# Imine Hydrolysis Reactions in Copper(II) Complexes of *NN'*-Ethylenebis-(thiophen-2-carbaldimine) and -(pyridine-2-carbaldimine)

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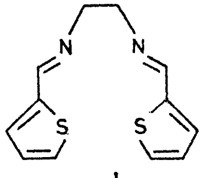
The hydrolysis of copper(II) complexes containing the ligands *NN'*-ethylenebis-(thiophen-2-carbaldimine) and -(pyridine-2-carbaldimine) has been studied. Two distinct reactions, involving each imine function in turn, have been observed for the former and, with evidence provided by the other ligand, have allowed a reassessment of the reasons for the occurrence of hydrolysis in Cu$^{II}$ complexes. An electronic basis, with initial polarisation of the imine groups, is suggested.

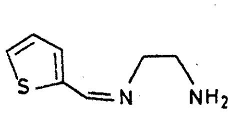
RECENTLY there have been several reports describing solvolysis reactions of copper(II) complexes containing co-ordinated imine groups which usually produce complexes with amine donors.[1–8] The reactions have been considered to be a consequence of electronic forces,[1] although a different argument based on steric interactions has also been advanced particularly for complexes containing the ligand *NN'*-ethylenebis(pyridine-2-carbaldimine).[3] When complexed with Cu$^{II}$ this ligand undergoes partial solvolysis involving addition across one, or both, of its imine functions [2,3] since, it is said, the steric strain in the square-planar ligand system is relieved by formation of the more flexible COR–NH linkage. Research [4] with similar ligands has been quoted as verifying the hypothesis that strain is the major cause of subsequent solvolysis.

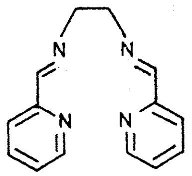
However, the realisation that such reactions are not confined to one type of ligand, and that they appear to be specific to copper in many instances, suggests that a steric origin may not be of paramount importance. We have now studied the hydrolysis of *NN'*-ethylenebis-(thiophen-2-carbaldimine), a ligand known to hydrolyse rapidly [5–8] on complex formation with Cu$^{II}$, and present evidence suggests that such solvolysis reactions are mainly of electronic origin with steric effects being of a minor nature. It has been possible to retard solvolysis sufficiently to observe two distinct cleavage reactions involving each imine linkage in turn. As subsequent crystal-structure determinations [9,10] have verified that the thiophen sulphur atoms are not co-ordinated to the metal centre, it is apparent that steric arguments cannot be applied in this instance and yet similar hydrolysis reactions have been found to occur.

## EXPERIMENTAL

The ligand *NN'*-ethylenebis(thiophen-2-carbaldimine) (L$^1$) was prepared by condensing thiophen-2-carbaldehyde (2.24 g) with excess of ethylenediamine (en) (0.62 g), recrystallisation being effected from ethanol or diethyl ether to produce straw-coloured needles of m.p. 88—89 °C (lit.,[6] 92 °C). Complexes of L$^1$ were initially prepared by mixing L$^1$ (2.48 g) with copper(II) chloride dihydrate (1.71 g) or copper(II) perchlorate hexahydrate (2.48 g) in 1 : 1 ratios in methanol. The two salts produced light and dark green needles respectively and these were washed with dry diethyl ether before being placed in a desiccator over silica gel. Recrystallisation was not possible because of the tendency of the complexes to hydrolyse. Since different stoicheiometries have been reported [7,8] for these complexes the preparations were repeated at 1 : 2 copper to ligand ratios. With perchlorate as anion the same dark green precipitate was obtained; with chloride, however, no precipitation occurred and subsequent hydrolysis reactions produced a mixture of L$^1$, thiophen-2-carbaldehyde, and en salts of Cu$^{II}$. Thus only one product is obtained from each salt regardless of the component ratios.


