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Interaction of Mercury(II) Cyanide with Ligands Containing Nitrogen Donor Atoms

ÉVA CS. PORZSOLT, M. T. BECK and A. BITTO
Department of Physical Chemistry, Kossuth Lajos University, 4010 Debrecen, Hungary
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The stabilities of complexes formed in aqueous solution between mercury(II) cyanide and various amines were studied pH-metrically at 25° C and an ionic strength of 0.1M. The results point to chelate and statistical effects, the different donor abilities of the NH_2 and NH groups, and the high stability of five-membered rings.

Introduction

It was earlier shown that mercury(II) cyanide reacts with various coordinatively saturated inert cyano complexes to yield heteropolynuclear complexes containing cyanide bridges[1]. As regards its complex-forming properties, it appeared of interest to study how $Hg(CN)_2$ reacts with various compounds containing nitrogen but not cyanide. The present paper reports on equilibrium studies of systems containing certain mono- and polydentate amines and $Hg(CN)_2$.

The interaction of $Hg(CN)_2$ and similar, but sulfur-containing ligands has already been studied[2,3]; and here too, mixed ligand complexes of the type $Hg(CN)_2X$ are formed.

Experimental

Chemicals

$Hg(CN)_2$: Merck DAB 6, recrystallized three times from water; ethylamine: BDH, analytical reagent; ethylenediamine: Reanal, monohydrate, freshly distilled; 1,3-diaminopropane: Fluka AG, distilled twice *in vacuo,* with passage of N_2; diethylenetriamine and triethylenetetramine: Baker Chem. Co., freshly distilled *in vacuo.* 1,10-penanthroline: Reanal, p.a; 2,2′-dipyridyl: Reanal, p.a.; pyridine: Reanal, analytically pure; $HClO_4$: VEB Laborchemie Apolda, 60%; NaOH: Chemapol, Prague; $KHCO_3$: Reanal, p.a., recrystallized and dried in CO_2 atmosphere; $NaClO_4$: Reanal, analytically pure, recrystallized twice from water; $AgClO_4$: prepared from $AgNO_3$ *via* Ag_2O, the latter being well washed, dried and dissolved in the equivalent amount of perchloric acid.

The equilibrium constants were determined by pH-metric titrations. The mentioned interaction of mercury(II) cyanide can conveniently be studied in the pH range between 2 and 10.6; below pH 10.6 formation of the hydroxo–cyano mixed ligand complex is not significant[4], while above pH 2 decomposition of $Hg(CN)_2$ by acids is negligible[5]. $Hg(CN)_2$ interacts with various anions[6–8], but not with perchlorate or fluoride[9]; accordingly, pure, freshly-distilled free amines were used instead of amine salts; the ionic strength was adjusted with sodium perchlorate, and perchloric acid was employed as titrant acid.

As a consequence of the fairly low stabilities of the mixed ligand complexes formed, to attain well-measurable pH changes a large $Hg(CN)_2$ excess has to be applied.

The composition of the solutions: 10 ml x*M* amine stock solution (x = 0.01–0.1); 1.0 ml 2.5*M* $NaClO_4$; y ml 0.25*M* $Hg(CN)_2$ (y = 0–14); (14–y) ml H_2O.

These solutions were titrated with 0.25*M* $HClO_4$, added in 0.05 ml portions from a microburette, under thermostatted conditions at 25° C. N_2 was bubbled through the solution. The change in the initial ionic strength of 0.1*M* was negligible during the titration.

The pH was measured with a Radiometer pH4 pH-meter using a glass electrode. Because of thc interfering reaction between $Hg(CN)_2$ and chloride a Wilhelm electrode was used[10] for reference electrode, filled with 0.01*M* $AgClO_4$ + 2.99*M* $NaClO_4$ solution into which a silver electrode was immersed. Applying this electrode the liquid junction potential has been eliminated.

A complex molecular species was accepted as existing if its concentration exceeded 8–10% of the total amine concentration – at least in a certain pH range. The ionic product of water ($K_w = 2.1 \times 10^{-4}$) was obtained by pH-metric titration of 0.1*M* $NaClO_4$ (as used for adjustment of the ionic strength) with NaOH of known concentration.

The protonation constants of the free amines and the stability constants of the mixed ligand complexes formed were calculated from the titration curves obtained. The approximate values of the constants were calculated with the methods of Irving and Rossotti[11] and Schwarzenbach[12,13] while the accurate values were computed by

Newton, Raphson and Sayce iteration, by means of the SCOGS[14,15] program modified by Nagypál[16].

