Thermodynamics of Complex Formation in Aqueous Solution. Reactions of Copper(II) with Ethylenediamine, *NN'*-dimethylethylenediamine, and *NN*-dimethylethylenediamine: log *K*, Δ*H*, and Δ*S* Values

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Equilibria in 0·5M-KNO_3 at 25° between copper(II) and the ligands (L) ethylenediamine (en), *NN'*-dimethylethylenediamine (dmen) and *NN*-dimethylethylenediamine (admn), have been investigated by e.m.f., calorimetric, and spectrophotometric measurements. In all these systems the same four complex species have been found. The equilibrium constants for $Cu^{2+} + nL \rightleftharpoons [CuL_n]^{2+}$ (n = 1 or 2) and $nCu^{2+} + nL + 2OH^- \rightleftharpoons [Cu_n(OH)_2L_n]^{(2n-2)+}$ (n = 1, hydrolysis; n = 2, olation) have been obtained from potentiometric data using a computer. The enthalpies of reaction were obtained by calorimetric measurements using two different kinds of calorimeters. Spectrophotometric measurements have been carried out and the spectra of individual complexes (n = 1 or 2; L = dmen, admn) have been calculated. *N*-methyl substitution reduces the heat of reaction and increases the positive entropy changes.

THE study of equilibria in aqueous solution of copper complexes with basic ligands such as amines presents experimental difficulties because of the presence of a large number of protonated, polymeric, and hydroxo-species. Recently the identification of these compounds and the determination of stability constants have been made possible by the use of computers. Nevertheless, regarding the hydroxo-complexes, there is often poor agreement between results. This is because of, in our opinion, the ease of formation of supersaturated solutions in regions of high pH. The stability of these solutions depends on the temperature and ionic strength. Some hydroxo-complexes have been isolated and the structure of one of these, from *X*-ray analysis, has shown the existence of the binuclear unit $Cu(OH)_2Cu$, containing two hydroxo-bridges.[1] $[Cu_2(OH)_2]^{2+}$ is also the dominant

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[1] Y. Iitaka, K. Shimizu, and T. Kwan, *Acta Cryst.*, 1966, **20**, 803.

species in the hydrolysis of copper(II) ions.[2] We have studied the influence of steric hindrance on formation of hydroxo-complexes of copper(II) and have chosen as ligands: ethylenediamine (en), *NN'*-dimethylethylenediamine (dmen), and *NN*-dimethylethylenediamine (admn). The results are compared with those of *NNN'N'*-tetramethylethylenediamine (tmen) previously reported.[3] The increase in steric hindrance on nitrogen, lowers the stability of the 1 : 2 copper–diamine complexes and causes considerable ΔH changes. For this reason, it is useful to study the formation of copper(II) complexes either by e.m.f. or calorimetric measurements. Several studies on these systems have been made,[4] but a complete thermodynamic investigation with rigorous mathematical treatment has not yet been reported.

EXPERIMENTAL

The purification of the diamines and the preparation and standardization of their solutions have been described.[5] By adding hydrochloric acid to an aqueous alcoholic solution of dmen, the amine hydrochloride was obtained. The product was recrystallized from aqueous alcohol and dried to constant weight at 60° *in vacuo* (Found: Cl, 43·9. Calc. for $C_4H_{14}N_2Cl_2$: 44·0%). Solutions of copper nitrate and potassium hydroxide were prepared and stored as reported.[3]

E.m.f. and Calorimetric Measurements.—The potentiometric apparatus and method have been described.[6] Basicity constants of diamines and ionic product of water determined in the same conditions (0·5M-KNO_3 at 25·0 °C) have been reported.[5]

The results of calorimetric measurements are shown in Table 1. For the Cu^{II}–en system a rotating ampoule calorimeter [7] was employed; for Cu^{II}–dmen and Cu^{II}–admn

TABLE 1

Calorimetric results for the copper(II)–diamine systems in 0·5M-KNO_3 at 25·0 °C [a]

