

Study of the effect of nature of ligand on reproportionation constants of ternary complexes

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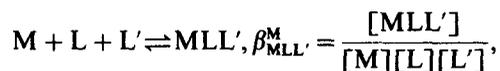
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Abstract. The stability constants of ternary M(II) complexes, $[MLL']$, where M refers to Cu(II) or Ni(II), L refers to ethylenediamine (en), 1,3-diaminopropane (1,3-pn), N,N-dimethylethylenediamine (N,N-dimen), N,N-diethylethylenediamine (N,N-dien) and L' refers to catechol, catechuic acid, tiron, pyrogallol, *o*-aminophenol, *o*-phenylenediamine, oxalic acid, malonic acid, glycine, α -alanine, β -alanine, have been determined potentiometrically using the SCOGS computer program. Log K_{reprop} (reprop. – reproportionation) of ternary complexes have been calculated. The effect of the nature of the ligand on K_{reprop} values has been discussed for these ternary complexes and the fact that K_{reprop} is not a proper measure of the stability of the ternary complex has been indicated.

Keywords. Reproportionation constant; ternary complexes; nature of ligand.

1. Introduction

Ternary complexes have attracted the attention of chemists mainly because of their importance as models for biological systems (Martell 1973; Sigel 1973, 1980; Fischer *et al* 1977). Their study however is important from a fundamental chemistry point of view as well. The effects of the structural features of the complex and the nature of the ligand on the stability of the ternary complex and associated binary complexes is of great significance (Bhattacharya 1981). The formation of a ternary complex can be considered to take place in three different ways, as follows:



Hence $\log K_{MLL'}^{ML} = \log \beta_{MLL'}^M - \log K_{ML}^M$,

$\log K_{MLL'}^{ML'} = \log \beta_{MLL'}^M - \log K_{ML'}^M$.

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One method of representing the stability of the ternary complex is in terms of $\Delta \log K = \log K_{\text{MLL}'}^{\text{ML}} - \log K_{\text{ML}'}^{\text{ML}}$, i.e. the difference in the tendency of L to bind to a free metal ion and to a metal ion bound to another ligand L'. On statistical considerations $\Delta \log K$ is expected to be negative, as when the ligand combines with a free metal ion, it has more coordination positions available for binding than when it combines with a metal ion already bound to another ligand. Thus, the value of $\Delta \log K$ depends on the coordination number of the metal ion and the denticity of the ligand. It is also affected by non-statistical factors like the nature of the ligands L and L'. A less negative value of $\Delta \log K$ indicates increased stability of the ternary complex because of factors other than statistical.

The other approach to express the stability of the ternary complex on a quantitative basis is based on the disproportionation constant, $K_{\text{reprop.}}$, as defined by the following equation:

$$\text{ML}_2 + \text{ML}'_2 \rightleftharpoons 2 \text{MLL}', K_{\text{reprop.}} = \frac{[\text{MLL}']^2}{[\text{ML}_2][\text{ML}'_2]}$$

$$\log K_{\text{reprop.}} = \log K_{\text{MLL}'}^{\text{ML}'} - \log K_{\text{ML}_2}^{\text{ML}} + \log K_{\text{MLL}'}^{\text{ML}} - \log K_{\text{ML}'_2}^{\text{ML}'}$$

