Co-ordinating Properties in Aqueous Solution of the Oxygen Atom in Bis-2-aminoethyl Ether

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The stability constants of the Ni^{II}, Cu^{II}, and Zn^{II} complexes with bis-2-aminoethyl ether (oden) have been determined at 25 °C in 0·5M-KNO_3 and the enthalpies of reaction determined calorimetrically under the same conditions. The results are compared with those for diethylenetriamine (den). In all the complexes investigated the co-ordination of the oxygen atom is achieved. The simple M^{II}(oden) complexes are less stable than the corresponding den complexes, and the determining factor in the destabilisation is a less favourable enthalpic contribution. Thus we might consider the co-ordination of the ether oxygen atom as an endothermic process. The results obtained for the hydroxo-species $[Cu(OH)(oden)]^+$ and $[Zn(OH)(oden)]^+$ are different from results previously obtained for similar species. Explanations are suggested.

MANY ligands contain more than one kind of donor atom and the nature of the interaction with the metal ion is influenced by the differing properties of these donor atoms, *e.g.* the radius, polarisability, and electronegativity, *etc.* The co-ordinating properties of such ligands have been mainly studied in the solid state or in non-aqueous solvents.[1] We have undertaken the present work with a view to understanding the co-ordinating behaviour in aqueous solution of an ether-type oxygen atom inserted into the skeleton of a diamine. For this purpose we have studied the reactions of bis-2-aminoethyl ether (oden) with the Ni^{2+}, Cu^{2+}, and Zn^{2+} ions. Here the donor property of the ether oxygen is enhanced by taking advantage of the chelate effect.

The stability constants of the complexes were determined by a potentiometric method at 25 °C in 0·5M-KNO_3. The enthalpies of reaction were determined calorimetrically under the same conditions. The results were compared with those for diethylenetriamine (den) [2] which has an NH group in place of O. In this way it is possible to evaluate the differences, from a thermodynamic point of view, between the two donor atoms. Ciampolini and his co-workers have studied the complexes formed by the ligand bis(2-dimethylaminoethyl) ether,[3] both in the solid state and in various non-aqueous solvents. For the nickel(II) and copper(II) complexes in non-co-ordinating solvents they proposed a five-co-ordinate trigonal bipyramidal structure (this implies complete participation of the O atom in the donor atom set) whilst they suggested that in non-co-ordinating solvents such as MeOH and EtOH a six-co-ordinate species was formed. Recently Reilley and his co-workers [4] showed that all three donor atoms of oden were co-ordinated to Ni^{2+} in aqueous solution.

The ligand oden has been studied previously using a potentiometric method by Fernelius and his co-workers.[5]

EXPERIMENTAL

Materials.—The amine oden was prepared according to the method already described.[5] It was purified as the hydrochloride which was recrystallised from ethanol and dried to constant weight at 60 °C *in vacuo* (Found: Cl, 40·1%. $C_4H_{14}Cl_2N_2O$ requires Cl, 40·0%). Solutions of potassium hydroxide, nitric acid, and metal nitrate were obtained and standardised as previously described.[6]

E.M.F. Measurements.—The potentiometric titrations were performed using a Radiometer PHM 52 digital potentiometer, a Radiometer G 2025/B glass electrode, a 0·1M-calomel electrode and a salt bridge containing 0·5M-KNO_3 solution, following the procedure previously described.[7] All the potentiometric measurements were carried out at 25 °C in 0·5M-KNO_3. The protonation constants were derived from 47 data points obtained from three titrations. For the Ni^{2+}, Cu^{2+}, and Zn^{2+} metal complexes 124, 198, and 133 data points respectively were used. The concentration conditions used are given in Table 1. The ligand–metal ratios varied between 1 : 1 and 1 : 0·2. The programme LEAST which was used to calculate the constants has been described elsewhere.[8] The protonation constants and the experimentally measured ionic product of water ($\log K_1 = 9{\cdot}888$; $\log K_2 = 9{\cdot}146$; $\log K_w = -13{\cdot}758$) were held constant during the calculation of the complex formation constants. The details of the protonation results will be reported elsewhere.

Calorimetric Measurements.—The measurements were carried out with a LKB 8700/2 titration calorimeter. For the copper(II) and zinc(II) complexes the calorimetric vessel contained *ca.* 90 ml of a solution containing the diamine hydrochloride and an equimolar amount of metal nitrate. The heats of formation of the nickel(II) complexes

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[1] R. Morassi and L. Sacconi, *J. Chem. Soc.* (*A*), 1971, 1487 and references therein.