The abbreviations used are as follows: etn = ethylamine; dpn = 1,3-diaminopropane; en = ethylenediamine; dien = diethylenetriamine; trien = triethylenetetramine.

The compositions of the complexes found are denoted by three-digit numbers: the first digit is the number of protons, the second is the number of amines, and the third is the number of mercury(II) cyanide molecules within the complex molecule.

Results

1,10-phenanthroline, 2,2'-Dipyridyl, Pyridine

When mercury(II) cyanide is added to the aqueous solutions of 1,10-phenanthroline (phen) or 2,2'-dipyridyl (bipy), white precipitates are formed; derivatographic analysis shows these to be $Hg(CN)_2 \cdot phen$ and $Hg(CN)_2 \cdot bipy$[17]. The possibility of pH-metry is excluded by the very slight solubilities of these precipitates. With pyridine even in the presence of a 20-fold excess of mercury(II) cyanide there is also no measurable pH-metric effect, although $Hg(CN)_2 \cdot 2C_5H_5N$ solid complex can be prepared[18] from solid $Hg(CN)_2$ and anhydrous pyridine.

Ammonia, Ethylamine

Although with ammonia $Hg(CN)_2$ forms a solid compound of composition $Hg(CN)_2 \cdot NH_3$[18] a 20-fold excess of $Hg(CN)_2$ in aqueous solution did not lead to measurable pH differences.

In the case of ethylamine there is a slight difference between the titration curves of solutions containing and not containing $Hg(CN)_2$, as can be seen in Figure 1*: With the assumption of the protonation of ethylamine (110) and the formation of the 1:1 complex (011), well agreeing constant values were obtained for the whole of the titration curve. The average values were: $\log K_{110} = 10.61 \pm 0.02$ and $\log K_{011} = 0.75 \pm 0.06$.

1,3-Diaminopropane

The titration curves for 1,3-diaminopropane in the presence and absence of $Hg(CN)_2$ respectively are given in Figure 2.

When only the (011) complex was assumed, the value obtained for its stability constant increased constantly during the titration from pH 9.8 on. However, when also the (111) complex was taken into consideration the calculated curve agreed well with the experimentally measured one, as shown in Table I.

The concentration distribution of the molecular species formed is shown in Figure 3 as a function of pH.

The constants were determined as: $\log K_{110} = 10.47 \pm 0.05$; $\log K_{210} = 8.55 \pm 0.1$; $\log K_{011} = 1.08 + 0.1$; $\log K_{111} = 0.25 \pm 0.1$.

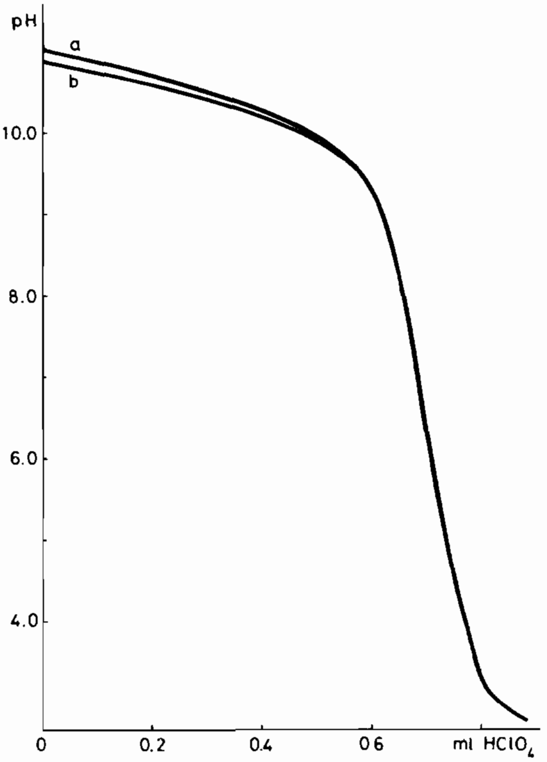

Figure 1. Effect of $Hg(CN)_2$ on the pH change during titration of $7.3 \times 10^{-3} M$ ethylamine with $0.2545 M$ $HClO_4$. $[Hg(CN)_2]$: (a) $0 M$; (b) $0.1 M$; T = 25° C; I = $0.1 M$.