	Calorimetric ampoule			Titrant added		
H^+ [b] (mmol)	$Cu(NO_3)_2$ (mmol)	diamine (mmol)	Vol (ml)	(ml)	$Cu(NO_3)_2$ (mmol)	Q [c] (cal)
admn [a]						
0·0000	0·0000	1·7783	87·80	2·50	0·8003	15·700
0·0014	0·8003	1·7783	90·30	2·50	0·8003	1·859
0·0028	1·6005	1·7783	92·80	2·50	0·8003	0·103
0·0043	2·4008	1·8883	95·30	2·50	0·8003	−0·020
−0·9976	0·0320	2·9460	92·39	1·50	0·4802	9·007
−0·9962	0·5122	2·9460	93·89	1·50	0·4802	8·823
−0·9948	0·9923	2·9460	95·39	1·50	0·4802	8·300
−0·9938	1·4725	2·9460	96·89	1·50	0·4802	7·290
1·2290	0·0320	3·0173	88·11	2·00	0·6402	12·267
1·2302	0·6722	3·0173	90·11	2·00	0·6402	8·424
1·2313	1·3124	3·0173	92·11	2·00	0·6402	0·592
1·2325	1·9526	3·0173	94·11	2·00	0·6402	0·279
dmen [a]						
0·0096	0·0320	2·2126	84·99	2·00	0·6404	13·528
0·0120	1·3124	2·2126	88·99	2·00	0·6404	0·980
−0·0013	0·0320	2·5287	86·37	2·00	0·6404	13·502
0·0011	1·3124	2·5287	90·37	2·00	0·6404	0·806
−1·0014	0·0320	3·0182	88·28	2·00	0·6404	13·216
2·2309	0·6722	1·9008	81·70	2·00	0·6404	0·256
1·1030	0·0320	1·9448	81·35	2·00	0·6404	2·453
1·1042	0·6722	1·9448	83·41	2·00	0·6404	0·628
1·1054	1·3124	1·9448	85·45	2·00	0·6404	0·177
−0·9657	0·0320	3·2111	89·87	2·00	0·6404	13·210
0·0189	1·0099	1·0733	85·94	1·70	0·8558	4·940
0·0130	1·0378	1·0856	86·01	1·80	0·9061	5·216
0·0140	1·1581	1·2114	94·87	1·80	0·9061	5·238
−0·0892	1·1581	1·2114	96·67	0·50	0·2517	1·233
0·0150	1·1969	1·2520	98·05	1·70	0·8558	4·976
en [d,e]						
HNO_3	Ampoule	Dewar vessel				
0·0210	3·2531	3·2641				41·27
0·0211	3·2631	3·2661				41·78
0·0211	3·2607	3·2609				41·50
0·0210	3·2596	6·5379				83·08
0·0210	3·2591	6·5371				82·77
0·0210	3·2585	6·5351				83·07

[a] Measurements performed with a titration calorimeter LKB 8700/2. [b] Negative values are referred to OH^- mmol. [c] These values have been corrected for heat of dilution of titrant in 0·5M-KNO_3. [d] Measurements performed with a rotating ampoule calorimeter. [e] The initial volume of the solution in the calorimeter was 159·9 ml, the final volume 168·5 ml for the first three measurements, 170·4 ml for the other measurements.

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[2] D. D. Perrin, *J. Chem. Soc.*, 1960, 3189.

[3] E. Arenare, P. Paoletti, A. Dei, and A. Vacca, preceding paper.

[4] L. G. Sillen and A. E. Martell, 'Stability Constants,' Special publication No. 17, The Chemical Society, London, 1964.

[5] P. Paoletti, R. Barbucci, A. Vacca, and A. Dei, *J. Chem. Soc.* (*A*), 1971, 310.

[6] A. Vacca and D. Arenare, *J. Phys. Chem.*, 1967, **71**, 1495. 5955.

[7] P. Paoletti, R. Usenza, and A. Vacca, *Ricerca sci.*, 1965, **35** (II-A), 201.

systems the titration calorimeter LKB 8700/2 was used. For the Cu^{II}–dmen system calorimetric titrations were carried out either on a solution of free amine or on a solution of amine hydrochloride. The formation of chloro-complexes was neglected for the following reasons: (*a*) the ratio $Cl^- : Cu^{2+}$ was never higher than 2 : 1, (*b*) the concentration of chloride ion was always lower than 2.5×10^{-2}M, (*c*) the stability constants of the copper chloride complexes reported in the literature are very small.

