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A Thermodynamic Investigation of the Coordinating Ability of N-(2-hydroxy ethyl)ethylenediamine towards Copper(II) and Nickel(II) in Aqueous Solution

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The heats of ligand protonation and of complex formation of the ligand N-(2-hydroxyethyl)ethylenediamine (Etolen) with Nickel(II) and Copper(II) have been calorimetrically measured at 25° C in 0.5M $NaClO_4$ solution; the corresponding entropy values have also been calculated. Thermodynamic parameters associated with protonation of the ligand Etolen are compared to those of similar amine ligands and the effect of the hydroxy group in Etolen has been evaluated. Enthalpy and entropy effects associated with the formation of Nickel(II) and Copper(II) complexes with Etolen are compared to similar terms for complex formation with the ligand 2,2'-diaminoethylether (Oden). Complexes of the latter ligand contain a coordinated etheral oxygen and are used as a comparison to determine the effect of the hydroxyl group in Etolen.

The entropy term for formation of the hydroxy complex $[Cu(OH)_2Etolen]$ is considerably larger than those associated with the formation of other analogous complexes. This is due to a probable opening of the chelate branch containing the alcoholic group during hydrolysis.

Introduction

The coordinating properties of the ligand Etolen N-(2-hydroxyethyl)ethylenediamine have been previously investigated by a variety of spectroscopic techniques, both in the solid state and in non-aqueous solution.[1] In some instances the ligand acts as a tridentate (through two nitrogen and one oxygen atoms) while in other cases the ligand acts as a bidentate (coordinating only through two nitrogen atoms), for example in the compound $CuEtolen_2(ClO_4)_2$ the ligand is bonded by three donor atoms (2 N and 1 O)[2] while in the compound $CuEtolen_2Cl_2$ the hydroxy group is not coordinated (only 2 N) and there are two free branches of the ligands *trans* to each other.[3]

In aqueous solutions the coordination properties of Etolen have been evaluated only by determination of the stability constants[4] and little is known about the coordinate bond strengths or about the geometry of the complexes in solution. The present study was undertaken to determine whether or not the hydroxy group of the ligand Etolen is coordinated to the metal ions Cu(II), Ni(II) in aqueous solution. Recently a complete thermodynamic investigation has shown that a ligand containing an etheral oxygen and two nitrogens (2,2'-diaminoethylether) can coordinate through all three donors in aqueous solution.[5] From a comparison of the two stereochemically similar ligands Oden and Etolen, the coordinating properties of the oxygen can be evaluated. The enthalpies of successive protonation of Etolen have been measured and are compared to those for other ligands containing similar electron withdrawing groups.

Experimental

Materials

N-(2-hydroxyethyl)ethylenediamine was obtained commercially. It was purified as the hydrochloride, formed by adding hydrochloric acid to an alcoholic solution of the amine. The product was recrystallised from alcohol and then dried to constant weight at 60°C *in vacuo* (Found: Cl 40.1%. Calc. for $C_4H_{14}N_2OCl_2$, Cl 40.0%). The solutions of metal ions and of sodium hydroxyde were prepared and standardised as previously described.[6]

Calorimetric Measurements

Calorimetric measurements were carried out in a titration calorimeter LKB 8700/2 by the technique previously described.[7] For the protonation measurements, different volumes of a standard solution of sodium hydroxide were added to *ca.* 90 ml of a solution containing the amine hydrochloride and a slight excess of perchloric acid. For the formation of metal complexes, the calorimetric vessel contained also an equimolar amount of metal ion. The heats of formation of the two Nickel(II) complexes were determined by an indirect method already described.[7]

TABLE I. Calorimetric Results for the Protonation and Metal Complex Formation of Etolen in 0.5*M* $NaClO_4$ at 25 °C.

