Copper(II)-assisted Hydrolysis of 2,4,6-Tris(2-pyridyl)-1,3,5-triazine. Part 3.† Crystal Structures of Diaqua[bis(2-pyridylcarbonyl)amido]copper(II) Nitrate Dihydrate and Aquabis(pyridine-2-carboxamide)copper(II) Nitrate Monohydrate‡

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Copper(II) has been found to promote the hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) to yield [bis(2-pyridylcarbonyl)amido]copper(II) and free pyridine-2-carboxamide, $NC_5H_4CONH_2$. The compounds $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_2]NO_3{\cdot}2H_2O$ (**1**) and $[Cu(NC_5H_4CONH_2)_2(H_2O)][NO_3]_2{\cdot}H_2O$ (**2**), where $(NC_5H_4CO)_2N^-$ is the bis(2-pyridylcarbonyl)amide anion (L), were grown from aqueous solutions of tptz and copper(II) nitrate. Crystals of (**1**) and (**2**) are triclinic, space group $P\bar{1}$ and $Z = 2$, with $a = 6.811(1)$, $b = 10.211(1)$, $c = 12.039(1)$ Å, $\alpha = 88.65(1)$, $\beta = 82.32(1)$, and $\gamma = 89.79(1)$° for (**1**) and $a = 11.622(3)$, $b = 11.280(3)$, $c = 8.007(3)$ Å, $\alpha = 90.33(2)$, $\beta = 101.85(4)$, and $\gamma = 115.28(3)$° for (**2**). The copper(II) ion is five-co-ordinate in both structures and its co-ordination geometry is near square pyramidal. The three nitrogen atoms of the $(NC_5H_4CO)_2N^-$ ligand and the oxygen atom of a water molecule form a distorted square plane around the copper ion in complex (**1**), whereas such a basal plane is built by the pyridine nitrogen and oxygen atoms of two carboxamides in (**2**). The axial position is filled by a water molecule in both cases. The proton association and acid dissociation constants of the complex $[CuL(H_2O)]^+$ [equations (i) and (ii)] have been determined by potentiometry in aqueous solution: log K_1 =

$$[CuL(H_2O)]^+ + H^+ \overset{K_1}{\rightleftharpoons} [Cu(HL)(H_2O)]^{2+} \qquad \text{(i)}$$

$$[CuL(H_2O)]^+ \overset{K_2}{\rightleftharpoons} [CuL(OH)] + H^+ \qquad \text{(ii)}$$

1.83(1) and log $K_2 = -8.80(1)$ (25 °C, 0.1 mol dm^{-3} $NaNO_3$). The co-ordination of L to copper(II) decreases the basicity of the imide nitrogen atom as shown by the low value of log K_1. The value of the hydroxo stability constant falls within the range established for hydroxocopper(II) complexes with N-donor tridentate ligands. A discussion of the factors which determine the nature of the isolated products of this copper(II)-promoted hydrolysis is made in the light of the available structures.

Copper(II)-assisted hydrolysis of 2,4,6-triaryltriazines such as 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpmtz) was observed for the first time by Lerner and Lippard.[1,2] They showed that the hydrolysis of these triazines yielded the [bis(arylcarbonyl)amido]copper(II) complexes and free pyridine-2-carboxamide. Very recently, some of us reported the crystal structures of two complexes of formula $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]X$ ($X = ClO_4$ or CF_3SO_3)[3,4] in which the two main products of the copper(II)-promoted hydrolysis of tptz were present as ligands. On the basis of structural data, it has been suggested that angular strain at the carbonyl-carbon atoms in co-ordinated bis(2-arylcarbonyl)amido ligands could be responsible for the hydrolysis of these normally stable 2,4,6-triaryl-1,3,5-triazines.[2–4] Kinetic and thermodynamic data have revealed that such a reaction probably occurs *via* nucleophilic attack at the triazine ring by OH^- or H_2O.[5] This mechanism is strongly supported by the observed angular strain. The isolation of copper(II) complexes containing co-ordinated tptz was precluded by the role of this metal ion in tptz hydrolysis. However, the hydrolytic reaction can be inhibited if N-donor tridentate ligands are bound to copper(II) as illustrated recently by the determination of the structure of [bis(2-pyridylcarbonyl)amido][2,4,6-tris(2-pyridyl)-1,3,5-triazine]copper(II) trifluoromethanesulphonate.[4] This compound is, as far as we are aware, the first example of a structural determination of a copper(II) complex containing tptz as a ligand.