TABLE I. Titration curve measured by acid titration of the 1,3-diaminopropane – $Hg(CN)_2$ mixture at 25° C and an ionic strength of $0.1 M$, and the curve calculated with the aid of the stability constants obtained. [dpn] = $0.01018 M$, $[Hg(CN)_2]$ = $0.10 M$, $[HClO_4]$ = $0.2545 M$.

pH Measured	ml $HClO_4$ Measured	ml $HClO_4$ Calculated	Δ ml
10.400	0.300	0.3098	0.0098
10.333	0.350	0.3543	0.0043
10.260	0.400	0.4043	0.0043
10.197	0.450	0.4477	–0.0023
10.126	0.500	0.4968	–0.0032
10.054	0.550	0.5465	–0.0035
9.980	0.600	0.5970	–0.0030
9.905	0.650	0.6473	–0.0027
9.830	0.700	0.6964	–0.0034
9.747	0.750	0.7491	–0.0009
9.665	0.800	0.7994	–0.0006
9.576	0.850	0.8520	0.0020
9.487	0.900	0.9028	0.0028
9.315	1.000	0.9975	–0.0025

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* The detailed data of all the titrations are available on request from the authors.

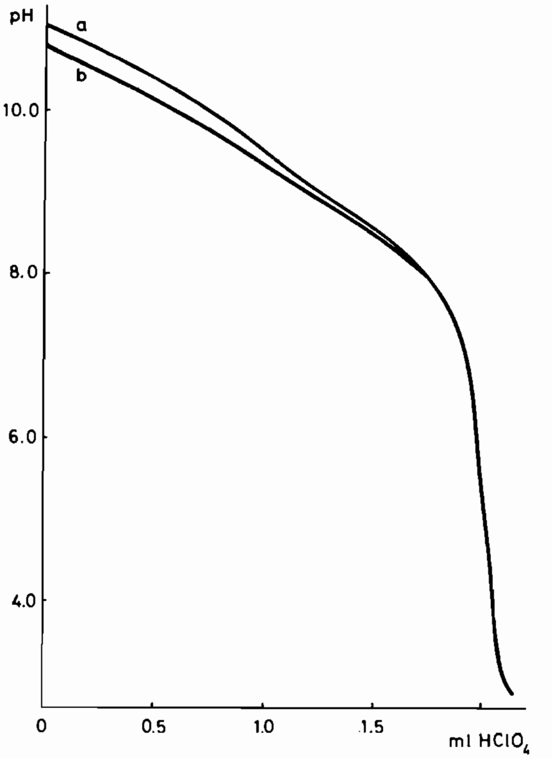

Figure 2. Effect of $Hg(CN)_2$ on the pH change during titration of $1.018 \times 10^{-2} M$ 1,3-diaminopropane with $0.2545 M$ $HClO_4$. $[Hg(CN)_2]$: (a) $0 M$, (b) $0.1 M$; T = 25° C; I = $0.1 M$.

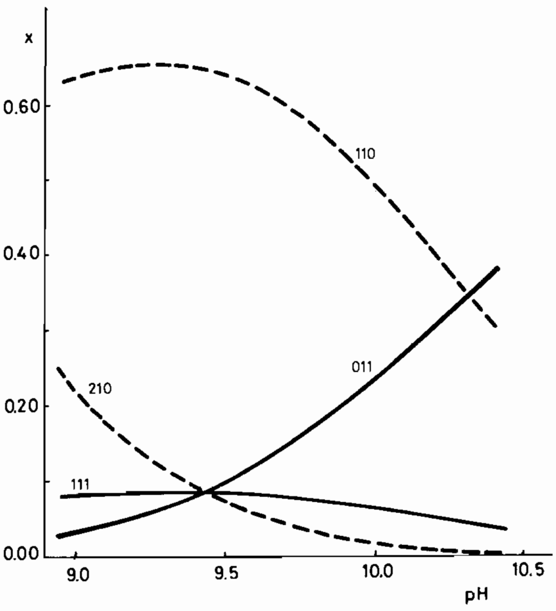

Figure 3. Mol fractions of the molecular species present in the 1,3-diaminopropane–$Hg(CN)_2$ systems referred to the total amine concentration, as a function of pH. [dpn] = $1.018 \times 10^{-2} M$; $[Hg(CN)_2] = 0.10 M$; T = 25° C; I = $0.1 M$.