[2] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1961, 2994.

[3] M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1967, **6**, 445.

[4] R. F. Evilia, D. C. Young, and C. N. Reilley, *J. Co-ordination Chem.*, 1973, **3**, 17.

[5] J. R. Lotz, B. P. Block, and W. C. Fernelius, *J. Amer. Chem. Soc.*, 1959, **64**, 541.

[6] R. Barbucci, P. Paoletti, and A. Vacca, *J. Chem. Soc.* (*A*), 1970, 2202.

[7] E. Arenare, P. Paoletti, A. Dei, and A. Vacca, *J.C.S. Dalton*, 1972, 736.

[8] A. Sabatini and A. Vacca, *J.C.S. Dalton*, 1972, 1693.

were determined by an indirect method. The calorimetric vessel contained *ca.* 90 ml of a solution of the complexes prepared 24 h earlier. The complex was destroyed by adding an excess of nitric acid. All the measurements were carried out with the reaction system thermostatted at 25·000 ± 0·001 °C. The enthalpy changes were calculated with an IBM 1130 computer using an appropriate Fortran IV programme and were corrected for the heat of dilution determined under the same conditions. The results of the calorimetric measurements are in Table 2. The stepwise heats of protonation used to calculate the enthalpies of complex formation are: $-\Delta H^\circ_1 = 12{\cdot}11$ and $-\Delta H^\circ_2 = 12{\cdot}96$ kcal mol^{-1}. The details of the protonation results will be reported elsewhere.

TABLE 1

Experimental details of the potentiometric measurements. Initial concentrations (mol l^{-1} × 10^2)

Cation	L : M ratio	[L]	[M]	[H$^+$]	pH range
Ni^{2+}	1·1	0·9930	0·8822	2·176	3·0—7·8
	6·3	1·0770	0·1709	2·343	3·0—11·2
	1·2	1·0250	0·8890	2·225	3·0—8·1
	5·9	0·9713	0·1634	2·062	3·0—11·1
	3·0	1·0840	0·3563	2·355	3·0—10·3
	2·5	0·9756	0·3840	2·113	3·0—10·0
Cu^{2+}	2·0	0·9334	0·4748	2·103	3·0—6·1
	4·0	1·0290	0·2603	2·263	3·0—10·7
	4·9	1·1670	0·2390	2·509	3·0—10·7
	8·0	0·9642	0·1197	2·102	3·0—10·8
Zn^{2+}	5·7	1·1504	0·2032	2·493	3·0—10·1
	6·6	1·0429	0·1570	2·269	3·0—10·4
	3·5	1·3146	0·3763	2·820	3·0—9·4
	7·0	1·1269	0·1604	2·439	3·0—10·0
	9·4	1·4441	0·1529	3·068	3·0—10·6
	4·4	1·1902	0·2715	2·572	3·0—9·9

RESULTS AND DISCUSSION

Nickel(II)*-oden Complexes.*—The thermodynamic functions relative to the formation of the two Ni^{2+} complexes formed with oden are shown in Table 3. As can be seen, the stability constants for the oden complexes are appreciably smaller than the corresponding constants for the den complexes. The fact that the two constants are also smaller than those for the analogous ethylenediamine complexes, $[Ni(en)]^{2+}$ and $[Ni(en)_2]^{2+}$,[9] can probably be attributed to a destabilising effect of the ether oxygen. We might consider, as a hypothesis, the possibility that the oden ligand is not completely co-ordinated to the Ni^{2+} ion which would lead either to the formation of eight-membered chelate rings or to the existence of free ends. This hypothesis, however, can be excluded on the basis of the results obtained by Reilley and his co-workers.[4] N.m.r. spectra in aqueous solution have in fact shown that oden behaves as a tridentate ligand towards the Ni^{2+} ion. The lower stability of both the oden complexes compared with those of den can be attributed essentially to the less favourable enthalpy contribution (see Table 3). A comparison between the entropy values found for the oden and the den complexes reveals some significant differences. These probably arise from the different degree of solvation of the complexes formed with the two ligands. It can be seen from the data in the Table that for oden the values of $-\Delta H^\circ_1$ and $-\Delta H^\circ_2$ are the same within experimental error, whilst in the case of den the second stage of complex formation is appreciably more exothermic than the first. The latter behaviour is that usually found in systems of this kind when the effects of steric hindrance are negligible.[10]