Spectrophotometric Measurements.—Spectra of the simple and hydroxo-complexes in 0·5M-KNO_3 at 25·0 °C were recorded on a Beckman DK-2A spectrophotometer fitted with 1-cm stoppered silica cells. Experimental results are shown in Table 2.

Calculations.—Calculation * of the constants was carried out using a program for an IBM 1130 computer, with the same assumptions for the complex species, as has been already described.[3]

As for the Cu^{II}–tmen system the calculations were commenced assuming that only the (presumed) most stable complexes are present at equilibrium. Later new species have been tried one at a time, but the relative formation constants have been varied together with those of the other complex species until the best agreement between experimental and calculated data was obtained. The new species was retained or rejected according to the criteria already described.[3]

The enthalpies of formation have been obtained from calorimetric measurements using a published method of calculation.[8] The spectra of the individual complexes $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[Cu_2(OH)_2L_2]^{2+}$, and $[Cu(OH)_2L]$ were calculated at 30 wavelengths by using a least-squares method to resolve the combined spectra of 10 solutions whose composition is shown in Table 2.

TABLE 2

Experimental details of the spectrophotometric measurements

Analyt. concentrations (mmol l^{-1})			Degree of formation (%)[a]				$\lambda_{max.}$ (nm) and optical density	
H^+	Cu^{2+}	dmen	$[CuL]^{2+}$	$[CuL_2]^{2+}$	$[Cu_2(OH)_2L_2]^{2+}$	$[Cu(OH)_2L]$		
0·41	19·05	17·15	86·5	0·7	0·7	0·0	662	0·92
−23·35[b]	16·90	20·66	0·0	18·4	64·3	17·2	575	1·17
−9·74	17·71	25·46	1·3	43·3	55·3	0·0	562	1·47
−8·39	16·08	22·93	5·3	42·1	52·6	0·0	562	1·25
−30·91	14·98	20·70	0·0	23·9	42·7	33·1	562	1·11
−20·72	14·55	22·84	0·0	40·6	39·1	20·2	562	1·09
−21·33	14·31	21·16	0·0	34·8	43·3	21·2	562	1·06
−8·41	9·91	18·45	0·0	66·4	24·2	9·1	562	0·88
0·50	15·35	31·36	0·0	98·1	1·9	0·0	550	1·71
0·88	9·10	17·14	13·2	82·8	3·8	0·0	550	0·86
		admn						
0·0	10·85	11·59	58·0	0·5	0·4	0·0	700	0·40
0·0	10·77	16·62	54·8	0·4	0·4	0·0	700	0·38
0·0	10·52	15·48	38·8	0·1	0·2	0·0	700	0·29
−32·77[b]	18·96	23·09	0·0	12·7	56·4	30·6	580	1·40
−16·17	14·66	16·26	0·0	9·5	83·2	7·2	580	1·06
−17·90	9·99	16·69	0·0	33·9	38·0	27·9	580	0·93
−22·57	10·36	13·09	0·0	13·4	50·2	36·3	580	0·75
−13·73	10·57	11·75	0·0	9·1	77·6	12·7	580	0·74
0·0	10·75	21·83	0·0	97·1	2·3	0·0	560	1·67
0·0	10·30	24·57	0·0	98·8	0·9	0·2	560	1·61
−8·94[b]	10·63	17·50	0·0	49·9	39·5	8·9	560	1·15

[a] The remainder being free metal ion. [b] Negatives values are referred to OH^- mmol.

RESULTS AND DISCUSSION

Stability Constants and Curve Fitting.—For the Cu^{II}–en system, the complex species retained in the calculation were $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[Cu_2(OH)_2L_2]^{2+}$, and $[Cu(OH)_2L]$ and the corresponding stability constants have been calculated. Other species tried in the calculation, but not retained were $[CuL_3]^{2+}$ and $[Cu(OH)L_2]^+$. The species tried in the Cu–admn and Cu–dmen systems were: $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[Cu_2(OH)_2L_2]^{2+}$, $[Cu(OH)_2L]$, $[Cu(OH)L]^+$, $[Cu_3(OH)_4L_2]^{2+}$, and $[Cu_2(OH)_2L]^{2+}$. Only the first four species were retained. In other words, all the systems have the same number and same type of complexes. The formation of a greater number of hydroxo-complexes in Cu–tmen system [3] is due to the lack of formation of the 1 : 2 complex. Figure 1 shows the distribution curves of the titration curves for the Cu^{II}–en, Cu^{II}–dmen, and Cu^{II}–admn systems. It is clear from an examination of these curves that the range of hydroxo-complexes is larger with the bulkier ligands such as dmen and admn. The complex $[Cu(OH)_2(en)]$ has a stability constant a little higher than 3 times the relative standard deviation. We must remember that a criterion [3] used to reject a complex species is that its stability constant is smaller than three times the standard deviation. Nevertheless the distribution curves reveal a small trace of this complex and it was not possible to obtain a larger amount owing to precipitation of copper(II) hydroxide.