L$^1$


L$^2$


L$^3$

When an excess of solvent was used perchlorate precipitation did not immediately occur and the solution turned purple overnight. Careful solvent control allowed crystallisation of a purple complex at this stage, and i.r. spectra, to be discussed later, showed that thiophen moieties were present. Analyses (Table 1) confirmed that a complex of formula [Cu(L$^2$)$_2$][ClO$_4$]$_2$ rather than [Cu(en)$_2$][ClO$_4$]$_2$ had formed (L$^2$ = *N*-2-aminoethylthiophen-2-carbaldimine). The complex [Cu(L$^1$)$_2$][ClO$_4$]$_2$ also decomposed in the crystalline state, exposure to air for 36 h or more producing a purple-grey powder with an elemental analysis consistent with the formula [Cu(L$^2$)$_2$][ClO$_4$]$_2$. That the original dark green complex was [Cu(L$^1$)$_2$][ClO$_4$]$_2$ was confirmed in an independent copper analysis on a freshly prepared sample by precipitating copper(I) thiocyanate [11] {Found: Cu, 8.30. Calc. for [Cu(L$^1$)$_2$][ClO$_4$]$_2$ : Cu, 8.35. Calc. for [Cu(L$^2$)$_2$][ClO$_4$]$_2$ : Cu, 11.15%}.

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[1] L. F. Lindoy, *Quart. Rev.*, 1971, **25**, 379.

[2] C. M. Harris and E. D. McKenzie, *J. Chem. Soc. (A)*, 1969, 746.

[3] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, 1956, **78**, 1137.

[4] M. Cressey, E. D. McKenzie, and S. Yates, *J. Chem. Soc. (A)*, 1971, 2677.

[5] G. L. Eichhorn and I. M. Trachtenberg, *J. Amer. Chem. Soc.*, 1954, **76**, 5183.

[6] G. L. Eichhorn and J. C. Bailar, jun., *J. Amer. Chem. Soc.*, 1953, **75**, 2905.

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[8] M. P. Coakley, L. H. Young, and R. A. Gallagher, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1449.

[9] A. T. Morcom and C. E. F. Rickard, unpublished work.

[10] G. D. Beckingsale and T. N. M. Waters, unpublished work.

TABLE 1

Analytical data (%)

| | C | H | N | Cl |
|---|---|---|---|---|
| Calc. for $[Cu(L^1)_2][ClO_4]_2$ | 37.95 | 3.20 | 7.40 | 8.35 |
| Calc. for $[Cu(L^2)_2][ClO_4]_2$ | 29.45 | 3.55 | 9.80 | 12.4 |
| Found (for decomposed $L^1$ complex) | 29.8 | 3.85 | 9.40 | 12.5 |
| Found (for purple crystals) | 30.05 | 4.30 | 9.70 | 12.45 |
| Calc. for $[Cu(L^3)][ClO_4]_2$ | 33.6 | 2.80 | 11.2 | 12.7 |
| Calc. for $[Cu_2(L^3)_2][ClO_4]_2$ | 40.7 | 3.40 | 13.55 | 11.45 |
| Found (green form) | 37.2 | 3.90 | 12.65 | 11.95 |
| Found (blue form) | 36.5 | 4.00 | 12.45 | 12.15 |
| Calc. for $[Cu_2(L^3)Cl_2]Cl$ | 33.15 | 2.80 | 11.05 | 27.95 |
| Calc. for $[Cu_2(L^3)Cl_2]Cl_2\cdot\frac{1}{2}MeOH$ | 33.3 | 3.35 | 10.35 | 26.3 |
| Found (green form) | 32.75 | 3.45 | 10.55 | 25.85 |
| Calc. for $[Cu(L^3)]Cl_2$ | 35.1 | 3.75 | 15.05 | 19.0 |
| Calc. for $[Cu(L^3)]Cl_2\cdot OH_2$ | 43.0 | 4.10 | 14.35 | 18.2 |
| Calc. for $[Cu(L^3)]Cl_2\cdot 2OH_2$ | 41.15 | 4.45 | 13.7 | 17.35 |
| Found (blue form) | 43.05 | 4.25 | 14.65 | 17.9 |

The chloride complex was confirmed by analysis as $[Cu(L^1)]Cl_2$ rather than $[Cu(L^1)_2]Cl_2$. It is stable for several months as a solid but alcoholic solutions slowly turn blue and eventually deposit blue crystals of a mixture of $[Cu(L^2)]Cl_2$ and $[Cu(en)]Cl_2$. It was impossible to crystallise a pure sample of the $L^2$ complex analogous to that obtained with perchlorate. Formation of $[Cu(L^2)]Cl_2$ has nevertheless been confirmed by recent structural data,[9] a dimeric $[Cu_2(L^2)_2Cl_2]Cl_2$ species with bridging chloride ions being found.