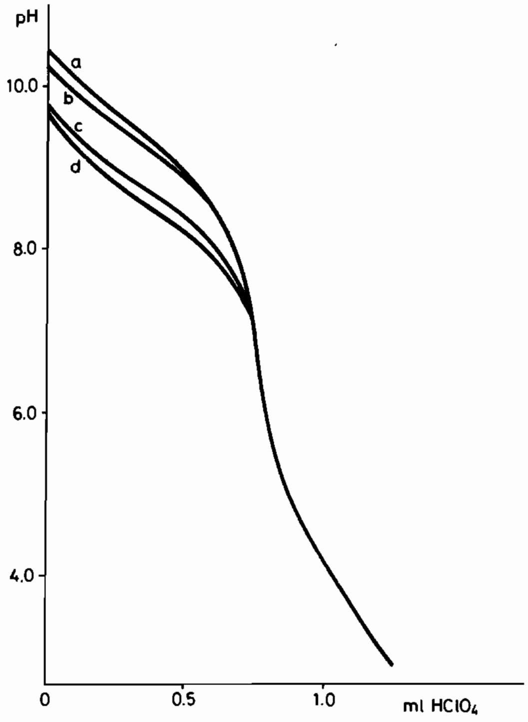

Figure 4. Effect of $Hg(CN)_2$ on the pH change during titration of $9.34 \times 10^{-3} M$ ethylenediamine with $0.2545 M$ $HClO_4$. $[Hg(CN)_2]$: (a) $0 M$; (b) $0.01 M$; (c) $0.05 M$; (d) $0.10 M$; I = $0.1 M$.

TABLE II. Titration curve measured by acid titration of the ethylenediamine – $Hg(CN)_2$ system at 25° C and an ionic strength of $0.1 M$, and the curve calculated with the aid of the constants obtained. [en] = $0.0093 M$, $[Hg(CN)_2] = 0.05 M$, $[HClO_4] = 0.2545 M$.

pH Measured	ml $HClO_4$ Measured	ml $HClO_4$ Calculated	Δ ml
9.958	0.100	0.1033	0.0033
9.698	0.200	0.1896	–0.0104
9.481	0.300	0.2816	–0.0184
9.282	0.400	0.3803	–0.0197
9.089	0.500	0.4833	–0.0167
8.882	0.600	0.5924	–0.0076
8.651	0.700	0.7020	0.0020
8.378	0.800	0.8083	0.0083
8.070	0.900	0.9049	0.0049
7.777	1.000	0.9932	–0.0068

Ethylenediamine, Diethylenetriamine, Triethylenetetramine

The titration curves for ethylenediamine are given in the presence and absence of $Hg(CN)_2$ in Figure 4; the data of one of these curves are given together with those of the calculated one in Table II and the distribution diagram is presented in Figure 5.

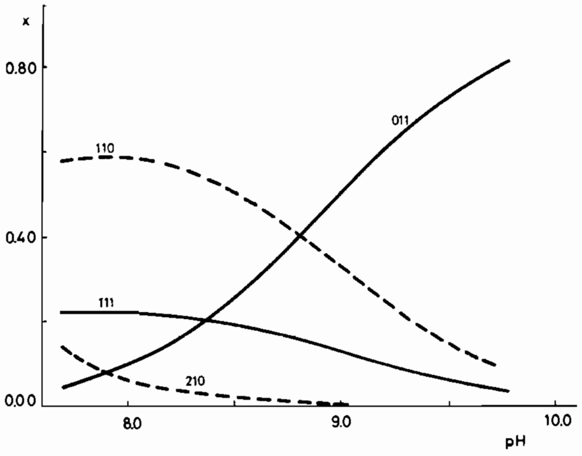

Figure 5. Mol fractions of the molecular species formed in the ethylenediamine–$Hg(CN)_2$ system referred to the total amine concentration, as a function of pH. [en] = 9.34 × 10^{-3} *M*; $[Hg(CN)_2]$ = 0.10*M*; I = 0.1*M*; T = 25° C.