On statistical considerations, the value of $K_{\text{reprop.}}$ is expected to be 4, i.e. $\log K_{\text{reprop.}} = 0.6$ (Dewitt and Watters 1954; Kida 1956; Schubert and Sharma 1969). The advantage of considering $\log K_{\text{reprop.}}$ is its firm statistical basis. It does not depend on the coordination number of the metal ion or the denticity of the ligand as in case of $\Delta \log K$. However, $\log K_{\text{reprop.}}$ does not indicate the absolute stability of the complex, but its relative stability with respect to the complexes ML_2 and ML'_2 . If for electrostatistical or stereochemical reasons the stability of ML_2 or ML'_2 is less, more of MLL' is formed and the value of $\log K_{\text{reprop.}}$ is higher than 0.60. Thus in a mixed ligand complex containing a neutral L and a negatively charged ligand L', $\Delta \log K$ is not affected by the electrostatic or entropy factor. However, these external factors are likely to have an appreciable effect on the formation of binary complexes ML_2 and ML'_2 and in turn on the $\log K_{\text{reprop.}}$ value. As ML_2 and ML'_2 are additional species which do not interfere in the formation of mixed ligand complex MLL' , the value $K_{\text{reprop.}}$, depending on such species, gives a misleading picture of the intrinsic tendency towards ternary complex formation and is not the proper measure of the stability of the ternary complex (Brookes and Pettit 1977). Such a defect does not occur in $\Delta \log K$ value.

In order to study the deviation of the $\log K_{\text{reprop.}}$ and $\Delta \log K$ values of the ternary complexes from the statistical expectations, and to understand the role of the nature of the ligand, formation constants of ternary complexes MLL' , where M = Cu(II) or Ni(II), L = en, 1,3-pn, N,N-dimen, N,N-dien and L' = catechol, catechuic acid, tiron, pyrogallol, o-aminophenol, o-phenylenediamine, oxalic acid, malonic acid, glycine, α -alanine, and β -alanine have been determined and the values of $\Delta \log K$ and $\log K_{\text{reprop.}}$ have been calculated. Some of the protonation constants and formation constants for binary complexes have been reported earlier (Huber *et al* 1971; Martell and Smith 1977; Odani and Yamuchi 1984). But all the protonation constants and binary constants have been redetermined to obtain the values under experimental conditions similar to that for the ternary complexes. In cases where the conditions used by the previous workers are comparable with ours, the values of the formation constants obtained by us are comparable to those of previous workers.

2. Experimental

All the reagents used were of AR grade and the titrations were carried out using an Orion Research microprocessor ionalyzer/901 with an accuracy of ± 0.001 pH units. The proton–ligand formation constants of the binary complexes CuL , CuL_2 , NiL , NiL_2 and NiL_3 were determined in aqueous media at 25°C and $I = 0.2 \text{ M NaClO}_4$ using the SCOGS computer program (charges on the species have been omitted for simplicity) (Sayce 1968, 1971; Sayce and Sharma 1972). In the case of the proton–ligand complexes, the formation constants of the L , LH and LH_2 species, and the formation constants of the binary complexes L , LH , LH_2 , M , ML , ML_2 were considered. The ML_3 species was also considered in case of Ni(II) complexes. (These values of formation constants are not presented in the paper, but can be obtained from the Editor or authors on request.) These refined values were used as fixed parameters for the refinement of the formation constants of the ternary complexes MLL' . For the determination of the formation constant of the ternary complexes MLL' , the following sets of solutions (50 cm^3) having $\text{M:L:L}'$ in the ratio 1:2:2 and 1:3:3 were prepared and titrated against standard alkali:

- (i) 0.02 M HClO_4 , 0.002 M metal perchlorate, 0.004 M ligand (L), 0.004 M ligand (L') and 0.17 M NaClO_4 .
- (ii) 0.02 M HClO_4 , 0.002 M metal perchlorate, 0.006 M ligand (L), 0.006 M ligand (L') and 0.166 M NaClO_4 .

Titrations of each set were carried out twice to check the reproducibility of the data. In the case of catechol and its derivatives, titrations were carried out under nitrogen. The species considered for the calculation of formation constants of ternary complexes were L , LH , LH_2 , L' , L'H , L'H_2 , M , ML , ML_2 , ML' , ML'_2 and MLL' . ML_3 and ML'_3 species were also considered in the case of Ni(II) complexes.

The formation constants $\log K_{\text{MLL}'}^{\text{M}}$, $\Delta \log K$ and $\log K_{\text{reprop.}}$ are presented in table 1.