Reilley *et al.*[4] found that the complex formation reaction between Ni^{2+} and a triamine involved the formation of two isomers, one meridional and one facial, in the first stage. They also demonstrated that the isomerisation reaction meridional $\rightleftharpoons$ facial is exothermic in the case of $[Ni(oden)]^{2+}$ but involves no enthalpy change in the case of $[Ni(den)]^{2+}$. In the $[NiL_2]^{2+}$ complexes on the other hand the two tridentate ligands are arranged equatorially. This has also been confirmed by recent *X*-ray studies.[11] Thus the second stage of complex formation involves the conversion of the complex which is present in the facial form into the meridional form. This transformation which is endothermic for oden leads to a decrease in the heat of formation of $[Ni(oden)_2]^{2+}$.

Copper(II)*-oden Complexes.*—Copper(II) forms three complexes with oden of formulae $[Cu(oden)]^{2+}$, $[Cu(oden)_2]^{2+}$, and $[Cu(OH)(oden)]^+$, *i.e.* the same types of complex which are found with den. First let us look at the data for the two simple complexes. The oden complexes are appreciably less stable than the corresponding den complexes (see Table 3). Here too, as we previously saw for Ni^{2+}, the destabilisation which must be attributed to the presence of the ether oxygen is revealed by the appreciably lower value of the enthalpy contribution for both stages. For the oden complexes the value of the entropy of formation is less for the second stage than for the first, as is also the case for the den complexes, although the difference is less pronounced. Not only is the heat of formation of $[Cu(oden)]^{2+}$ less than that of $[Cu(den)]^{2+}$ but it is also less than that of $[Cu(en)]^{2+}$.[9] If the possibility of incomplete co-ordination by the three donor atoms of oden is excluded, then it is reasonable to assume that co-ordination of the oxygen atom is an endothermic process. The lower value of $-\Delta H^\circ_2$ relative to $-\Delta H^\circ_1$, can be explained by assuming that the second molecule of ligand is only co-ordinated through two donor atoms, preferably N and O. This is the same hypothesis that has been advanced for $[Cu(den)_2]^{2+}$ in aqueous solution.[2] Alternatively it is possible that co-ordination of the second molecule of ligand weakens the Cu–N bonds. This view finds support in the structural data

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[9] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1960, 4553.

[10] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta Rev.*, 1973, **7**, 43.

[11] P. Paoletti, S. Biagini, and M. Cannas, *Chem. Comm.*, 1969, 513.

TABLE 2

Calorimetric results for the metal complex formation of oden in 0·5M-KNO_3 at 25 °C

					Titrant added		
					HNO_3		
	H^+ mmol	M^{2+} mmol	oden mmol	Vol./ml	ml	mmol	Q/cal [a]
Ni^{2+}	1·1729	0·1638	0·9965	87·46	5·00	4·8120	8·791
	1·7079	0·1555	0·9573	80·66	5·00	4·8120	2·058
	1·8314	0·1667	1·0265	86·49	5·00	4·8120	2·139
	2·6623	0·2967	1·7092	81·63	5·00	4·8120	7·467
	2·6940	0·3003	1·7296	82·60	5·00	4·8120	7·443
	0·5488	0·1792	0·9616	76·29	5·00	4·8120	15·156
	0·5943	0·1940	1·0412	82·60	5·00	4·8120	16·337
	0·6223	0·2032	1·0903	86·49	5·00	4·8120	17·106
	0·3655	0·1624	0·9064	72·89	5·00	4·8120	16·184
	1·1722	0·1637	0·9957	87·41	5·00	4·8120	8·766
	0·9696	0·1354	0·8236	72·30	5·00	4·8120	7·141
	1·1100	0·2040	1·2474	84·06	5·00	4·8120	15·034
Cu^{2+}					KOH		
	2·3327	0·1928	1·0994	95·57	1·00	0·5886	4·317
	5·9572	0·4901	2·7060	92·60	2·50	1·4715	12·763
	6·0957	0·4132	2·6563	91·17	2·50	1·4715	14·590
	4·6242	0·4132	2·6563	93·67	2·50	1·4715	4·268
	5·9840	0·3898	2·7044	93·13	2·50	1·4715	12·930
	4·5125	0·3898	2·7044	95·63	2·50	1·4715	2·862
	3·0410	0·3898	2·7044	98·13	2·50	1·4715	1·431
	6·3366	0·6300	2·8844	91·16	2·50	1·4715	12·885
	3·3936	0·6300	2·8844	96·16	2·50	1·4715	1·663
	6·1735	0·5567	2·8166	92·73	2·50	1·4715	12·583
	4·7025	0·5567	2·8166	95·23	2·50	1·4715	5·167
	3·2305	0·5567	2·8166	97·73	2·50	1·4715	1·460
	4·4926	0·3935	2·6903	99·10	2·50	1·4715	2·935
	3·0211	0·3935	2·6903	101·60	2·50	1·4715	1·379
Zn^{2+}							
	5·7687	0·4443	0·6359	95·10	2·50	1·4715	9·647
	4·2972	0·4443	2·6359	97·60	2·50	1·4715	3·702
	2·8257	0·4443	0·6359	100·10	2·50	1·4715	1·669
	3·9568	0·3310	2·4344	94·20	2·50	1·4715	2·910
	2·4853	0·3310	2·4344	96·70	2·50	1·4715	1·571
	4·7507	0·3000	2·3061	91·05	2·50	1·4715	5·569
	3·2792	0·3000	2·3061	93·55	2·50	1·4715	1·927
	1·8077	0·3000	2·3061	96·05	2·50	1·4715	1·460
	4·6040	0·2925	2·8725	93·03	2·50	1·4715	2·233
	3·1325	0·2925	2·8725	95·53	2·50	1·4715	1·494
	6·1803	0·2901	2·9780	92·99	2·50	1·4715	6·400
	4·7088	0·2901	2·9780	95·49	2·50	1·4715	2·065
	3·2373	0·2901	2·9780	97·97	2·50	1·4715	1·493