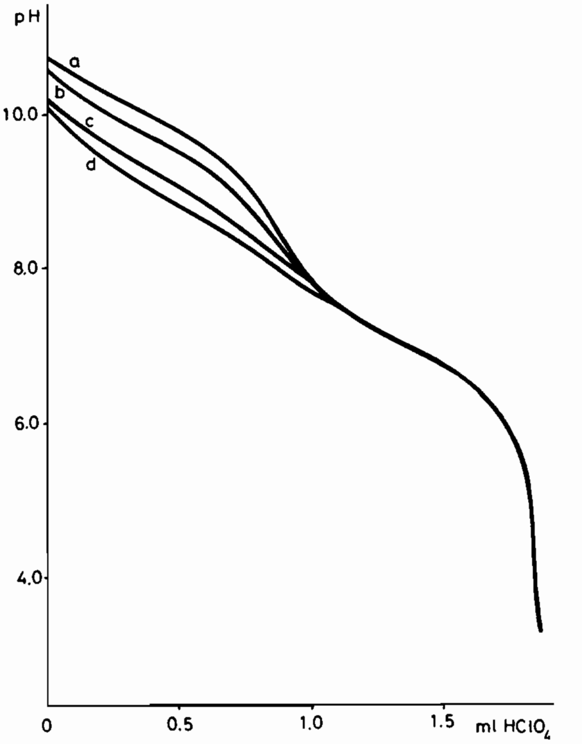

Figure 6. Effect of $Hg(CN)_2$ on the pH change during titration of 3.92 × 10^{-3}*M* diethylenetriamine with 0.2545*M* perchloric acid. $[Hg(CN)_2]$: (a) 0*M*; (b) 0.004*M*; (c) 0.04*M*; (d) 0.08*M*; T = 25° C; I = 0.1*M*.

The various protonation and stability constants were found to be: $\log K_{110} = 9.90 \pm 0.04$; $\log K_{210} = 7.01 \pm 0.04$; $\log K_{011} = 2.12 \pm 0.1$; $\log K_{111} = 0.60 \pm 0.06$.

The titration curves for the dien–$Hg(CN)_2$ system are given in Figure 6, the comparison of the experimental and calculated curves in Table III, and the concentration distribution of the molecular species found in Figure 7.

The protonation and stability constants found were: $\log K_{110} = 9.64 \pm 0.1$; $\log K_{210} = 8.86 \pm 0.1$; $\log K_{310} = 4.36 \pm 0.1$; $\log K_{011} = 2.52 \pm 0.08$; $\log K_{012} = 0.52 \pm 0.1$; $\log K_{111} = 1.68 \pm 0.2$.

TABLE III. Titration curve measured by acid titration of the diethylenetriamine – $Hg(CN)_2$ mixture at 25° C and an ionic strength of 0.1*M*, and the curve calculated from the constants obtained. [dien] = 0.00392*M*, $[Hg(CN)_2]$ = 0.08*M*, $[HClO_4]$ = 0.2545*M*.

pH Measured	ml $HClO_4$ Measured	ml $HClO_4$ Calculated	Δ ml
9.285	0.100	0.1060	0.0060
9.098	0.150	0.1543	0.0043
8.947	0.200	0.2026	0.0026
8.819	0.250	0.2499	–0.0009
8.699	0.300	0.2987	–0.0013
8.477	0.400	0.3951	–0.0049
8.363	0.450	0.4447	–0.0053
8.240	0.500	0.4960	–0.0040
8.112	0.550	0.5451	–0.0049
7.951	0.600	0.5990	–0.0010
7.748	0.650	0.6529	0.0029

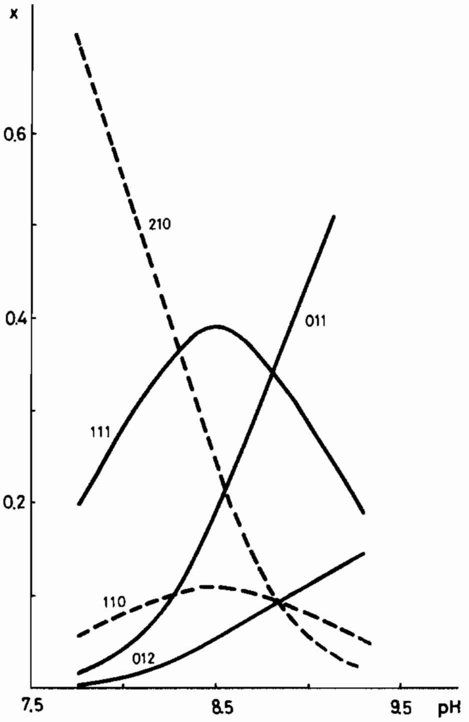

Figure 7. Mol fractions of the molecular species formed in the diethylenetriamine–$Hg(CN)_2$ system referred to the total amine concentration, as a function of the pH. [dien] = 3.92 × 10^{-3}*M*; $[Hg(CN)_2]$ = 0.08*M*; T = 25° C; I = 0.1*M*.