The ligand *NN'*-ethylenebis(pyridine-2-carbaldimine) ($L^3$) was prepared by condensing pyridine-2-carbaldehyde (2.14 g) with en (0.62 g) in ethanol.[3] Rapid cooling in a refrigerator resulted in straw-coloured needles of m.p. 65 °C (lit.,[3] 68 °C). Copper(II) complexes using both perchlorate (1.31 g) and chloride (0.85 g) salts were prepared by addition of a methanolic solution to $L^3$ (1.19 g) in 1 : 1 ratios. With perchlorate as anion dark blue crystals were at first obtained but later preparations under supposedly identical conditions produced a black semicrystalline precipitate and a light green powder. I.r. spectra suggested that these three products were different forms of the same complex and analytical data were consistent with this, although some impurity was apparently present. Harris and McKenzie [2] reported $[Cu_2(L^3)_3][ClO_4]_4$ as a contaminant and the higher C, H, and N percentages and lower Cl value found here are consistent with the formation of a complex with a ligand to copper ratio greater than unity and are inconsistent with a simple hydrolytic impurity. In the absence of suitable crystals for *X*-ray structural analysis, solutions of the $Cu^{II}$ complexes eventually decomposing to en salts, no further deductions were possible. With chloride as anion a green powder initially precipitated but blue crystals also began to form quite rapidly. To isolate the powder the reaction solution was filtered immediately, elemental analysis then verifying that a complex $[Cu_2(L^3)Cl_2]Cl_2$ rather than $[Cu(L^3)]Cl_2$ had formed in agreement with predictions of Harris and McKenzie [2] but not of Busch and Bailar.[3] Analysis of the blue crystals revealed a complex $[Cu(L^3\cdot OH_2)]Cl_2$, and indicated that partial hydrolysis across one C=N linkage had taken place.

Thus reactions with the ligand $L^3$ are in general agreement with the conclusion of Harris and McKenzie [2] rather than Busch and Bailar.[3] However, we find no verification for the suggested nature of the contaminants present, nor did we have success with the suggested improvement in technique [2] to remove such species.

Kinetic data for the hydrolysis of the ligands and their copper(II) perchlorate complexes were obtained using 50% methanol–water or spectroscopic (but undried) methanol as solvents. Changes were followed on a Unicam SP 800A visible–u.v. spectrometer. The solution concentrations were *ca.* $5 \times 10^{-3}$M for complexes and *ca.* $10^{-5}$M for the ligands, spectra being obtained at suitable intervals until the hydrolysis was complete.*

## RESULTS AND DISCUSSION

The synthetic work has revealed that two separate hydrolyses occur with complexes derived from $L^1$ and that these involve each of the C=N linkages in turn. Except for one report [7] of a $Ni^{II}$ complex, no complexes containing the ligand $L^2$ have been observed in this reaction. Identification of such products has, however, an important bearing on later discussions of steric strain.

I.r. spectra obtained for complexes of $L^1$, $L^2$, and en are consistent with their formulations (see Table 2). As already observed, the presence of thiophen rings is indicated by strong 'aromatic' bands in the region 700—800 $cm^{-1}$. The appearance of a broad δ(NH) absorption at 1 580 $cm^{-1}$ and a ν($NH_2$) doublet in the region 3 200—3 300 $cm^{-1}$ confirms the initial hydrolysis reaction and final cleavage to en salts is verified by loss of both ν(C=N) and 'aromatic' bands. An interesting feature of the spectrum of $[Cu(L^2)_2][ClO_4]_2$ is the splitting of the perchlorate band at 1 100 $cm^{-1}$ ($\nu_3$) in place of the single absorption observed with $[Cu(L^1)_2](ClO_4)_2$. This suggested that the perchlorate groups are bound to the copper centre, and a strong bonding interaction has since been confirmed by *X*-ray crystallography.[10]