As a part of our study of the copper(II)-promoted hydrolysis reaction of tptz we now describe the synthesis, structure, and spectral characterization of the copper(II) complexes $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_2]NO_3{\cdot}2H_2O$ (**1**) and $[Cu(NC_5H_4CONH_2)_2(H_2O)][NO_3]_2{\cdot}H_2O$ (**2**). Each compound contains as ligand only one of the two main products of the copper(II)-

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† Part 2 is ref. 4.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Crystal data for complexes (**1**) and (**2**)

	(**1**)	(**2**)
Formula	$C_{12}H_{16}CuN_4O_9$	$C_{12}H_{16}CuN_6O_{10}$
M	423.8	467.7
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	6.811(1)	11.622(3)
b/Å	10.211(1)	11.280(3)
c/Å	12.039(1)	8.007(3)
α/°	88.65(1)	90.33(2)
β/°	82.32(1)	101.85(4)
γ/°	89.79(1)	115.28(3)
U/Å^3	830.2(2)	923.7(6)
Z	2	2
D_c/g cm^{-3}	1.695	1.681
F(000)	434	462
Crystal size (mm)	0.29 × 0.17 × 0.12	0.09 × 0.09 × 0.12
Standard reflections	114, 132, 232	600, 060, 005
μ(Mo-K_α)/cm^{-1}	13.71	12.40
Maximum, minimum transmission factors	0.86, 0.71	2.45, 0.64
Reflections collected	3 243	3 260
Independent reflections[a]	2 883	3 004
No. of parameters refined	300	326
$R[=\Sigma(\lVert F_o\rvert - \lvert F_c\rVert)/\Sigma\lvert F_o\rvert]$	0.026	0.034
$R'\{=[\Sigma w(\lVert F_o\rvert - \lvert F_c\rVert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$	0.029[b]	0.034[c]

[a] $I \geqslant 2.0\sigma(I)$ for (**1**), $\geqslant 1.5\sigma(I)$ for (**2**). [b] $w = 4F_o^2/[\sigma_c^2 + (0.02F_o^2)^2]$. [c] Unit weights.

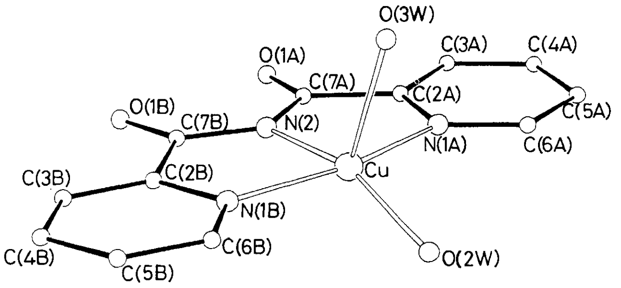

Figure 1. View of the cationic species $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_2]^+$ with the atom-numbering scheme. Hydrogen atoms are not shown

assisted hydrolysis of tptz. We also report on the acid–base behaviour of the cationic species $[CuL(H_2O)]^+$ [L being the bis(2-pyridylcarbonyl)amido ligand $(NC_5H_4CO)_2N^-$] in aqueous solution. Studies of the formation of mono- and polynuclear species of such a complex with extended bridging ligands are in progress.[6]

Experimental

Materials and Measurements.—The reagents $Cu(NO_3)_2\cdot 3H_2O$ and tptz were purchased from Merck and used as received. I.r. spectra were obtained on KBr pellets in the 4 000—225 cm^{-1} region using a Perkin-Elmer 1750 FTIR spectrophotometer, e.s.r. spectra on a ER 2000 Brüker spectrometer equipped with a nitrogen cryostat. Potentiometric titrations were performed with a previously described assembly.[7] Carbonate-free NaOH and 0.1 mol dm^{-3} $NaNO_3$ were used as titrant and background electrolyte respectively. The temperature of all solutions was held at 25.0 °C by circulating constant-temperature water through the water-jacketed titration cell. The computer program SUPERQUAD[8] was used to process potentiometric data and calculate both proton and hydroxo stability constants.

