (ii), (iii) and all possible combinations have to be rejected. Calculations performed by the iso-concentration function method and analysis of the sum of the weighted squares of residuals obtained by joint treatment of all measured series ($C_{enH_2(ClO_4)_2}$ = (0.3333, 0.25, 0.15, 0.05 M) $\gg C_{Hg(ClO_4)_2}$, $3 \leq pH < 7$) confirmed this conclusion. For the particular models the values are: SSR(i) = 2.15×10^{-4}, SSR(ii) = 0.27, SSR(iii) = 0.57, respectively. Under such circumstances, analysis of possible reasons for discrepancies between the model postulated by us (model (i): $Hg(enH)^{3+}$, $Hg(en)^{2+}$, $Hg(en)(enH)^{3+}$, $Hg(en)_2^{2+}$) and that proposed by Watters and Mason[13] ($Hg(en)^{2+}$, $Hg(enH)_2^{3+}$, $Hg(en)(enH)^{3+}$, $Hg(en)(OH)^+$, $Hg(en)_2^{2+}$, $Hg(en)(enH)_2^{4+}$) seems to be justified. Comparison of the stability constant ratios determined by Watters and Mason revealed constants

$$\beta_{100}/\beta_{020} = 10^{14.3\pm 0.1}/10^{12.9\pm}0.1 = 10^{1.4},$$

$$\beta_{200}/\beta_{120} = 10^{23.3\pm 0.1}/10^{22.3\pm 0.3} = 10^{1.1},$$

$$\beta_{101}k_{B_1}/\beta_{110} = 10^{23.8\pm 0.3}\, 10^{-4}/10^{18.6\pm 1} = 10^{1.2},$$

within the limits of $\{\beta_{ijk}\}$ determination error. This means that (*7a*) and (*8a*) are fulfilled and hence

$$\beta_{100}/\beta_{020} = \beta_{200}/\beta_{120} = \beta_{101}k_{B_1}/\beta_{110} = \gamma C_{enH_2(ClO_4)_2} = \text{const.} \qquad (18)$$

Assuming that the γ value ($= k_1^H k_{12}^H = 10^{2.8}$, 0.1 M $NaClO_4$)[13] is constant, we obtain $C_{enH_2(ClO_4)_2}$ equal to 0.04 M. This value is practically equal to the expected one, *i.e.*, $C_{enH_2(ClO_4)_2}$ = 0.05 M (considering the 20% error in β_{020}, and thus in $C_{enH_2(ClO_4)_2}$ determination). This supports the hypothesis, assumed here, that β_{100} and β_{020}, β_{120} and β_{200}, β_{101} and β_{110} were estimated from two experimental series with the same $C_{enH_2(ClO_4)_2}$ (= 0.05 M, *c.f.*, Ref. 13). In addition, analysis of the sum of the weighted squares of residuals for the available part of Watters and Mason's data confirmed the above conclusion.[14] This revealed that the existence of only $Hg(en)^{2+}$, $Hg(en)(enH)^{3+}$ and $Hg(en)_2^{2+}$ could be statistically justified,[14] under Watters and Mason experimental conditions.[13] It does not mean, however, that for any system with bidentate ligand (L) the stability constants for $M(LH)_2^{4+}$, $M(L)(LH)_2^{4+}$ and $M(L)(OH)^+$ complexes, the simultaneous presence of $M(L)^{2+}$, $M(L)_2^{2+}$ and $M(L)(LH)^{3+}$, cannot be determined (*e.g.*, by iso-concentration function procedures). However, the relations reported here (Eq. (*11*), (*12*)) show when the coexistence of those complexes should not be postulated.

If $C_{enH_2(ClO_4)_2}$ is not constant for each experimental point, the possibility of determination of a final model for complexation equilibria depends on the range of γ changes and on the overall precision of potential measurements (σ_E). Results of the reexamination of the Cd(II)-ethanediamine system by DC/tast polarography (old data in Ref. 15) reveal that the following models for complexation equilibria are numerically equivalent for a 3.6% change in the γ value and $\sigma_E \simeq 0.9$ mV): (i), $Cd(enH)^{3+}$, $\log\beta_{01} = 1.92 \pm 0.15$; $Cd(en)^{2+}$, $\log\beta_{10} = 6.26 \pm 0.38$; $Cd(en)(enH)^{3+}$, $\log\beta_{11} = 7.89 \pm 0.18$; $Cd(en)_2^{2+}$, $\log\beta_{20} = 11.65 \pm 0.08$; SSR(i) = $5.20\, 10^{-2}$, σ_E(i) = 0.93 mV; (ii), $Cd(enH)^{3+}$, $\log\beta_{01} = 1.90 \pm 0.16$;