Thermodynamic Functions.—In Tables 3 and 4 we have reported the thermodynamic functions $\Delta G°$, $\Delta H°$, and $\Delta S°$ for complex formation of 1 : 1, 1 : 2, and

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* The computer output with all the points of the titration curves, the results of the potentiometric measurements, and the details of the calculation have been deposited with the National Lending Library in Supplementary Publication No. SUP 20300 (20 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[8] A. Vacca and P. Paoletti, *J. Chem. Soc.* (*A*), 1968, 2378.

hydroxo-species. The corresponding values for tmen are also listed in the Tables.

We have obtained the heats of reaction for the Cu^{II}–dmen system by two different techniques, the first ('classical') consists in adding the metal-ion solution to the amine solution and the second ('potentiometric') consists in adding potassium hydroxide to a solution containing copper(II) ion, diamine hydrochloride, and appropriate amounts of acid or base. The results obtained from the two techniques are in agreement and the enthalpy changes have been calculated using all the data together. In contrast, for the Cu^{II}–en system we have obtained slightly different values for the enthalpies of complex formation according to the procedure employed. The values in Table 3 obtained with the 'classical' method, are in agreement with the literature results. The values obtained with the second, 'potentiometric' procedure are $-12{\cdot}0$ kcal mol^{-1} for ΔH_1 and $-12{\cdot}6$ kcal mol^{-1} for ΔH_2. It is surprising that the second heat is slightly more exothermic than the first one. In most of the systems examined by us, however, a slight increase in the heat for each successive step was found, as shown by the Mn^{II}–, Fe^{II}–, Co^{II}–, and Ni^{II}–en systems.[9] Because the heats of reaction depend on the values of stability constants and heats of protonation of diamine, ionic product of water, corresponding heat of dissociation, and on the values of the stability constants of the complexes, it is very probable that an error in one of these quantities affects the heat of complex formation found, according to the method employed.

TABLE 3

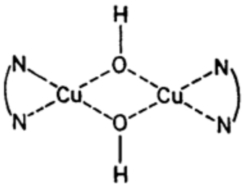
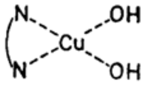
Thermodynamic functions of simple complex formation in 0·5M-KNO_3 at 25·0 °C [a]

Reaction		en	meen [b]	dmen	admn	tmen [c]
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	$-\Delta G^\circ$ (kcal mol^{-1})	14·435(3)	14·210(8)	13·786(1)	12·659(4)	10·059(1)
	$-\Delta H^\circ$ [d] (kcal mol^{-1})	12·56(5)	11·53(6)	11·10(1)	9·82(3)	6·17(2)
	ΔS° (e.u.)	6·3(2)	9·0(2)	9·0(1)	9·5(1)	13·0(1)
$[CuL]^{2+} + L \rightleftharpoons [CuL_2]^{2+}$	$-\Delta G^\circ$ (kcal mol^{-1})	12·482(7)	11·872(27)	9·755(7)	9·588(12)	
	$-\Delta H^\circ$ [d] (kcal mol^{-1})	12·64(9)	12·2(1)	9·67(2)	9·48(7)	
	ΔS° (e.u.)	−0·5(3)	−1·0(4)	0·3(1)	0·4(3)	

[a] Numbers in parentheses associated with all values are standard deviations in the last significant figure. [b] meen: *N*-Methylethylenediamine; our unpublished results. [c] Values taken from ref. 3. [d] Previous results for the copper(II)–ethylenediamine system: $-\Delta H_1 = 13{\cdot}0$ and $-\Delta H_2 = 12{\cdot}4$ (1M-KNO_3, at 25 °C), I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 1407; $-\Delta H_{1-2} = 25{\cdot}16$ (0·1M-KCl, 25 °C), T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 1954, 2304; $-\Delta H_1 = 12{\cdot}6$ and $-\Delta H_2 = 12{\cdot}6$ ($\mu \longrightarrow 0$, 25 °C), H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*A*), 1967, 1441; $-\Delta H_1 = 12{\cdot}45$ and $-\Delta H_2 = 12{\cdot}2$ (0·30M in ClO_4^- at 25 °C), F. Holmes and D. R. Williams, *J. Chem. Soc.*, 1967, 1702.