Metal	Calorimetric Ampoule			Titrant Added			Q^a
	H^+ mmol	M^{2+} mmol	Etolen mmol	Vol ml	NaOH ml	mmol	cal
H^+	3.1414		1.4887	90.5	1.00	0.4630	3.098
	2.5714		1.2041	95.5	1.00	0.4630	3.141
	2.6784		1.4887	91.5	2.00	0.9260	2.937
	2.1084		1.2041	96.5	2.00	0.9268	2.891
	3.0971		1.4672	92.6	1.00	0.4630	3.070
	2.6341		1.4672	93.6	2.00	0.9260	2.891
	2.7764		1.3063	94.5	1.00	0.4630	3.071
	2.3134		1.3063	95.5	2.00	0.4630	2.903
	4.8368		2.3349	91.7	2.00	0.9260	4.594
	3.9108		2.3349	93.7	2.00	0.9260	2.927
	2.8443		2.2665	95.8	2.00	0.9260	2.537
					$HClO_4$		
Ni^+	2.1226	0.2367	1.4315	89.87	8.00	2.2648	5.621
	1.4249	0.2329	1.3636	89.87	8.00	2.2648	10.135
	2.3505	0.2226	1.6936	92.48	8.00	2.2648	8.091
	1.1637	0.2096	1.2306	90.07	8.00	2.2648	10.327
	1.1824	0.2130	1.2504	91.51	8.00	2.2648	10.516
	1.9554	0.2214	1.3216	89.68	8.00	2.2648	5.229
	1.9869	0.2249	1.3429	91.13	8.00	2.2648	5.281
					NaOH		
Cu^{2+}	5.8381	0.4058	2.8374	94.40	2.00	0.9260	8.317
	4.9121	0.4058	2.8374	96.40	2.00	0.9260	7.010
	3.9861	0.4058	2.8374	98.40	2.00	0.9260	3.408
	5.7914	0.4849	2.8141	94.94	2.00	0.9260	8.381
	4.8654	0.4849	2.8141	96.94	2.00	0.9260	7.374
	3.9394	0.4849	2.8141	98.94	2.00	0.9260	4.683
	5.4230	0.4481	2.6256	92.52	3.00	1.3893	12.102
	4.2081	0.4392	2.4854	94.29	2.00	0.9260	7.295
	3.2821	0.4392	2.4854	96.29	2.00	0.9260	3.883
	5.8013	0.4210	2.8190	92.50	3.00	1.3893	11.969
	4.4120	0.4210	2.8190	95.50	3.00	1.3893	7.049
	4.7360	0.9806	2.8312	68.19	2.00	0.9260	7.602
	4.2801	1.0051	2.8393	94.90	3.00	1.3893	11.404
	4.3012	1.0470	2.8449	95.01	3.00	1.3893	11.404
	4.7470	1.1216	2.8366	96.24	2.00	0.9260	7.600
	3.8212	1.1216	2.8366	98.24	2.00	0.9260	7.642
	4.3000	1.0745	2.8443	96.37	3.00	1.3893	11.391
	4.8351	1.4801	2.8807	94.85	2.00	0.9260	7.557
	3.9091	1.4801	2.8807	96.85	2.00	0.9260	7.599
	4.0206	1.5204	2.7048	96.31	3.00	1.3893	11.408
	4.0304	0.4481	2.6256	95.52	3.00	1.3893	7.649

[a] Corrected for the heat of dilution of the titrant in 0.5*M* $NaClO_4$.

All the measurements were carried out with the reaction system thermostatted at 25.000 ± 0.001 °C. The heats of formation were calculated with an IBM 1130 computer and an appropriate program.[7] The concentration equilibrium constants used with Etolen were those reported in 0.5*M* Na ClO_4 at 25 °C.[4a] The detailed results are shown in Table I.

Results and Discussion

Protonation

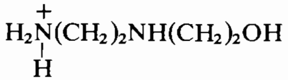
Protonation in Etolen may occur at both the primary and secondary nitrogens. Thermodynamic parameters for the protonation of this ligand are given in Table II and compared to the values obtained for the ligand

TABLE II. Thermodynamic Functions of Protonation and of Complex Formation with Etolen in 0.5*M* $NaClO_4$ Aqueous Solution at 25 °C.[a]