TABLE 2

I.r. data ($cm^{-1}$)

| Compound | ν(OH) | ν(NH) | (νC=N) | δ(NH) | ν($ClO_4$) |
|---|---|---|---|---|---|
| $L^1$ | | | 1 630 | | |
| $[Cu(L^1)_2][ClO_4)_2$ | | | 1 615 | | 1 100 |
| $[Cu(L^2)_2][ClO_4]_2$ | | 3 260,<br>3 225 | 1 625 | 1 580 | 1 140,*<br>1 100,<br>1 080,<br>1 020 * |
| $[Cu(L^1)]Cl_2$ | | | 1 635,<br>1 615 | | |
| $[Cu(L^2)]Cl_2$ | | 3 250,<br>3 220 | 1 620 | 1 570 | |
| $L^3$ | | | 1 645,<br>1 585 | | |
| $[Cu(L^3)][ClO_4]_2$ | | | 1 653,<br>1 600 | | 1 100 |
| $[Cu_2(L^3)Cl_2]Cl_2\cdot\frac{1}{2}MeOH$ | 3 450 | | 1 640,<br>1 595 | | |
| $[Cu(L^3)]Cl_2\cdot OH_2$ | 3 380 | 3 250 | 1 595 | 1 590 | |

* Finely resolved doublet.

Visible and u.v. spectroscopy have been used to study the hydrolysis reactions in water and methanol solutions. Because of the similarity of the spectra of $L^1$ and thiophen-2-carbaldehyde it was necessary to study the position of the *d–d* envelope as the main guide to hydrolysis reactions for $L^1$ and $L^2$ complexes (see Table 3).

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* 1M = 1 mol $dm^{-3}$.

[11] A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis,' 2nd edn., Longmans, Green and Co., London, 1959, p. 430.

All but one of the complexes produced similar spectra in methanol and water, $[Cu(L^1)_2][ClO_4]_2$ showing evidence of immediate hydrolysis in water. Kinetic data obtained in undried spectroscopic methanol solution and 50% methanol–water (Table 4) verified that a fast hydrolysis reaction did indeed occur, the *d–d* absorption band for $[Cu(L^1)_2][ClO_4]_2$ quickly shifting to higher energies typical of $[Cu(L^2)_2][ClO_4]_2$ and $[Cu(en)_2][ClO_4]_2$. The rate constants showed good agreement with those obtained for $[Cu(L^1)_2]Cl_2$.[5,6]

TABLE 3

U.v.–visible spectra (cm$^{-1}$) [a]

| Complex | | | | | Solvent |
|---|---|---|---|---|---|
| $[Cu(L^1)_2][ClO_4]_2$ | 16 100 (40) | | 34 700 (20 500) | 38 800 (33 500) | MeOH |
| $[Cu(L^1)_2][ClO_4]_2$ | 15 800 (50) | 18 800 [b] (70) | 33 900 (30 000) | 37 900 (55 000) | $H_2O$ |
| $[Cu(L^2)_2][ClO_4]_2$ | | 18 300 (80) | 34 400 (14 900) | 38 600 (29 800) | MeOH |
| $[Cu(L^2)_2][ClO_4]_2$ | | 18 700 (90) | 34 000 (19 300) | 38 200 (37 000) | $H_2O$ |
| $[Cu(L^1)]Cl_2$ | 15 200 (50) | | 34 100 | 27 400 | |
| $[Cu(L^1)]Cl_2$ | 15 400 (50) | | 34 000 (12 400) | 38 000 (24 800) | $H_2O$ |
| $[Cu(L^2)]Cl_2$ | 15 500 (60) | | 34 000 (5 100) | 39 200 (5 600) | MeOH |
| $[Cu(L^3)][ClO_4]_2$ | 16 500 (150) | | 33 500 (10 200)<br>34 800 (15 600) | 36 100 (16 900)<br>37 600 (15 600) | $H_2O$ |
| $[Cu(L^3)]Cl_2$ | 14 400 (100) | 26 700 [c] (140) | 32 900 (3 000)<br>35 300 (10 900) | 39 700 (14 800)<br>43 900 (16 400) | MeOH |
| $[Cu(L^3)]Cl_2$ | 16 000 (100) | 27 000 [c] (100) | 33 400 (10 000)<br>34 800 (12 000) | 38 800 (10 000)<br>42 900 (20 000) | $H_2O$ |
| Ligand | | | | | |
| Thiophen-2-carbaldehyde | | | 34 400 (5 600) | 38 500 (11 300) | MeOH |
| $L^1$ | | | 35 000 (23 700) | 38 800 (26 200) | MeOH |
| $L^3$ | | | 35 000 (5 300) | 37 000 (12 600)<br>42 900 (19 900) | MeOH |