TABLE 4

Thermodynamic functions for the olation and hydrolysis of CuL^{2+} complex in 0·5M-KNO_3 at 25·0 °C [a]

		dmen	admn	tmen [b]
Olation $2[CuL]^{2+} + 2\,OH^- \rightleftharpoons [Cu_2(OH)_2L_2]^{2+}$ 	$-\Delta G^\circ$ (kcal mol^{-1})	20·49(1)	21·03(2)	20·81(3)
	$-\Delta H^\circ$ (kcal mol^{-1})	11·2(1)	11·2(3)	9·4(2)
	ΔS° (e.u.)	31(1)	33(1)	38·3(8)
Hydrolysis $[CuL]^{2+} + 2\,OH^- \rightleftharpoons [Cu(OH)_2L]$ 	$-\Delta G^\circ$ (kcal mol^{-1})	11·33(2)	11·99(5)	12·44(3)
	$-\Delta H^\circ$ (kcal mol^{-1})	7·4(4)	5·9(5)	5·6(1)
	ΔS° (e.u.)	13(2)	20(2)	23·0(4)

[a] Numbers in parentheses associated with all values are standard deviations in the last significant figure. [b] Values taken from ref. 3.

The uncertainty in heat of formation of the complex $[Cu(en)]^{2+}$ made it impossible to measure the heat of olation and of hydrolysis. In this system, the region of formation of hydroxo-complexes is very narrow. However, in the systems Cu–dmen and Cu–admn, it is also possible to calculate the heat of formation of the

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

$[Cu_2(OH)_2L_2]^{2+}$ and $[Cu(OH)_2L]$ species. In Figure 1 we see that the amount of complex $[Cu(OH)_2L]$ increases with increasing pH, and in calorimetric measurements it is possible to get higher pH values than in potentiometric measurements with a glass electrode.

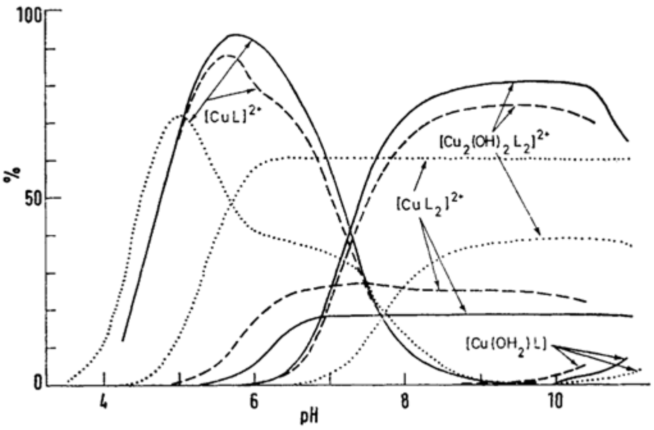

FIGURE 1 Distribution curves of copper(II) complexes: (· · · ·) L = ethylenediamine (en), metal : ligand ratio 1 : 1·5; $[Cu^{2+}]$ = 5·331 mmol l^{-1}; (——) L = *NN'*-dimethylethylenediamine (dmen), metal : ligand ratio 1 : 1·2 $[Cu^{2+}]$ = 9·810 mmol l^{-1}; (– – – –) L = *NN*-dimethylethylenediamine (admn), metal : ligand ratio 1 : 1·3 $[Cu^{2+}]$ = 5·734 mmol l^{-1}

CONCLUSION

The stability constant of the 1 : 1 copper(II)–diamine complex diminishes with increasing substitution of methyl groups on the nitrogen atoms (Table 3). This diminution in stability is undoubtedly a consequence of the decrease in the heat of formation on passing from 12·56 kcal mol^{-1} for en to 6·17 kcal mol^{-1} for the tmen. This decrease in the heat of reaction is due to steric repulsions and to the probable formation of less strong M–N bonds. However, these reactions are accompanied by liberation of water molecules of hydration and this is an endothermic effect. On the other hand, the increase of steric crowding favours this desolvation process as we can see from the increasing positive contribution of the reaction entropy. This term contributes to stabilization of the complex, but it is not enough to compensate the decreasing enthalpic contribution. It is known the two substituents on the nitrogen atom occupy two non-equivalent positions, the so-called axial and equatorial positions.[10] A methyl group will repel the co-ordinated water molecules to a different extent depending on its position.