[a] Corrected for heats of dilution.

TABLE 3

Thermodynamic functions of the formation of metal complexes with the ligand oden in 0·5M-KNO_3 at 25 °C. For comparison those relative to the ligand den are also reported [a]

	oden				den			
		kcal mol^{-1}				kcal mol^{-1}		
Reaction [b]	log K [c]	$-\Delta G^{\circ}$ [c]	$-\Delta H^{\circ}$ [c]	ΔS° [c] cal mol^{-1} K^{-1}	log K	$-\Delta G^{\circ}$	$-\Delta H^{c}$	ΔS° cal mol^{-1} K^{-1}
$Ni + L \rightleftharpoons NiL$	5·895 (5)	8·039 (7)	6·7 (2)	4·5 (7)	10·60	14·45	11·85	8·5
$NiL + L \rightleftharpoons NiL_2$	3·62 (2)	4·94 (3)	6·5 (5)	−5 (2)	7·99	10·90	13·45	−8·5
$Cu + L \rightleftharpoons CuL$	8·970 (5)	12·232 (7)	9·53 (6)	9·1 (3)	15·80	21·55	18·00	12·0
$CuL + L \rightleftharpoons CuL_2$	3·78 (3)	5·15 (4)	4·5 (2)	2 (1)	5·21	7·10	8·15	−3·5
$CuL + OH \rightleftharpoons Cu(OH)L$	5·48 (2)	7·47 (3)	9·3 (3)	−6 (1)	4·50	6·14	2·70	11·5
$Zn + L \leftrightharpoons ZnL$	5·74 (1)	7·83 (1)	4·8 (1)	9·9 (5)	8·80	12·00	6·45	18·5
$ZnL + L \rightleftharpoons ZnL_2$	4·12 (3)	5·62 (4)	7·3 (2)	−4 (1)	5·50	7·50	10·15	−9·0
$ZnL + OH \rightleftharpoons Zn(OH)L$	5·11 (3)	6·97 (4)	−0·4 (5)	25 (2)				
$ZnL + 2OH \rightleftharpoons Zn(OH)_2L$	8·37 (3)	11·41 (4)						

[a] Ref. 2. [b] The charges of ions are omitted. [c] Standard deviations in parentheses.