The deviation in the $\log K_{\text{MLL}'}^{\text{M}}$ values have been shown in brackets. These indicate random errors in the titration, dependent on the precision of the instruments. The concentration of the species obtained from the output of the computer data for the system [Cu-en-catechol] as representative have been plotted in figure 1.

As precipitation occurs at higher pH, computer refinement of $\log K_{\text{Cu(ox)}_2}^{\text{Cu(ox)}}$ and $\log K_{\text{NiLL}'}^{\text{Ni}}$, where $\text{L}' = \text{oxalic acid (ox)}$, malonic acid, or *o*-phenylenediamine was not possible.

3. Results and discussion

In the case of the CuLL' complex, where $\text{L} = \text{ethylenediamine}$ or $1,3\text{-diaminopropane}$ and $\text{L}' = \text{catechol}$, catechuic acid, pyrogallol or tiron, it is observed that $\log K_{\text{reprop.}}$ is much higher than the expected value of 0.60 and the value of $\log K_{\text{reprop.}}$ is not in keeping with the value of $\Delta \log K$. The value of $\Delta \log K$ is negative as expected from statistical considerations. However, the values of $\log K_{\text{reprop.}}$ are higher, because catechol and its derivatives form charged ions and the value of $K_{\text{ML}_2}^{\text{M}}$ is lowered because of electrostatic repulsion between the two ligand ions. Moreover, neutral CuLL' is entropy-stabilized compared to the charged ions CuL_2^{n+} and $\text{CuL}_2'^{n-}$. This leads to a large value of $K_{\text{reprop.}}$. In cases where $\text{L} = 1,3\text{-diaminopropane}$ forming a

Table 1. Mixed ligand stability constants, $\Delta \log K$ and $\log K_{\text{reprop}}$ in aqueous media, $\mu = 0.2 \text{ M}$ (NaClO_4) at 25°C .