In the complex with the symmetric isomer (dmen) both the methyl groups occupy the position with the lower steric hindrance (probably the equatorial position). In the admn complex one of the two methyl groups has to occupy the more hindered position (probably the axial position) and this accounts for the lower heat of formation.

In the second step, the heat of reaction either does not change or only slightly increases for the less hindered amines ethylenediamine and *N*-methylethylenediamine (meen), and decreases for the others.

Here again the two isomers dmen and admn show different behaviour. For dmen the heat of reaction diminishes markedly (1·4 kcal mol^{-1}), whereas for admn the diminution is only 0·3 kcal mol^{-1}. This can be explained assuming the two dimethylamino-groups in $[Cu(admn)_2]^{2+}$ are disposed in a *trans*-position in the co-ordination plane.

On passing from the first to the second step the entropy of formation decreases as usual in stepwise reactions. For the reaction of olation, as well as for the reaction of hydrolysis, we can observe the same trend noted in the formation of the simple complexes, *i.e.* the heat of reaction diminished while the entropy increases in passing from dmen to tmen through admn. In the hydrolysis reaction, two metal–hydroxide bonds are formed, while in the olation, four such bonds are formed. Nevertheless the heat of olation is less than twice the heat of hydrolysis and this is probably because the two hydroxide ions act as bridges. The entropy changes of both reactions are strongly positive, as generally observed in reactions where neutralization of electric charge occurs.

The visible absorption spectra of simple and hydroxo-copper(II) complexes with the two isomeric amines admn and dmen are shown in Figure 2. The frequencies of maxima of the dmen and admn complexes are the same in the compounds of the same stoicheiometry, in apparent disagreement with the calorimetric results. The differences in the enthalpies of complex formation

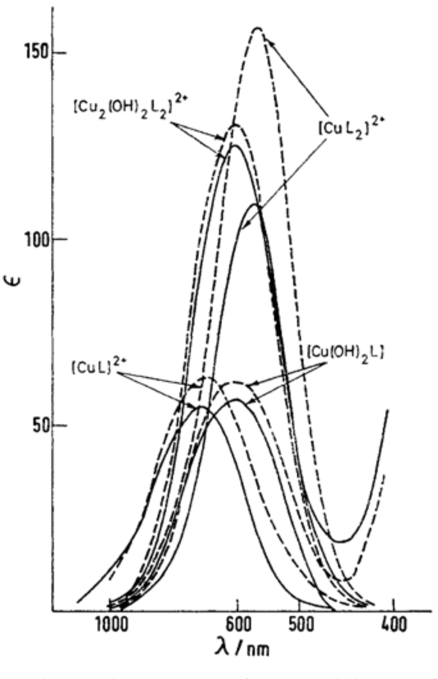

FIGURE 2 Electronic spectra of copper(II) complexes, calculated as described in the text. (——) L = *NN'*-dimethylethylenediamine (dmen); (– – – –) L = *NN*-dimethylethylenediamine (admn)

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[10] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168.

suggest that the strength of the co-ordinate bonds, and hence the ligand field, is different in the complexes with the two ligands admn and dmen. However, small changes in the ligand field are not detectable by spectral measurements, but only by direct measurements of the heat of reaction. (For example, the difference in the ΔH values of formation of the 1 : 1 complex with dmen and admn is 1·28 kcal mol^{-1}, which corresponds to *ca.* 0·5 kK.) For each ligand the frequencies of maxima decrease in the order $CuL_2 > Cu_2(OH)_2L_2 = Cu(OH)_2L > CuL$. The two hydroxo-complexes, monomer and dimer, have the same maximum absorption frequency but different molar extinction coefficients.

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