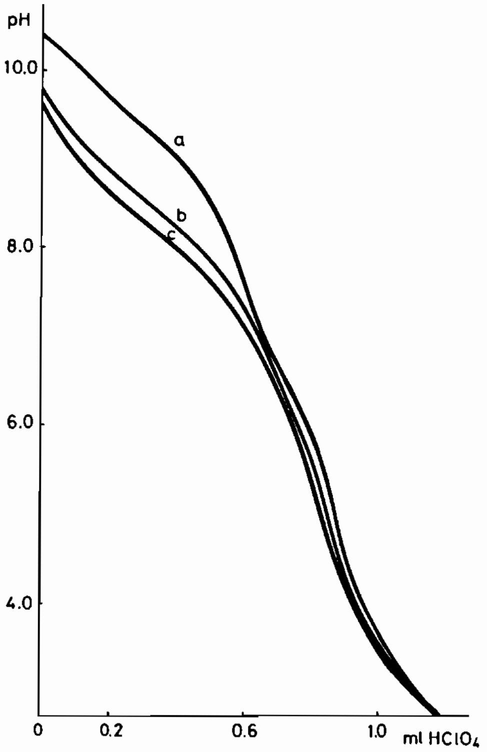

Figure 8. Effect of $Hg(CN)_2$ on the pH change during titration of $3.054 \times 10^{-3} M$ triethylenetetramine with $0.2545 M$ $HClO_4$. $[Hg(CN)_2]$: (a) $0 M$; (b) $0.04 M$; (c) $0.08 M$; $T = 25° C$; $I = 0.1 M$.

TABLE IV. Titration curve measured by acid titration of the triethylenetetramine – $Hg(CN)_2$ mixture at 25° C and an ionic strength of $0.1 M$, and the curve calculated from the constants obtained. $[trien] = 0.00305 M$, $[Hg(CN)_2] = 0.04 M$, $[HClO_4] = 0.2545 M$.

pH Measured	ml HClO₄ Measured	ml HClO₄ Calculated	Δ ml
9.227	0.100	0.1020	0.0020
9.026	0.150	0.1494	−0.0006
8.854	0.200	0.1986	−0.0014
8.695	0.250	0.2500	0.0000
8.552	0.300	0.2969	−0.0011
8.404	0.350	0.3496	−0.0004
8.251	0.400	0.3998	−0.0002
8.073	0.450	0.4525	0.0024
7.880	0.500	0.5006	0.0006
7.630	0.550	0.5516	0.0016
7.338	0.600	0.5956	−0.0044

The titration curves for trien in the presence and absence of $Hg(CN)_2$ are presented in Figure 8, the fit of the calculated and the experimental curves can be judged from Table IV and the concentration distribution diagram is given in Figure 9.

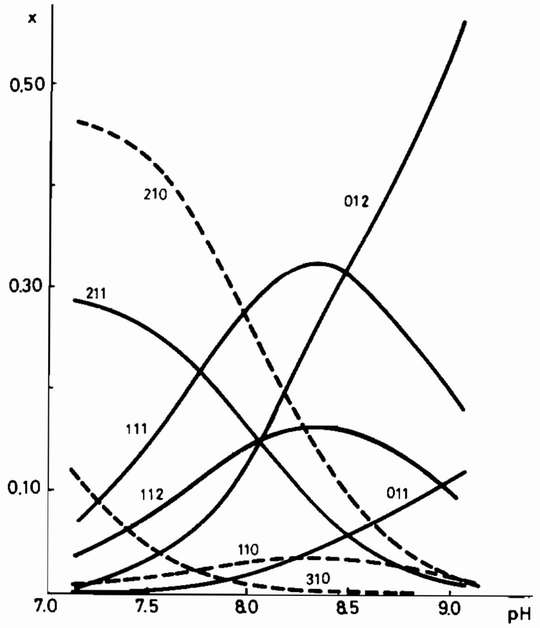

Figure 9. Mol fractions of the molecular species present in the triethylenetetramine–$Hg(CN)_2$ system referred to the total amine concentration, as a function of pH. $[trien] = 3.054 \times 10^{-3} M$; $[Hg(CN)_2] = 0.08 M$; $T = 25° C$; $I = 0.1 M$.