recently reported for some Cu^{2+}/den complexes;[12] it is found that when there is only one molecule of den co-ordinated to the metal ion, the average Cu–N distance is shorter than when two molecules of den are co-ordinated. It should also be noted that the ratio of the values of ΔH°_1 and ΔH°_2 is more or less constant for the den and oden complexes. When we come to the hydroxo-complex [Cu(OH)(oden)]$^+$, we find that its formation constant is greater than that of the corresponding den complex by one logarithmic unit. The difference is even more pronounced in the ΔH° and ΔS° values. There is no parallel to the high value of ΔH° and the low value of ΔS° in any system of this type which has been studied to date. This type of reaction in which there is a decrease in charge is normally accompanied by the liberation of large numbers of solvent molecules, which leads to low values of $-\Delta H^\circ$ and relatively high values of ΔS°.[13] It had been shown, furthermore, that the thermodynamic functions associated with the addition of an OH$^-$ ion to a [CuL]$^{2+}$ complex are practically independent of the type of tridentate ligand involved (den, bis-3-aminopropylamine or dpt, and 3-azahexane-1,6-diamine or 2,3 tri).[10]

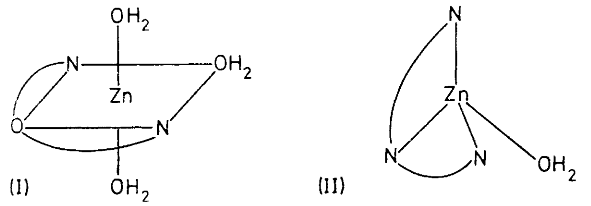

FIGURE 1 Configurations of zinc(II) chelates: (I), [Zn(oden)]$^{2+}$; and (II), [Zn(den)]$^{2+}$

Zinc(II)-*oden Complexes*.—There are four complexes formed between the Zn^{2+} ion and the ligand oden: [ZnL]$^{2+}$, [ZnL$_2$]$^{2+}$, [Zn(OH)L],$^+$ and [Zn(OH)$_2$L]. Only the first two complexes are also found in the Zn/den system[2] whilst with dpt and 2,3-tri[10] the species [Zn(OH)L]$^+$ was also formed. The thermodynamic functions associated with complex formation are shown in Table 3. It was not possible to determine the enthalpy of formation of the dihydroxo- species, [Zn(OH)$_2$(oden)] since a sufficient concentration could not be obtained in the calorimeter before precipitation of the hydroxide occurred. From a comparison of the thermodynamic functions for the formation of the simple complexes of den and oden we see that, in this case too, the lower stability of the oden complexes is a consequence of a less favourable enthalpic contribution. For the first stage of complex formation we notice that the entropy term makes a not negligible contribution to the destabilisation of the oden complex relative to the den complex. This result is easily explained when it is remembered that for the [Zn(den)]$^{2+}$ complex a tetrahedral structure was proposed,[2] whilst in all probability the [Zn(oden)]$^{2+}$ complex is octahedral. Such a structure would allow the retention of a larger number of molecules of water (see Figure 1). Another piece of evidence which supports the idea of an octahedral structure for the [Zn(oden)]$^{2+}$ is to be found in the thermodynamic functions for the formation of the hydroxo-complex [Zn(OH)L]$^+$. The addition of a hydroxyl ion is a spontaneous process ($\Delta G^\circ < 0$) with a heat term which is practically zero within experimental error and a large positive entropy change. This indicates that the Zn^{2+} ion goes from an octahedral configuration to one of lower co-ordination number, probably tetrahedral, with the subsequent release of a number of water molecules. This latter process is endothermic and takes place with an increase in entropy. Our hypothesis for the structures of the [ZnL]$^{2+}$ and [Zn(OH)L]$^+$ complexes receives support from other