[a] Absorption coefficients ($\varepsilon$/l mol$^{-1}$ cm$^{-1}$) are given in parentheses. [b] Due to partial hydrolysis to $[Cu(L^2)_2][ClO_4]_2$. [c] Shoulder on a more intense absorption.

TABLE 4

Rate data in a methanol–water (1 : 1) at 293 K

| Compound | $k$/s$^{-1}$ | Wavelength of measurement ($\lambda$/nm) |
|---|---|---|
| $[Cu(L^1)_2][ClO_4]_2$ | $1.3 \times 10^{-3}$ | 570 |
| | $2.2 \times 10^{-3}$ [a] | 670 |
| | $2.1 \times 10^{-3}$ [b] | 560 |
| $[Cu(L^2)_2][ClO_4]_2$ | $1.1 \times 10^{-3}$ | 380 |
| | *ca.* $10^{-3}$ [b] | 380 |
| $[Cu(L^3)][ClO_4]_2$ | $4.2 \times 10^{-5}$ | 450 |
| $L^1$ [c] | $1.1 \times 10^{-3}$ | 285 |
| $L^3$ | $2.1 \times 10^{-4}$ | 235 |

[a] Obtained in undried methanol solution. [b] Obtained at pH 8.6. [c] Stable in MeOH over 24 h.

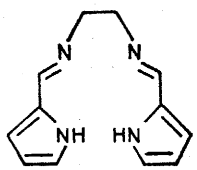
A spectral study of complexes involving $L^3$ was also undertaken. I.r. spectra for the three perchlorate complexes (Table 2) showed two $\nu$(C=N) bands at 1 600 and 1 653 cm$^{-1}$, consistent with partial cleavage across only one of the imine linkages. No splitting in the perchlorate bands was observed for these complexes. The green chloride complex showed similar bands at 1 595 and 1 640 cm$^{-1}$; however, only one band, at 1 595 cm$^{-1}$, remained for the blue chloride complex. It was the absence of a second $\nu$(C=N) band that prompted Busch and Bailar [3] to propose a complex in which both aliphatic imine groups had been partially hydrolysed, but this is incompatible with the analytical data.[2] Thus a shift in the second $\nu$(C=N) band to 1 600 cm$^{-1}$, where it would be hidden under the aromatic $\nu$(C=N) peak, as suggested by Harris and McKenzie,[2] is supported.

Visible and u.v. spectra (Table 3) did not produce the same clear shifts in absorption maxima found for $L^1$ complexes, but rate data were unequivocal in showing that the fast hydrolysis observed for $L^1$ complexes did not occur. It is pertinent at this stage, however, to compare both the rate constants for hydrolysis of the ligands $L^1$ and $L^3$ in company with their complexes before making an assessment in terms of 'electronic' arguments, all rate constants (first order) being shown in Table 4.

It has already been noticed that hydrolysis of $[Cu(L^1)_2]^{2+}$ to $[Cu(L_2)_2]^{2+}$ and subsequently to $[Cu(en)_2]^{2+}$ proceeds at a far greater rate than for $[Cu(L^3)]^{2+}$, the first-order rate constants differing by almost two orders of magnitude. Comparison with ligand solvolysis shows that the hydrolysis is accelerated when $L^1$ is complexed, particularly when smaller amounts of water are present, whereas $L^3$ itself hydrolyses at a faster rate than its copper complex. Such an observation is easily explained by noting that bond rupture, absent for the $L^1$ complex, must occur in the $L^3$ complex to allow hydrolysis to occur. The retardation rate does not, however, imply a steric origin for hydrolysis, whereas the acceleration in $L^1$ complexes does support an electronic mechanism.