Ligands(L')	$\log K_{\text{CuLL}}$	$\Delta \log K$	$\log K_{\text{reprop}}$	$\log K_{\text{NiLL}}$	$\Delta \log K$	$\log K_{\text{reprop}}$
	<i>Ethylenediamine-Cu²⁺-L'-systems</i>			<i>Ethylenediamine-Ni²⁺-L' systems</i>		
Catechol	23.56(0.04)	-0.13	3.26	16.14(0.06)	-0.23	3.91
Catechuic acid	22.58(0.03)	-0.24	3.66	15.54(0.04)	-0.53	2.87
Tiron	23.18(0.09)	-0.67	2.45	16.27(0.10)	-1.32	1.93
Pyrogallol	22.31(0.03)	-0.52	—	14.79(0.08)	-0.62	—
<i>o</i> -Aminophenol	18.12(0.10)	-0.40	1.82	12.10(0.02)	-0.28	0.90
<i>o</i> -Phenylenediamine	13.65(0.04)	-0.82	0.54	—	—	—
Oxalic acid	14.15(0.03)	-0.72	0.96	—	—	—
Malonic acid	14.42(0.05)	-0.74	1.13	—	—	—
Glycine	17.05(0.02)	-0.90	0.81	13.05(0.04)	-0.78	0.90
α -Alanine	17.23(0.03)	-0.73	0.79	12.60(0.01)	-0.90	0.94
β -Alanine	15.91(0.10)	-0.83	0.67	12.16(0.05)	-0.93	1.10
1,3-Diaminopropane	18.46(0.10)	-1.28	0.85	14.06(0.03)	-1.35	0.92
	<i>1,3-Diaminopropane-Cu²⁺-L' systems</i>			<i>1,3-Diaminopropane-Ni²⁺-L' systems</i>		
Catechol	22.72(0.10)	-0.65	3.31	15.03(0.01)	-0.77	3.93
Catechuic acid	21.76(0.10)	-0.74	3.37	14.51(0.04)	-0.99	3.05
Tiron	22.33(0.04)	-1.20	2.48	15.18(0.07)	-1.84	1.99
Pyrogallol	21.68(0.10)	-0.83	—	13.86(0.01)	-0.98	—
<i>o</i> -Aminophenol	17.70(0.10)	-0.50	2.71	11.45(0.05)	-0.36	1.84
<i>o</i> -Phenylenediamine	13.08(0.04)	-1.07	1.13	—	—	—
Oxalic acid	13.60(0.05)	-0.95	1.59	—	—	—
Malonic acid	13.86(0.04)	-0.98	1.74	—	—	—
Glycine	16.57(0.04)	-1.06	1.58	11.98(0.01)	-1.28	1.00
α -Alanine	16.73(0.05)	-0.91	1.52	11.55(0.01)	-1.38	1.08
β -Alanine	15.45(0.10)	-0.97	1.48	11.08(0.06)	-1.44	1.18
Ethylenediamine	18.46(0.10)	-1.28	0.85	14.06(0.01)	-1.35	0.92
	<i>N,N-Dimethylethylenediamine-Cu-L'</i>			<i>N,N-Dimethylethylenediamine-Ni-L'</i>		
Catechol	22.50(0.01)	-0.09	4.27	14.81(0.04)	-0.30	4.55
Catechuic acid	21.12(0.03)	-0.60	3.87	14.16(0.01)	-0.65	3.41
Tiron	22.10(0.00)	-0.65	3.42	14.78(0.03)	-1.55	2.25
Pyrogallol	20.80(0.01)	-0.90	—	13.25(0.04)	-0.90	—
<i>o</i> -Aminophenol	16.66(0.05)	-0.76	2.03	10.70(0.05)	-0.42	1.40
<i>o</i> -Phenylenediamine	12.41(0.04)	-0.96	1.19	—	—	—
Oxalic acid	13.35(0.01)	-0.42	2.49	—	—	—
Malonic acid	13.39(0.03)	-0.67	2.57	—	—	—
Glycine	16.41(0.00)	-0.44	2.66	11.45(0.00)	-1.12	1.00
α -Alanine	16.49(0.02)	-0.37	2.44	11.13(0.02)	-1.11	1.30
β -Alanine	15.05(0.05)	-0.59	2.08	10.58(0.05)	-1.25	1.24
Ethylenediamine	18.07(0.00)	-0.89	1.47	13.57(0.01)	-1.15	1.00
1,3-Diaminopropane	16.52(0.04)	-1.39	1.56	12.79(0.03)	-1.36	1.68
	<i>N,N-Dimethylethylenediamine-Cu-L'</i>			<i>N,N-Dimethylethylenediamine-Ni-L'</i>		
Catechol	21.40(0.02)	-0.06	4.47	13.27(0.00)	-0.30	4.65
Catechuic acid	19.98(0.04)	-0.61	3.99	12.59(0.01)	-0.68	3.45
Tiron	21.07(0.01)	-0.55	3.76	13.20(0.00)	-1.59	2.27
Pyrogallol	19.70(0.04)	-0.90	—	11.71(0.02)	-0.90	—
<i>o</i> -Aminophenol	15.72(0.05)	-0.57	2.55	9.16(0.05)	-0.42	1.50
<i>o</i> -Phenylenediamine	11.56(0.05)	-0.68	1.89	—	—	—
Oxalic acid	11.99(0.01)	-0.25	2.17	—	—	—
Malonic acid	12.55(0.03)	-0.38	2.94	—	—	—
Glycine	15.33(0.01)	-0.39	2.90	9.96(0.01)	-1.07	1.20
α -Alanine	15.38(0.00)	-0.35	2.62	9.58(0.00)	-1.12	1.38
β -Alanine	14.11(0.04)	-0.40	2.60	9.02(0.04)	-1.27	1.30
Ethylenediamine	17.08(0.01)	-0.75	1.89	12.03(0.01)	-1.15	1.10
1,3-Diaminopropane	16.25(0.01)	-1.26	1.86	11.21(0.04)	-1.40	1.70