$Cd(enH)_2^{4+}$, $\log\beta_{02} = 3.57 \pm 0.33$; $Cd(enH)_3^{5+}$, $\log\beta_{03} = 5.07 \pm 0.23$; $Cd(enH)_4^{6+}$, $\log\beta_{04} = 6.19 \pm 0.08$; SSR(ii) = 5.50 10^{-3}, σ_E(ii) = 0.95 mV; (iii), $Cd(OH)^-$, $\log\beta_{001} = 8.75 \pm 0.14$; $Cd(OH)_2$, $\log\beta_{002} = 17.04 \pm 0.44$; $Cd(OH)_3^-$, $\log\beta_{003} = 25.62 \pm 0.16$; $Cd(OH)_4^{2-}$, $\log\beta_{004} = 33.33 \pm 0.09$; SSR(iii) = 5.22 10^{-3}, σ_E(iii) = 0.93 mV. To determine which of the three models mentioned above is the most probable statistically (apart from "chemical intuition"), a five-fold increase of measurement precision ($\sigma_E \cong 0.2$ mV) is required (with a 3.6% change in the γ value). This can be achieved replacing the polarographic measurements with a dropping mercury electrode by potentiometric determinations with a Cd(Hg) electrode (*c.f.*, polarographic model (i) and Cd(Hg) electrode results in Table II).

Acid Properties and Chelation Effects

Protonated complexes of the classical chelating ligands are in fact heteropolynuclear complexes (*e.g.*, $ZnenH^{3+}$, $enHgenH^{3+}$ or $HenAgenH^{3+}$), although in the examination of the complexation equilibria they are usually regarded as the simple mononuclear ($ZnenH^{3+}$, $Ag(enH)_2^{3+}$), or mixed ($Hg(en)(enH)^{3+}$, $Cd(en)_2(enH)^{3+}$) cases. Therefore, the dual dissociation of these complexes should be taken into account. The first leads to decomposition of the complex to the metal cation and the protonated ligand (protonated and chelating ligand for mixed complexes). The second reveals the acid character of $M(en)_i(enH)_j^{(2+j)+}$ complexes and for totally labile systems it proceeds in two stages. In the first stage the appropriate complex containing monodentate ethanediamine, $M(en)_i(enH)_{j-1}(en^*)^{(1+j)+}$, is formed as a result of proton transfer to a solvent molecule (*19*). In the second stage, chelate ring closure occurs and $M(en)_{i+1}(enH)_{j-1}^{(1+j)+}$ is formed (*20*). From electrometric data, only the cumulative dissociation constant, $\bar{K}_a$, for the overall process can be obtained (Eq. (*22*), Table III),

$$\begin{array}{c}
M(en)_i(enH)_j^{(2+j)+} + H_2O = M(en)_i(enH)_{j-1}(en^*)^{(1+j)+} + H_3O^+ \qquad (19) \\
M(en)_i(enH)_{j-1}(en^*)^{(1+j)+} = M(en)_{i+1}(enH)_{j-1}^{(1+j)+} \qquad (20) \\
\hline
M(en)_i(enH)_j^{(2+j)+} + H_2O = M(en)_{i+1}(enH)_{j-1}^{(1+j)+} + H_3O^+ \qquad (21)
\end{array}$$

. . . .

$$M(en)_i(enH)_j^{(2+j)+} + j\,H_2O = M(en)_{i+j}^{2+} + j\,H_3O^+ \qquad (22)$$

where the equilibrium constants are defined as follows in (*19a*) to (*22a*).