Synthesis.—A green suspension was formed when tptz (1 mmol) was added to an aqueous solution (30 cm^3) containing $Cu(NO_3)_2\cdot 3H_2O$ (1—1.3 mmol). Gentle boiling with stirring yielded a blue-green solution which became blue after heating for *ca.* 30 min. This colour change is due to the copper(II)-assisted hydrolysis of tptz. Evaporation of solvent at room temperature produced needle-like dark blue and polyhedral blue single crystals of complexes (**1**) and (**2**) respectively [Found: C, 33.85; H, 3.90; N, 13.25. Calc. for $C_{12}H_{16}CuN_4O_9$ (**1**): C, 34.00; H, 3.80; N, 13.20%. Found: C, 30.80; H, 3.70; N, 18.15. Calc. for $C_{12}H_{16}CuN_6O_{10}$ (**2**): C, 30.80; H, 3.40; N, 17.95%].

Crystallography.—Diffraction data were collected at 293 K, for (**1**) with an Enraf-Nonius CAD-4 diffractometer and for (**2**) with a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). The unit-cell parameters were in each case derived from least-squares refinement of 25 well centred reflections ($8 \leqslant \theta \leqslant 21°$). Intensity data were collected by the ω-scan technique in the 2θ range 4—52° for (**1**) and by the θ—2θ scan technique in the 2θ range 4—50° for (**2**). Examination of three standard reflections monitored throughout the data collection showed no significant decay. Lorentz and polarization corrections were applied. Absorption correction by the Gaussian integration method and an empirical absorption correction[9] were carried out for complexes (**1**) and (**2**) respectively. Based on the centric distribution of E values for (**1**) and (**2**), the space group $P\bar{1}$ was assumed and this choice was later confirmed by the successful refinements of both structures. Independent reflections with $I \geqslant 2.0\sigma(I)$ for (**1**) and $I \geqslant 1.5\sigma(I)$ for (**2**) were used for the structure refinements.

Structure solution and refinement. Both structures were solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in complex (**1**) were located from a Fourier difference map whereas they were included in calculated positions for (**2**). They were refined with isotropic thermal parameters in both structures. In the final least-squares cycles for (**1**) an extinction parameter was included and refined. The crystal data are listed in Table 1. All calculations on complex (**1**) were carried out using the Enraf-Nonius structure determination programs,[10] and on (**2**) by the XM84[11] and SHELX 76 systems.[12] Atomic scattering factors for neutral atoms and corrections for anomalous dispersion were taken from ref. 13. The final Fourier difference maps showed residual maxima and minima of 0.27 and −0.24 e Å^{-3} for (**1**) and 0.41 and −0.67 e Å^{-3} for (**2**). The final atomic co-ordinates for all non-hydrogen atoms of complexes (**1**) and (**2**) are given in Tables 2 and 3 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Molecular Structure of Complex (**1**).—Figure 1 shows a perspective view of the cationic species $[Cu\{NC_5H_4CO)_2N\}(H_2O)_2]^+$ with the atom-numbering scheme and Figure 2 a stereoscopic view of the unit cell. Selected bond lengths and non-bonded distances and angles are given in Table 4. The structure consists of mononuclear cationic species $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_2]^+$, unco-ordinated nitrate ions, and water of crystallization linked by ionic and hydrogen-bonding interactions.

The co-ordination polyhedron around copper(II) is best described as a distorted square pyramid. The basal positions are occupied by three nitrogen atoms [N(2), N(1A), and N(1B)] from the bis(2-pyridylcarbonyl)amido ligand and one oxygen