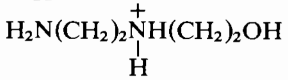
	Etolen[b]			Meen[d]			den[e]			Oden		
	$-\Delta G^{\circ c}$	$-\Delta H^\circ$	ΔS°	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°
$H^+ + L \rightleftarrows HL$	13.28	11.13(7)	7.2(2)	13.83	11.25	8.7	13.35	11.20	7.2	13.48	12.11	4.6
$H^+ + HL \rightleftarrows H_2L$	9.33	10.07(14)	-2.5(5)	9.90	10.34	-1.5	12.25	11.95	1.0	12.47	12.96	-1.6
$H^+ + H_2L \rightleftarrows H_3L$							5.80	7.20	-4.7			
$Ni + L \rightleftarrows NiL$	9.50	7.78(13)	5.8(4)				14.40	11.85	8.5	8.03	6.70	4.5
$NiL + L \rightleftarrows NiL_2$	7.95	8.31(23)	-1.2(8)				10.75	13.45	-8.5	4.93	6.52	-5.3
$Ni + 2L \rightleftarrows NiL_2$	17.45	16.09(10)	4.6(4)				25.15	25.30	0.0	12.96	13.22	-0.8
$Cu + L \rightleftarrows CuL$	14.09	11.09(3)	10.06(10)	14.21	11.53	9.0	21.5	18.00	12.0	12.2	9.53	9.1
$CuL + L \rightleftarrows CuL_2$	10.57	1.06(53)	31.9 (1.8)	11.86	12.2	-1.0	7.1	8.15	-3.5	5.15	4.51	2.2
$Cu + 2L \rightleftarrows CuL_2$	24.66	12.15(51)	42.0 (1.7)	26.07	23.73	8.0	28.6	26.15	8.5	17.35	14.04	11.3
$CuL + 2OH^- \rightleftarrows Cu(OH)_2L$	24.06	12.34(10)	39.3 (4)									

[a] ΔG° and ΔH° are expressed in Kcal. mol^{-1}, ΔS° in cal. mol^{-1}. deg.$^{-1}$. [b] The values in parentheses are the standard deviations. [c] Values taken from ref. 4a. [d] Ref. 6 and 7. [e] Ref. 9 and 10. [f] Ref. 5.

N-methyl ethylenediamine (Meen)[8] and diethylenetriamine (den)[9] and 2,2′-diaminoethylether (Oden).[5] It is observed that all three thermodynamic ΔG°, ΔH°, ΔS° are for both protonation steps lower than those for Meen. The differences are in each case higher for the ΔG° values rather than the ΔH° values, a larger entropy contribution favouring the protonation of Meen. The difference $\Delta H^\circ_1 - \Delta H^\circ_2$ *i.e.* the enthalpy value referred to the reaction $LH_2^{2+} + L \rightleftarrows 2LH^+$, is very similar for both ligands. Previously a method to calculate the percentage of the two tautomeric protonated species



$$H_2\overset{+}{\underset{\substack{|\\ H}}{N}}(CH_2)_2NH(CH_2)_2OH$$



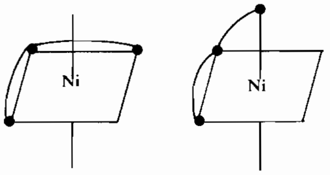
$$H_2N(CH_2)_2\overset{+}{\underset{\substack{|\\ H}}{N}}H(CH_2)_2OH$$

from ΔH° values has been shown.[8] In this case the similarity of the enthalpy values for both ligands allow us to assume that the percentage of the two tautomeric species must be approximately equal both in Meen and Etolen.

The entropy terms for both the protonation steps of Etolen are smaller than for Meen. This has been related to the presence of the alcoholic oxygen which strongly hinders dehydration during the protonation process. This effect is similar to that caused by the presence of a NH_2 group, in fact both ΔH°_1 and ΔS°_1 of den are similar to those values for Etolen.

Nickel(II)–Etolen Complexes

Thermodynamic functions for the formation of $[Ni\,Etolen]^{2+}$ and $[NiEtolen_2]^{2+}$ are reported in Table II. It is seen that $\Delta H^\circ_2 > \Delta H^\circ_1$ by 0.5 Kcal.mol^{-1}. A similar inequality is found also in Ni(II)–den complexes[10], but not in Ni(II)–Oden complexes (where $\Delta H^\circ_2 \simeq \Delta H^\circ_1$).[5] Reaction of a tridentate ligand with Ni(II) to give complexes $[NiL]^{2+}$ gives rise to the possibility of two isomers, one meridional and the other facial:

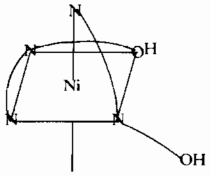


meridional *facial*

For the $[Niden]^{2+}$ case it has been shown that the isomerisation reaction *meridional* ⇄ *facial* is athermic while it is exothermic for the $[NiOden]^{2+}$ case.[11] However in the formation of $[NiL_2]^{2+}$ complexes ($NiL + L \rightleftarrows NiL_2$), the two tridentate ligands are generally equatorially placed and therefore the *facial* → *meridional* transformation must occur at the same time as the addition of the second ligand molecule. Since the percentage difference of isomers and therefore also the thermodynamic parameters of the isomerisation reaction are not known for the NiEtolen case, we can only make a comparison of the overall thermodynamic functions for formation of NiL_2 species: $Ni + 2L \rightleftarrows NiL_2$. It is noted that ΔH_{den} (25.30) > ΔH_{Etolen} (16.09) > ΔH_{Oden} (13.27).