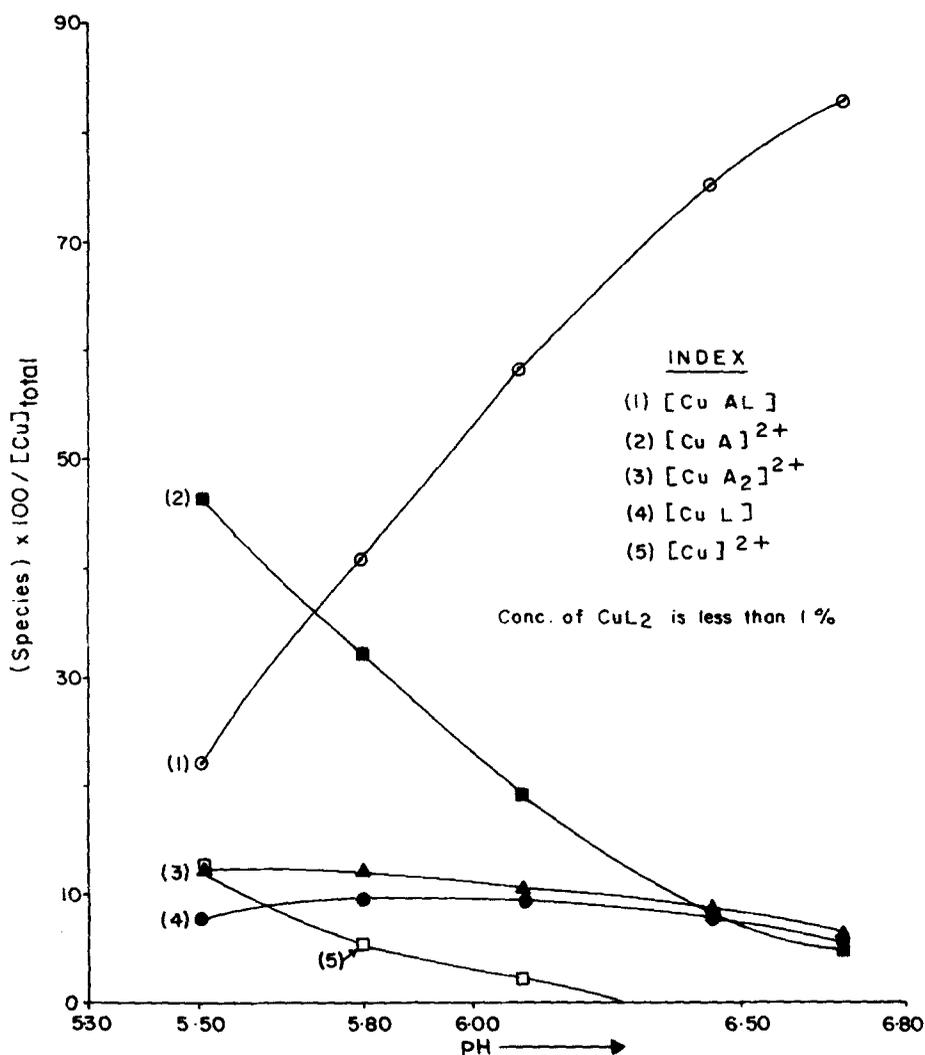
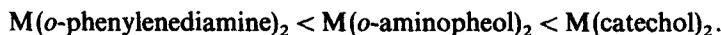


Figure 1. Distribution diagram for the $[Cu-en(A)-catecholate(L)]$ ternary system showing the formation percentages relative to total concentration of the metal as a function of pH.

six-membered ring, an unstable 6,6-membered ML_2 complex is formed. Thus both ML_2 and ML'_2 are less stable and therefore more of MLL' is formed, resulting in higher $\log K_{reprop.}$ values than the complex $[Cu(ethylenediamine)(L')]$.