Table 2. Final atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for complex (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.285 44(1)	0.035 97(2)	0.705 17(2)	C(4B)	0.379 1(4)	−0.381 6(2)	0.871 0(2)
O(1A)	0.256 3(2)	−0.077 0(1)	0.389 5(1)	C(5B)	0.370 7(3)	−0.275 2(2)	0.938 8(2)
N(1A)	0.244 2(2)	0.172 3(1)	0.589 1(1)	C(6B)	0.349 3(3)	−0.152 1(2)	0.893 3(2)
C(2A)	0.231 6(3)	0.123 7(2)	0.487 0(2)	C(7B)	0.305 9(3)	−0.210 4(2)	0.598 3(2)
C(3A)	0.198 5(3)	0.201 4(2)	0.397 5(2)	N(2)	0.279 8(2)	−0.078 7(1)	0.579 7(1)
C(4A)	0.181 3(3)	0.335 5(2)	0.411 2(2)	N(3)	0.152 5(3)	0.240 4(2)	1.055 7(1)
C(5A)	0.195 8(3)	0.385 8(2)	0.514 0(2)	O(31)	0.172 5(3)	0.121 9(2)	1.038 2(2)
C(6A)	0.225 4(3)	0.302 4(2)	0.601 5(2)	O(32)	0.185 6(3)	0.318 6(2)	0.974 2(1)
C(7A)	0.255 8(3)	−0.023 0(2)	0.478 6(2)	O(33)	0.103 5(3)	0.279 7(2)	1.150 8(1)
O(1B)	0.307 8(2)	−0.298 0(1)	0.531 6(1)	O(2W)	0.397 7(2)	0.147 8(1)	0.811 4(1)
N(1B)	0.330 8(2)	−0.133 2(2)	0.784 2(1)	O(3W)	−0.026 2(2)	0.065 9(2)	0.792 3(1)
C(2B)	0.334 1(3)	−0.238 1(2)	0.718 5(2)	O(4W)	0.631 4(2)	0.338 0(2)	0.714 9(1)
C(3B)	0.360 9(3)	−0.363 3(2)	0.758 9(2)	O(5W)	0.922 2(3)	0.438 0(2)	0.828 4(2)

Table 3. Final atomic co-ordinates with e.s.d.s in parentheses for complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.274 13(4)	0.155 01(4)	0.401 64(5)	C(5′)	0.114 8(4)	0.788 4(4)	−0.391 5(5)
O(1)	0.099 1(2)	0.096 5(2)	0.254 5(3)	C(6′)	0.125 3(3)	0.891 1(3)	−0.489 0(5)
N(1)	0.312 6(2)	0.309 4(3)	0.269 2(3)	C(7′)	0.469 1(3)	1.117 4(3)	−0.386 7(4)
C(2)	0.207 0(3)	0.303 6(3)	0.155 0(4)	N(2′)	0.583 1(3)	1.132 9(4)	−0.299 9(4)
C(3)	0.213 2(4)	0.403 5(4)	0.054 8(5)	N(3)	−0.109 0(3)	0.395 5(3)	−0.261 2(4)
C(4)	0.332 6(4)	0.513 2(4)	0.071 9(5)	O(31)	−0.005 2(3)	0.490 3(3)	−0.263 8(5)
C(5)	0.439 8(4)	0.518 0(4)	0.186 1(5)	O(32)	−0.112 1(4)	0.304 8(3)	−0.178 5(5)
C(6)	0.426 8(4)	0.414 6(4)	0.282 7(5)	O(33)	−0.214 1(3)	0.389 4(3)	−0.344 7(4)
C(7)	0.088 6(3)	0.177 2(3)	0.151 2(4)	N(4)	0.333 4(3)	0.111 9(3)	0.005 9(3)
N(2)	−0.020 9(3)	0.152 7(4)	0.041 7(4)	O(41)	0.440 8(3)	0.187 9(3)	−0.015 4(4)
O(1′)	0.455 1(2)	1.202 3(2)	−0.479 9(3)	O(42)	0.230 7(2)	0.104 8(3)	−0.090 2(3)
N(1′)	0.241 2(2)	0.993 4(3)	−0.482 4(3)	O(43)	0.322 8(3)	0.039 6(3)	0.125 3(3)
C(2′)	0.349 0(3)	0.995 7(3)	−0.378 8(4)	O(2W)	0.223 9(4)	1.240 4(4)	−0.382 6(5)
C(3′)	0.344 2(4)	0.896 1(4)	−0.278 3(5)	O(3W)	0.208 4(4)	1.472 7(4)	−1.364 8(5)
C(4′)	0.224 3(4)	0.791 1(4)	−0.285 1(5)				