$$K_a' = K_a/K_T = \frac{[M(en)_i(enH)_{j-1}(en^*)^{(1+j)+}][H_3O^+]}{[M(en)_i(enH)_j^{(2+j)+}]} \qquad (19a)$$

$$K_T = \frac{[M(en)_{i+1}(enH)_{j-1}^{(1+j)+}]}{[M(en)_i(enH)_{j-1}(en^*)^{(1+j)+}]} \qquad (20a)$$

$$K_a = K_a'K_T = \frac{\beta_{(i+1)(j-1)}}{\beta_{ij}k_1^H} = \frac{[M(en)_{i+1}(enH)_{j-1}^{(1+j)+}][H_3O^+]}{[M(en)_i(enH)_j^{(2+j)+}]} \qquad (21a)$$

$$\bar{K}_a = \prod_j (K_a'K_T)_j = \frac{\beta_{(i+j)0}}{\beta_{ij}(k_1^H)^j} \qquad (22a)$$

Comparison of the K_a values (for $j = 1 \bar{K}_a = K_a$) listed in Table III permits the following conclusions. All protonated complexes of zinc triad cations are stronger

TABLE III
Acid properties of 1,2-ethanediammonium and 2-aminoethylammonium cations as well as of protonated non- and partly-chelated complex cations in the zinc triad-1,2-ethanediamine-3 M (Na, H)ClO$_4$ systems

enH_2^{2+}	$+ H_2O = enH^+$	$+ H_3O^+$	$k_{a_1} = 1/k_{12}^H$	$= 10^{-7.93}$
enH^+	$+ H_2O = en$	$+ H_3O^+$	$k_{a_2} = 1/k_1^H$	$= 10^{-10.81}$
$Zn(enH)^{3+}$	$+ H_2O = Zn(en)^{2+}$	$+ H_3O^+$	$K_a = \beta_{100}/(\beta_{010}k_1^H)$	$= 10^{-5.35}$
$Cd(enH)^{3+}$	$+ H_2O = Cd(en)^{2+}$	$+ H_3O^+$		$= 10^{-6.30}$
$Hg(enH)^{3+}$	$+ H_2O = Hg(en)^{2+}$	$+ H_3O^+$		$= 10^{-2.882}$
$Zn(en)(enH)^{3+}$	$+ H_2O = Zn(en)_2^{2+}$	$+ H_3O^+$	$K_a = \beta_{200}/(\beta_{110}k_1^H)$	$= 10^{-5.86}$
$Cd(en)(enH)^{3+}$	$+ H_2O = Cd(en)_2^{2+}$	$+ H_3O^+$		$= 10^{-7.05}$
$Hg(en)(enH)^{3+}$	$+ H_2O = Hg(en)_2^{2+}$	$+ H_3O^+$		$= 10^{-5.591}$
$Zn(en)_2(enH)^{3+}$	$+ H_2O = Zn(en)_3^{2+}$	$+ H_3O^+$	$K_a = \beta_{300}/(\beta_{210}k_1^H)$	$= 10^{-8.74}$
$Cd(en)_2(enH)^{3+}$	$+ H_2O = Cd(en)_3^{2+}$	$+ H_3O^+$		$= 10^{-8.66}$

acids than the 2-aminoethylammonium cation (enH^+). The protonated, mixed complexes containing two chelating ethanediamine molecules, $M(en)_2(enH)^{3+}$, are stronger acids than enH^+, but weaker than the 1,2-ethanediammonium cation (enH_2^{2+}). The protonated complexes containing no more than one chelated ethanediamine molecule ($M(en)_i(enH)^{3+}$, $i = 0, 1$) are stronger acids than the enH_2^{2+} cation. For a given metal cation, the protonated complex, $M(enH)^{3+}$, is a stronger acid than the mixed $M(en)(enH)^{3+}$ species. It is noteworthy that not only $Zn(enH)^{3+}$ but also $Zn(en)(enH)^{3+}$ is a stronger acid than $Cd(enH)^{3+}$. Moreover, the acidity of $Zn(en)(enH)^{3+}$ is only slightly smaller than that of $Hg(en)(enH)^{3+}$, while that of $Hg(enH)^{3+}$ greatly exceeds the acidity of $Zn(enH)^{3+}$. Instead, the acid properties of $Cd(en)_2(enH)^{3+}$ are only slightly stronger than those of $Zn(en)_2(enH)^{3+}$. Generally, the observed acid dissociation constant of the protonated $M(en)_i(enH)_j$ complex, $\bar{K}_a$, will be higher, the lower is the product of its cumulative stability constant (β_{ij}) and of the first protonation constant of ethanediamine, and, simultaneously, the higher is the cumulative stability constant of the chelated complex, ($\beta_{(i+j)0}$), into which the protonated complex is decomposed (Table III). According to (*22a*) the acid properties of a given protonated complex are directly proportional to the tendency towards chelate ring closure (K_T). K_T values estimated from the Schwarzenbach[36] and Bjerrum[8] empirical relations are listed in Table IV. Comparison of K_T values and the chelation effects reveals that Zn(II) has the greater tendency to the chelation than Cd(II) under a tetrahedral configuration. That is the reason why the acid properties $Zn(enH)^{3+}$ and $Zn(en)(enH)^{3+}$ are stronger than those of $Cd(enH)^{3+}$. The chelation effect for Zn(II) decreases, while for Cd(II) increases with increase of the complexation degree (Table IV). Comparison of values for the β_{21}/β_{20} ratio (Table II) shows that Cd(II) has a greater tendency to achieve octahedral configuration than Zn(II). Therefore, the change of configuration is accompanied by inversion of acid properties: $Cd(en)_2(enH)^{3+}$ is a stronger acid than $Zn(en)_2(enH)^{3+}$.