Replacing a nitrogen atom by an oxygen atom in the tridentate ligand always gives rise to a less favourable enthalpy contribution to the formation of the NiL_2 complex. The entropy values are in the different order

$\Delta S_{Etolen} > \Delta S_{den} > \Delta S_{Oden}$. Especially outstanding is the difference between ΔS_{Etolen} and ΔS_{den} (see Table II). This difference supports the fact that in the [Ni Etolen$_2$]$^{2+}$ complex not all six donor atoms are coordinated but that there is present at least one free branch of the ligand, suggesting in this case a non-coordinated alcohol group.



Copper(II)–Etolen Complexes

Generally copper(II) complexes in aqueous solution are tetragonally distorted octahedral, the equatorial plane offering the four most favourable coordination sites.[12] Therefore a tridentate ligand like Etolen, prefers to place itself around the equatorial plane of the metal atom in a *meridional* configuration.

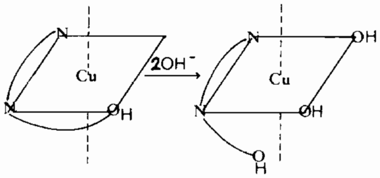
The heat of formation of [CuEtolen]$^{2+}$ is sligthly lower than that found for [CuMeen]$^{2+}$ and is much higher than that for [CuOden]$^{2+}$ (Table II). In the last compound coordination of the etheral oxygen causes an endothermic effect.[5] However that the entropy value for [CuEtolen]$^{2+}$ is between those for the analogous [Cuden]$^{2+}$ and [CuOden]$^{2+}$ (Table II), for which the full coordination of the three donor groups was shown[10], suggests that all three donor atoms of Etolen are coordinated to the metal ion. The enthalpy effect due to the alcoholic oxygen is therefore negligible.

The addition of the second ligand of Etolen to Copper(II) occurs with a very small enthalpy but with a favourable entropy term, so that the $\Delta G°$ value is not much different to that observed for the formation of [CuMeen$_2$]$^{2+}$.[13] The very low enthalpy value is very difficult to explain using a model of coordination by a second ligand molecule. Complexes of Copper(II) with tridentate ligands generally have the enthalpy of second step lower than that for the first[12] but never before has such a low value for a second step been observed. In fact the enthalpy for the second step is of the order found for various hydrogen bondings, however the decidedly high entropy value excludes such a possibility and therefore the formation of an inner sphere complex is suggested. Isolation of some solid complexes[14] and spectroscopic evidence, in aqueous solution too[15], confirm the existence of the [Cu Etolen$_2$]$^{2+}$ species.

In fact, crystal structures for [CuEtolen$_2$Cl$_2$] and [CuEtolen$_2$](ClO$_4$)$_2$ show that in the first of these compounds, Etolen acts as a bidentate coordinating through four nitrogen atoms in a square planar, the axial position being occupied by the chloride.[3] Etolen acts as a tridentate in the second compound and both alcoholic oxygens occupy axial positions. The lower coordinating ability of the perchlorate ion determines the full coordination of the Etolen ligand. While there is not apparent distortion of bond angles or lengths in the equatorial plane, the N–Cu–OH angle in [Cu Etolen$_2$](ClO$_4$)$_2$ is distorted and causes strain upon the axial alcoholic oxygen.[2]

Of the three hydroxy complexes [Cu(OH)Etolen]$^+$, [Cu(OH)$_2$Etolen], [Cu(OH)$_2$Etolen$_2$],[4a] enthalpy of hydrolysis could only be measured for [Cu(OH)$_2$ Etolen] (Table II). This latter enthalpy is decidedly higher than those found for complexes such as [Cu (OH)$_2$dimeen], [Cu(OH)$_2$adimeen], [Cu(OH)$_2$ tmeen][13] (dimeen = N,N′-dimethylethylenediamine, adimeen = N,N-dimethylethylenediamine, tmeen = N,N,N′,N′-tetramethylethylenediamine). The high $\Delta S°$ value seems consistent with the hypothesis of a hydrolysis reaction accompanied by the opening of one branch of a chelate ring.

The magnitude of the enthalpy excludes the opening of the amine branch. Therefore we conclude that the reaction is accompanied by the liberation of an alcoholic OH branch and the formation of a complex containing two nitrogens and two hydroxide ions.



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