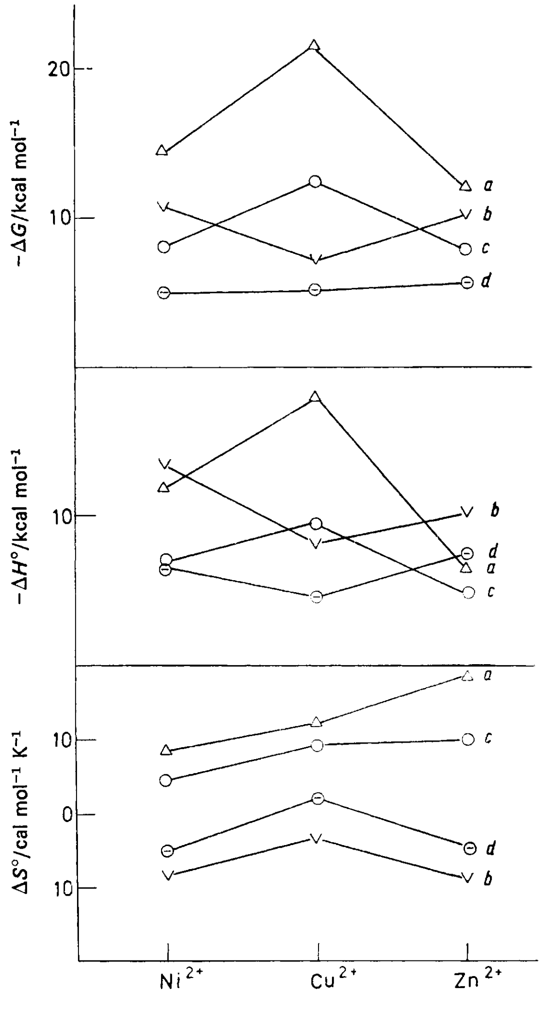

FIGURE 2 Plots of the thermodynamic functions of formation of *a*, [M(den)]$^{2+}$; *b*, [M(den)$_2$]$^{2+}$; *c*, [M(oden)]$^{2+}$; *d*, [M(oden)$_2$]$^{2+}$ ions *vs*. the atomic number of the metal

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[12] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 2233, 2493.

[13] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1972, 1099.

results which we have obtained, *e.g.* those for the analogous complexes of the ligand 2,3-tri.[14]

GENERAL CONCLUSIONS

In Figure 2 the values of the thermodynamic functions for the formation of the simple oden complexes of the types $[ML]^{2+}$ and $[ML_2]^{2+}$, together with the corresponding values for the den complexes which are included for comparison, are plotted against the atomic numbers of the metal ions. It will be noted that: (*i*) the oden complexes are always less stable than the corresponding den complexes, (*ii*) the complex formation reactions for oden are always less exothermic than those for the den complexes, and (*iii*) the entropy of formation of the 1 : 1 oden complexes is less than that of the analogous den complexes whilst the opposite is true for the 1 : 2 complexes. It is precisely because of this latter observation that it must be assumed that the determining factor in the destabilisation of the oden complexes must be sought in a less favourable enthalpic contribution. From a comparison of the heats of formation of the oden complexes with those for similar polyamine complexes, such as those of ethylenediamine,[9] one is forced to the conclusion that co-ordination of the ether oxygen atom is an endothermic process, *i.e.* it makes a positive contribution to ΔH° thus depressing the overall value of the heat of reaction.

For the 1 : 1 complexes a normal trend is found in the variation of the ΔG° and ΔH° values as a function of the atomic number of the metal ion. It should be noted that the enthalpies of formation of the complexes $[Zn(oden)]^{2+}$ and $[Zn(den)]^{2+}$ differ by 1·7 kcal mol^{-1}. The difference in the ΔG° values is enhanced (4·2 kcal mol^{-1}) because of very different ΔS° values. The explanations of these facts must be looked for in the fact that, as we have previously said, $[Zn(oden)]^{2+}$ is probably octahedral, and then more solvated than $[Zn(den)]^{2+}$ for which a tetrahedral structure was proposed.[2]

As far as the 1 : 2 complexes of oden and den are concerned, the values of $-\Delta G^\circ$ and $-\Delta H^\circ$ reach a minimum at Cu^{2+}, except for the value of $-\Delta G^\circ$ for oden. However we must remember in this case that the stability of the complex $[Ni(oden)_2]^{2+}$ is reduced as a result of the unfavourable enthalpy term due to the endothermic nature of the isomerisation reaction: facial $\rightleftharpoons$ meridional. If it were not for this fact the value of $-\Delta G^\circ{}_2$ would also reach a minimum at Cu^{2+}. The lower stability and the lower exothermicity of the Cu^{2+} complexes can be attributed to a smaller co-ordinate bond energy, due either to the fact that some of the ligand donor atoms occupy apical positions in the tetragonally distorted octahedron about the Cu^{2+} ion or to the fact that not all the six donor atoms are co-ordinated (free end). The results obtained for the hydroxo-species $[Cu(OH)L]^+$ and $[Zn(OH)L]^+$ are both different from each other and different from results previously obtained for such species. Previously it has been found that addition of an OH^- ion to a polyamine complex is accompanied by a variation in the thermodynamic functions which is not critically dependent on the type of polyamine complex. The explanation for such an anomaly must be looked for in a change of structure in going from the simple complex to the hydroxo-species and/or an appreciable variation in their ability to structure the solvent.

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[14] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, 1973, **7**, 157.