For the dissociation $Hg(enH)^{3+} + H_2O = Hg(en^*)^{2+} + H_3O^+$, the value of K_a' ($= \beta_{Hg(en^*)}/\beta_{01}k_1^H$) is equal to $10^{-10.7}$. This value is in satisfactory agreement with the estimate obtained from the relation $K_a' = K_a/K_T = 10^{-10.6}$–$10^{-10.8}$ (Tables III, IV, and (*19a*)). Rough values for the dissociation constant K_a' ($= K_a/K_T$) for $Cd(enH)^{3+}$ and $Zn(enH)^{3+}$ are equal to $10^{-9.3}$ and $10^{-9.45}$, respectively. K_a' values for $Hg(enH)^{3+}$, $Cd(enH)^{3+}$, $Zn(enH)^{3+}$ are significantly less than the value of the

TABLE IV

Values of the logarithms of equilibrium constants for tautomeric equilibria, $Hg(en^*)_i^{2+} \Leftrightarrow Hg(en)_i^{2+}$, and values of $\log \beta_{20}(en)/\beta_2(NH_3)$ for zinc triad complexes and chelation effects in 1,2-ethanediamine systems relative to ammonia

	Zn(II)	Cd(II)	Hg(II)
$\log K_T = \log \beta_{10}(en)/K_{Hg(en^*)}$			$7.73^{a,b}$
$\simeq \log \beta_{10}(en)/K_1(NH_3)$	$4.1^{c,b}$	$3.0^{d,b}$	$7.95^{a,b}$
$\log K_T = \log \beta_{20}(en)/\beta_{Hg(en^*)_2}$			$7.30^{a,b}$
$\simeq \log \beta_{20}(en)/\beta_2(NH_3)$	$7.5^{c,b}$	$6.5^{d,b}$	$8.17^{a,e}$
Chel $= \log \beta_{10}(en)/\beta_2(NH_3)$	$1.6^{c,b}$	$1.4^{d,b}$	$-1.0^{a,e}$
Chel $= \log K_{20}(en)/K_3K_4(NH_3)$	$1.2^{c,b}$	$3.0^{d,b}$	$7.4^{a,b}$
Chel $= \log K_{30}(en)/K_5K_6(NH_3)$		$4.72^{d,b}$	

[a,c,d] 3 M $NaClO_4$, 25°C. [a] Ref. 14. [c] Ref. 19. [d] Ref. 16. [b] 2 M NH_4NO_3, 22°C, Ref. 1. [e] 1 M $NaClO_4$, 25°C, Ref. 37.

first successive acid dissociation constant of enH_2^{2+} ($10^{-7.93}$). Therefore, in aqueous $enH_2(ClO)_4$ solutions, protonated ethanediamine complexes of the zinc triad cations can be formed. However, for compensation of the strong tendency towards chelation not only a sufficiently high $enH_2(ClO_4)_2$ concentration is required, but also a sufficiently low pH is necessary (*i.e.*, the $[enH^+]/[en]$ ratio should be sufficiently high, *c.f.*, Figures 1 and 2).

CONCLUSIONS

For labile systems it is impossible to distinguish between $M(en)_i(enH)_j$ and $M(en)_{(i-a)}(enH)_{(j+a)}(OH)_a$ complexes on the basis of static electrometric data alone (even for error-free data). To establish a final model for complexation equilibria, additional (X-ray and/or spectroscopic) structural data are necessary.