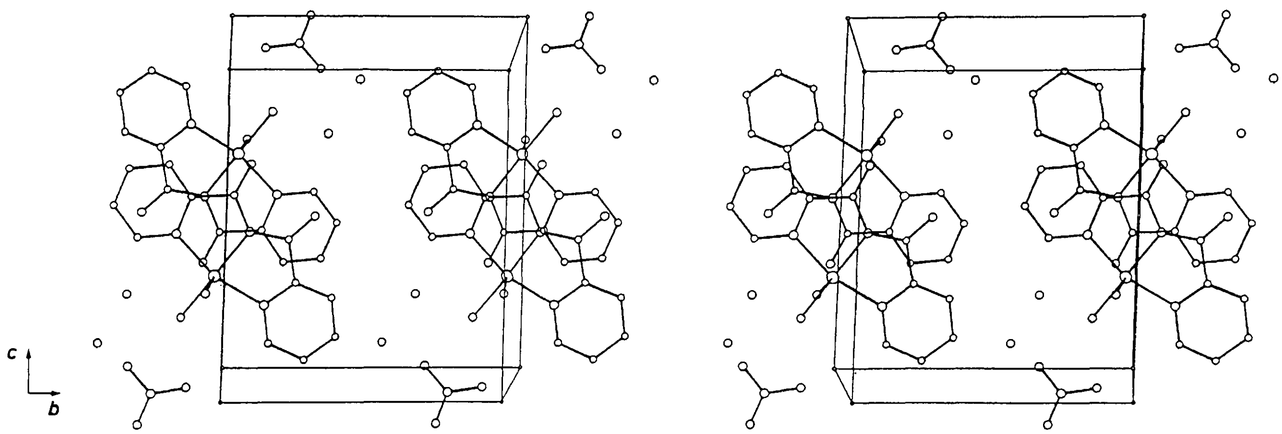

Figure 2. Stereoscopic view of the unit cell of complex (**1**) down the *a* axis

atom [O(2W)] of a water molecule. The Cu–N distances [1.938(1)—1.996(1) Å] are close to those reported for other [bis(2-arylcarbonyl)amido]copper(II) complexes,[2–4,14,15] whereas the Cu–O distances are 1.966(1) (basal) and 2.262(1) Å (apical). It should also be pointed out that the sixth position around Cu is screened by the proximity of a carbonyl oxygen atom of a symmetry-related molecule, Cu ··· O(1A^{II}) 3.302(1) Å. The basal atoms do not quite fall on a plane. Atoms N(1A) and N(1B) are 0.144 and 0.147 Å below while atoms O(2W) and N(2) are 0.123 and 0.167 Å above the mean plane through the four atoms. The copper atom lies 0.220 Å below this same plane. The plane defined by Cu, O(2W), and O(3W) makes an angle of 87.5° with the mean basal plane. The angles N(1A)–Cu–N(1B) and O(2W)–Cu–N(2) in the basal plane are 163.81(5) and 158.36(6)°, respectively. The significant deviation of the values of the angles N(2)–Cu–N(1A) [81.87(4)°] and N(2)–Cu–N(1B) [81.98(5)°] from the ideal value of 90° is due to the fact that such angles arise from the small bite size of the five-membered planar chelate ring.

The bis(2-pyridylcarbonyl)amido ligand is better described by two pyridylcarbonyl halves denoted A and B which form a dihedral angle of 1.5°, a value which is smaller than those reported for triaqua[bis(2-pyrimidylcarbonyl)amido]copper(II) nitrate dihydrate (2.9°)[2] and other [bis(2-pyridylcarbonyl)-

Table 4. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex (**1**)

Copper environment

Cu–N(1A)	1.994(1)	Cu–N(1B)	1.996(1)
Cu–N(2)	1.938(1)	Cu–O(2W)	1.966(1)
Cu–O(3W)	2.262(1)		
N(1A)–Cu–N(2)	81.87(4)	N(1B)–Cu–N(2)	81.98(5)
N(1A)–Cu–O(2W)	98.73(5)	N(1B)–Cu–O(2W)	95.86(5)
N(1A)–Cu–O(3W)	90.92(5)	N(1B)–Cu–O(3W)	95.55(5)
O(2W)–Cu–O(3W)	92.04(6)	N(2)–Cu–O(3W)	109.59(5)
N(2)–Cu–O(2W)	158.36(6)	N(1A)–Cu–N(1B)	163.81(5)