It is interesting to compare the $\log K_{reprop.}$ values for the $CuLL'$ complex where $L = ethylenediamine$, 1,3-diaminopropane and $L' = catechol$, *o*-aminophenol, *o*-phenylenediamine. $\Delta \log K$ values do not have significant differences, but the differences in $\log K_{reprop.}$ values are significant. This is because in the formation of ML'_2 complex, where $L' = catecholate$ anion, there is more charge repulsion between the L'^{2-} in the ML'_2 complex, than in the formation of the ML_2 complex where L' is mono-negative *o*-aminophenolate anion. In the formation of the ML_2 complex where $L' = o$ -phenylenediamine, there is no repulsion between the ligands. Hence destabiliz-

ation of the ML_2 complex is in the order



As a result $\log K_{\text{reprop.}}$ values of the ternary complexes are in the order



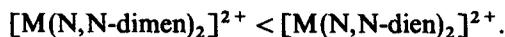
In the case of $[M(\text{ethylenediamine})(o\text{-phenylenediamine})]$ with two neutral ligands, with no electrostatic repulsion, the $\log K_{\text{reprop.}}$ value is closer to the expected value of 0.60.

A similar effect of the charge on L^{n-} is observed in complexes $CuLL'$ where $L = \text{ethylenediamine}$, 1,3-diaminopropane and $L^{n-} = \text{oxalate}$, malonate, amino acid or 1,3-pn. It is observed that $\log K_{\text{reprop.}}$ is maximum in cases where $L' = \text{ox}^{2-}$ ($\text{ox} = \text{oxalate}$). It is less when $L' = \text{amino acid monoanion}$ and least where $L' = \text{neutral 1,3-diaminopropane}$. This can be explained as follows.

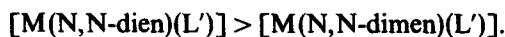
For complexes $CuLL'$, where $L = 1,3\text{-pn}$, $\log K_{\text{reprop.}}$ is greater than when $L = \text{ethylenediamine}$, as discussed earlier. In case of $[Cu(1,3\text{-pn})(\text{malonate})]$ complex, $K_{\text{reprop.}}$ is higher as both the binary complexes $[Cu(\text{malonate})_2]^{2-}$ and $[Cu(1,3\text{-pn})_2]^{2+}$ have two six-membered rings resulting in their lesser stability, leading to formation of more ternary complex.

$\Delta \log K$ and $\log K_{\text{reprop.}}$ values of the ternary complexes $[Ni\text{-en}L']$ and $[Ni(1,3\text{-pn})(L')]$ for different L' follow the same order as those of the $[Cu(\text{en})L']$ and $[Cu(1,3\text{-pn})L']$ complexes and this fact is in agreement with the above explanation.

A similar effect of the nature of L' leading to low or high $K_{\text{reprop.}}$ values is observed in complexes MLL' , where $M = Cu(II)$ or $Ni(II)$ and $L = N,N\text{-dimen}$ or $N,N\text{-dien}$ and L' are the ligands as described in $[M\text{-en}$ or $1,3\text{-pn } L']$ systems. However in the case of MLL' , where $L = N,N\text{-dimen}$ or $N,N\text{-dien}$, $\log K_{\text{reprop.}}$ is higher than in the case of the $[M(\text{en})(L')]$ complexes. This is because both the N -substituted diamine ligands (L) have two methyl groups ($-\text{CH}_3$) or two ethyl groups ($-\text{C}_2\text{H}_5$) on the nitrogens of the diamine and hence both the binary complexes $[M(N,N\text{-dimen})_2]^{2+}$ and $[M(N,N\text{-dien})_2]^{2+}$ are destabilized because of steric hindrance. As a result the formation of the ternary complex is maximum and $K_{\text{reprop.}}$ is high. The destabilization of the binary ML_2 complex is in the order



As a result $K_{\text{reprop.}}$ values of the ternary complexes are in the order



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