For labile systems it is also impossible to distinguish between $M(en)_i(enH)_j$ and $M(en)_{(i-a)}(enH)_{(j+2a)}$ complexes or between $M(en)_i(enH)_j$ and $M(en)_{(i-a)}(OH)_{(j+2a)}$, on the basis of electrometric measurements for a single series with constant total $enH_2(ClO_4)_2$ concentrations. The final selection of the correct model for complexation equilibria is possible only if the range of $C_{enH_2(ClO_4)_2}$ under investigation is sufficiently broad. In this case the application of the iso-concentration function procedure is recommended, because it does not require any *a priori* assumptions as to the composition or abundance of the complexes formed.[14,19] The application of the direct computer method requires the individual treatment of each measuring series alone, and next, of all series together (followed by a F-Snedecor test and goodness-of-fit statistics, χ^2), to be sure that there is no apparent indistinguishability of appropriate complexes (and for estimation of systematic errors).

The potentiometric method with an amalgam- or Hg-electrode supplies the most precise values of stability constants of the zinc triad cations-ethanediamine complexes and enables statistical verification. The precision of polarographic measurements for the Cd(II)-en system affords only a rough set of stability constants, although the reproducibility of the reversible reduction waves of Cd(II) is of the order 0.5 mV, and the slopes of logarithmic analyses are equal to 29.5–30.5 mV. *Quasi*-reversible reduction of Zn(II) complexes with ethanediamine proceeds according to the parallel charge transfer mechanism.[40] The high degree of irreversibility of the DC polarographic waves renders impossible the determination of real values of the reversible half wave potentials. As a consequence, the determination of the stability constant set for Zn(II)-ethanediamine complexes from polarographic data is impossible. For the Hg(II)-en system the well-shaped DC polarographic waves are observed only at great C_{en} excess. Therefore, determination of the full set of stability constants for the $Hg(en)_i(enH)_j^{(2+j)+}$ complexes from polarographic measurements is also impossible.

For the Hg(II)-en system the most reliable model consists of the complexes $M(enH)^{3+}$, $M(en)^{2+}$, $M(en)(enH)^{3+}$, and $M(en)_2^{2+}$, which coexist in labile equilibrium. For Cd(II)- and Zn(II)-en systems, in addition, the presence of $M(en)_2(enH)^{3+}$ and $M(en)_3^{2+}$ complexes should be included (Figure 2, Table II).

Acid properties of the protonated complexes decline along the series $Hg(enH)^{3+} \gg Zn(enH)^{3+} > Hg(en)(enH)^{3+} \geqslant Zn(en)(enH)^{3+} > Cd(enH)^{3+} > Cd(en)(enH)^{3+} > enH_2^{2+} > Cd(en)_2(enH)^{3+} \cong Zn(en)_2(enH)^{3+} \gg enH^+$. The above series reflects the compromise between the tendency to closure of the chelate ring and the ability to complex with the 2-aminoethylammonium cation.

Protonated partly-chelated complexes, $M(en)(enH)^{3+}$ and $M(en)_2(enH)^{3+}$, are important in acidic and close to neutral ethanediamine solutions. The planar $Hg(en)^{2+}$ chelate complex transforms to the tetrahedral $Hg(en)_2^{2+}$ species *via* the $Hg(en)(enH)^{3+}$ protonated complex, followed by the unstable $Hg(en)(en^*)^{2+}$ intermediate. Similarly, *via* the partly-chelated complexes, $M(en)_2(enH)^{3+} \rightarrow M(en)_2(en^*)^{2+}$, the tetrahedral $Zn(en)_2^{2+}$ and $Cd(en)_2^{2+}$ chelated complexes transform to the octahedral $Zn(en)_3^{2+}$ and $Cd(en)_3^{2+}$ ions.

Contrary to the significantly less labile Co(II)- and Ni(II)-en systems,[41–45] no information about the kinetics of chelate ring formation/opening have been reported for extremely labile zinc triad cations-ethanediamine systems. Therefore, only rough values of stability constants (based on Bjerrum's and Schwarzenbach's empirical relations) for the intermediate $M(en^*)_i^{2+}$ can be evaluated. Similarly, no structural data or thermodynamic quantities for protonated complexes coexisting under labile equilibria with the chelated species in aqueous solution have been obtained.

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