The protonation and stability constants found were: $\log K_{110} = 9.77 \pm 0.1$; $\log K_{210} = 9.04 \pm 0.1$; $\log K_{310} = 6.54 \pm 0.1$; $\log K_{410} = 3.34 \pm 0.1$; $\log K_{011} = 2.73 \pm 0.2$; $\log K_{012} = 1.81 \pm 0.2$; $\log K_{111} = 2.19 \pm 0.2$; $\log K_{112} = 0.82 \pm 0.1$; $\log K_{211} = 0.90 \pm 0.1$.

Discussion

$Hg(CN)_2$ interacts with the various amines through the residual affinity of thc Hg(II). In the titration of the $Hg(CN)_2$–amine systems with acid, not only the 1:1 complexes but also protonated and polynuclear complexes are formed. The protonation constants of

TABLE V. Stability constants of the mixed ligand complexes found in the $Hg(CN)_2$ – amine systems at 25° C and an ionic strength of $0.1 M$.[a]

Amine	$\log K_{ABC}$				
	011	012	111	112	211
etn	0.75	–	–	–	–
dpn	1.08	–	0.25	–	–
en	2.12	–	0.60	–	–
dien	2.52	0.52	0.68	–	–
trien	2.73	1.81	2.19	0.82	0.90

[a] A = H, B = amine, C = $Hg(CN)_2$.

TABLE VI. Statistical, experimentally determined and calculated increases of the stability constants of en, dien and trien (011) complexes, at 25° C and an ionic strength of 0.1 *M*.

Ligand	Donor Groups in the Chelate Ring	Number of Possible Chelate Rings	Stability Constants		
			Statist.	Measd.	Calcd.
en	NH_2 NH_2	1		131.8	
dien	NH NH_2	2	2 × 131.8	2.50 × 131.8	2.50 × 131.8[a]
trien	NH NH_2	2			
	NH NH	1	3 × 131.8	4.1 × 131.8	4.06 × 131.8[b]

[a] 2.50 = 2 × 1.25. [b] 4.06 = 2 × 1.25 + 1 × 1.25^2.

the amines determined in this paper are in good agreement with the literature data[19] indicating the high purity of the amines applied.

Table V lists the pH-metrically determined stability constants of the $Hg(CN)_2$–amine mixed ligand complexes.

Ethylamine, monoprotonated ethylenediamine and diaminopropane can behave as monodentate, while ethylenediamine, 1,3-diaminopropane, diethylenetriamine, triethylenetetramine and monoprotonated diethylenetriamine and triethylenetetramine as bi- or polydentate ligands towards $Hg(CN)_2$. The great difference between the stability constants of the compounds formed with mono- and polydentate ligands indicates a significant chelate effect. The resulting chelates contain five-membered rings; five-membered rings are similarly present in the molecules $Hg(CN)_2 \cdot$ phen and $Hg(CN)_2 \cdot$ dipy. The stability of the 1,3-diaminopropane (011) complex is similar to that of the ethylamine (011) complex rather than to that of the ethylenediamine (011) complex. Presumably this means that the probability of formation of a six-membered chelate ring is fairly low and the potentially bidentate 1,3-diaminopropane in this case behaves monodentately.

A more detailed comparison of the tabulated data shows that the stabilities of complexes with the same indices increase in parallel with the increase of the number of donor atoms in the ligand. However the extent of the increase is not comparable for most of the different compounds. This is possible only when the different analogous amines differ from each other not only in the number of donor groups but are bonded to the $Hg(CN)_2$ exactly the same way (monodentately or with chelate formation). These are fulfilled only in the case of etn, dpn (011) (monodentate) and en, dien, trien (011) (chelate) complexes. Though this gives us only a limited number of data for making generalizations, nevertheless one must consider that while in the case of etn, dpn (011) complexes the extent of the increase corresponds to the statistical one, in the second scrics it is higher. Its reason may be the different donor abilities of the nitrogen atoms in NH_2 and NH groups present in different numbers in the different amines of the second series. The ratio of the stability constants, presented in Table VI, shows that the ratio of the donor abilities of the NH_2 NH_2, NH NH_2, and NH NH groups is 1 : 1.25 : 1.25^2. It seems unlikely that these ratios are due to coincidence or experimental error.

Acknowledgments

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