We had also intended to make a study of the reaction at pH values >7 to verify that the same mechanism of hydrolysis applied to both complexes, and in particular that OH$^-$ attack would occur to cause an increase in the rate constant. Unfortunately $L^3$ complexes formed dark solutions in basic conditions, even at pH 8, and no hydrolysis data could be obtained. Initial reaction, however, appeared to be more rapid, as it did with $L^1$ complexes where an almost two-fold increase in rate constant was observed at pH 8.9.

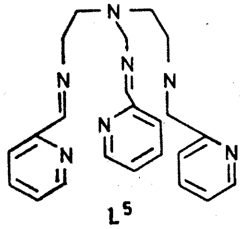
This preliminary kinetic evidence can now be added to the many unusual reactions of imines co-ordinated to Cu$^{II}$ and an assessment of such reactions can be made. The electronic argument is based on the charge separation that occurs across the imine linkage as a result of electron donation to the central metal ion; the imine carbon atom is then susceptible to nucleophilic attack by, for example, $OH^-$ or $OR^-$ from solvents. Thus many $Cu^{II}$ complexes are hydrolysed even though the ligands themselves are relatively stable. (In some instances where the reverse is true special stabilising features of complex formation are present which outweigh hydrolytic tendencies, a feature discussed in detail by Lindoy [1] in a recent review.) Steric causes have been postulated largely as a result of studies of $L^3$ and derivatives where it is said that partial hydrolysis to the more flexible COR–NH linkage occurs to relieve the strain imposed by quadridentate co-ordination. Consideration of the reactions of the $L^1$ and $L^2$ complexes throws considerable doubt on such a theory however. The establishment of the two distinct hydrolysis reactions suggests that the only difference between $L^1$ and $L^3$ systems is the more rapid hydrolysis of the former, which can be explained by noting that a chelate ring does not have to be broken in the bidentate complexes of $L^1$ since the sulphur atoms, unlike the ring nitrogens of $L^3$, do not co-ordinate. Steric arguments do not, therefore, apply to $L^1$ because there is no strain in the ligand system. Introduction of the known reactions of *NN'*-ethylenebis(pyrrole-2-carbaldimine) ($L^4$) also contradicts the steric hypothesis. Molecular models built for $L^1$, $L^3$, and $L^4$ show that when complexed with $Cu^{II}$ in a square-planar arrangement the order of steric strain is $L^4 > L^1 > L^3$, although $L^1$ does not, in practice, act as a quadridentate ligand. Little adjustment in the normal bond lengths and angles is needed to bond $L^4$ as a quadridentate ligand even though 1 : 1 complexes of $L^4$ are not only stable, with the pyrrole nitrogen donors apparently bonded to the copper centre, but also show no cleavage across their C=N linkages.[12-16] This resistance to hydrolysis in the presence of steric strain is clearly inconsistent with a steric argument for hydrolysis.



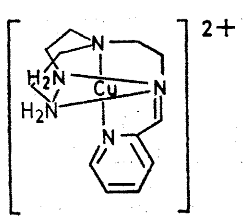
$L^4$

Three further hydrolysis reactions are significant in this context. Hydrolysis of *NN'*-ethylenebis(quinoline-8-carbaldimine) [17] is said to occur only where the ligand is required to be planar by metal-ion constraints because of consequent steric clashes between hydrogen atoms in the 2-positions of the quinoline rings. These, it is supposed, cause the imine functions to twist and subsequently cleave because of the loss of $\pi$ overlap. However, it is difficult to understand why the flexible en rings cannot twist to relieve some of the strain, and why the non-planar complexes should not hydrolyse when, presumably, strain and lack of $\pi$ delocalisation is also present. It seems far more likely that when the ligand is planar a greater charge separation occurs across the imine linkages, the maximum $\pi$ interaction in the chelate ring then being possible, and that, for the planar geometry only, this is just sufficient to cause hydrolysis to occur.

The most convincing argument for an electronic origin to account for cleavage of bound imine groups can be found in reactions [18] of the ligand $L^5$. This contains three aliphatic imine, three aromatic imine, and a tertiary amine nitrogen as potential donors. With many metal ions it co-ordinates through the six imine donors, but for $Cu^{II}$ only a subsequent hydrolysis occurs which involves two of the three equivalent aliphatic donors. In addition, the tertiary amine nitrogen atom is brought into the co-ordination sphere, occupying an axial position of a trigonal bipyramid as in (I). The suggested reason for this observation, namely that the driving force for the reaction is the tendency of $Cu^{II}$ to adopt a five-co-ordinate stereochemistry, is then an electronic one. The hypothesis is supported by the stability of one imine group, whereas a steric argument would require that one, or all, be hydrolysed.



$L^5$



(I)

A further example of the hydrolysis reaction occurring only in a $Cu^{II}$ complex has recently been reported.[19] It involves the thiazole ligand $L^6$. On complex formation with $Cu^{II}$ 1 mol of ligand is reduced to a thiazoline, whereas a further mol is hydrolysed across the C=N linkage and oxidised to a pyridinecarboxylate. The five-co-ordinate complex shown in (II) then results, co-ordination being through three imine linkages (two aromatic and one aliphatic) and an oxygen from the carboxylate ligand and from a co-ordinated water molecule. This peculiar redox reaction occurs only with $Cu^{II}$, and again supports the view that hydrolysis reactions are electronic in origin.

Thus in all instances where steric strain has been suggested as the fundamental cause of hydrolysis, several doubts have arisen and alternative electronic mechanisms can be proposed. These involve polarisation of the C=N linkage. This view also accounts for the stability of

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[12] R. E. Clarke and J. H. Weber, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1837.

[13] A. Chakravorty and T. S. Kannan, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1691.

[14] R. H. Holm, A. Chakravorty, and W. J. Theriot, *Inorg. Chem.*, 1966, **5**, 625.

[15] J. H. Weber, *Inorg. Chem.*, 1967, **6**, 258.

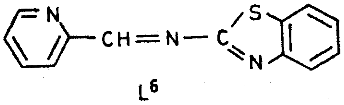
[16] K. N. Yeh and R. H. Baker, *Inorg. Chem.*, 1967, **6**, 830.

[17] J. Dekkers and H. A. Goodwin, *Austral. J. Chem.*, 1966, **19**, 2241.

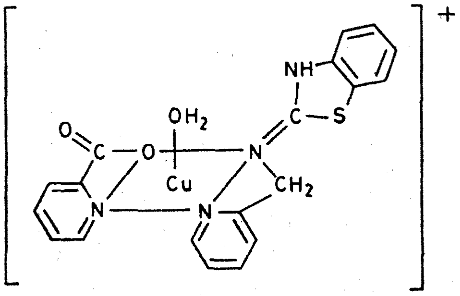
[18] E. C. Lingafelter, L. C. Andrews, R. M. Kirchner, N. J. Rose, and L. J. Wilson, *Co-ordination Chem. Rev.*, 1972, **8**, 55.

[19] A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *J.C.S. Dalton*, 1972, 2483.

$L^4$ complexes since $L^4$, on co-ordination, loses two protons and is effectively a 2— ion with the charge largely remaining on the pyrrole nitrogen atoms. The two negative charges effectively cancel the charge of the copper centre and polarisation of the imine groups does not occur to any great extent. By contrast, in the neutral ligands $L^1$ and $L^3$ where an electrostatic effect is absent, a charge-balancing mechanism to satisfy Pauling's electroneutrality principle [20] must involve a considerable degree of polarisation of the imine donors and a greater susceptibility to attack by nucleophiles.



$L^6$



(II)

Thus a simple electronic explanation can be advanced to account for hydrolysis reactions in copper(II)–imine systems, which is not to say that structural effects are always of no consequence.

[4/1878 *Received, 16th September, 1974*]

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[20] L. Pauling, 'The Nature of the Chemical Bond,' 2nd edn., Oxford University Press, 1940.