Bis(2-pyridylcarbonyl)amido ligand

N(1A)–C(2A)	1.350(2)	N(1B)–C(2B)	1.345(2)
C(2A)–C(3A)	1.366(2)	C(2B)–C(3B)	1.378(2)
C(3A)–C(4A)	1.386(2)	C(3B)–C(4B)	1.381(2)
C(4A)–C(5A)	1.367(2)	C(4B)–C(5B)	1.371(3)
C(5A)–C(6A)	1.375(2)	C(5B)–C(6B)	1.375(2)
C(6A)–N(1A)	1.345(2)	C(6B)–N(1B)	1.346(2)
C(2A)–C(7A)	1.511(2)	C(2B)–C(7B)	1.506(2)
C(7A)–O(1A)	1.217(2)	C(7B)–O(1B)	1.216(2)
C(7A)–N(2)	1.361(2)	C(7B)–N(2)	1.374(2)
Cu–N(1A)–C(2A)	113.9(1)	Cu–N(1B)–C(2B)	113.8(1)
Cu–N(1A)–C(6A)	128.1(1)	Cu–N(1B)–C(6B)	127.5(5)
C(2A)–N(1A)–C(6A)	118.0(1)	C(2B)–N(1B)–C(6B)	118.7(1)
N(1A)–C(2A)–C(7A)	115.3(1)	N(1B)–C(2B)–C(7B)	115.9(1)
N(1A)–C(2A)–C(3A)	122.5(1)	N(1B)–C(2B)–C(3B)	122.1(1)
C(7A)–C(2A)–C(3A)	122.2(1)	C(7B)–C(2B)–C(3B)	122.0(1)
C(2A)–C(3A)–C(4A)	118.9(1)	C(2B)–C(3B)–C(4B)	118.7(2)
C(3A)–C(4A)–C(5A)	119.1(2)	C(3B)–C(4B)–C(5B)	119.4(2)
C(4A)–C(5A)–C(6A)	119.3(1)	C(4B)–C(5B)–C(6B)	119.4(2)
C(5A)–C(6A)–N(1A)	122.2(1)	C(5B)–C(6B)–N(1B)	121.8(2)
C(2A)–C(7A)–O(1A)	121.2(1)	C(2B)–C(7B)–O(1B)	121.4(1)
C(2A)–C(7A)–N(2)	111.0(1)	C(2B)–C(7B)–N(2)	110.7(1)
O(1A)–C(7A)–N(2)	127.8(1)	O(1B)–C(7B)–N(2)	127.9(1)
Cu–N(2)–C(7A)	117.9(1)	Cu–N(2)–C(7B)	117.6(1)
C(7A)–N(2)–C(7B)	124.5(1)		

Nitrate group

N(3)–O(31)	1.238(2)	N(3)–O(33)	1.226(2)
N(3)–O(32)	1.248(2)		
O(31)–N(3)–O(32)	118.2(1)	O(32)–N(3)–O(33)	121.0(2)
O(31)–N(3)–O(33)	120.8(1)		

Hydrogen bonds

A[a]	D[b]	H	A ··· D	A ··· H–D
O(1A)	O(3W^{I})[c]	H(3W1)	2.858(2)	167(2)
O(1A)	O(4W^{II})	H(4W1)	3.026(2)	132(2)
O(1B)	O(4W^{II})	H(4W1)	2.980(2)	150(3)
O(31)	O(2W)	H(2W2)	2.955(2)	142(2)
O(31)	O(3W^{III})	H(3W2)	2.851(1)	177(2)
O(32)	O(2W)	H(2W2)	2.892(2)	157(2)
O(32)	O(5W^{IV})	H(5W2)	2.919(2)	169(2)
O(33)	O(5W^{V})	H(5W1)	2.903(2)	154(3)
O(4W)	O(2W)	H(2W1)	2.660(2)	177(2)
O(5W)	O(4W)	H(4W2)	2.764(2)	166(2)

[a] Acceptor atom. [b] Donor atom. [c] Symmetry translations: I $-x$, $-y$, $1 - z$; II $1 - x$, $-y$, $1 - z$; III $-x$, $-y$, $2 - z$; IV $x - 1, y, z$; V $1 - x$, $1 - y$, $2 - z$.

amido]copper(II) complexes (3.1—8.6°).[3,4,14,15] The need for short metal–nitrogen bonds is at the origin of the angular strain observed around the carbonyl carbon atoms C(7A) and C(7B). Although angular strain is also exhibited by (2,2′:6′,2″-terpyridyl)copper(II) complexes,[16—20] the stability of the pyridine ring when compared to the s-triazine ring precludes the above mentioned copper(II)-assisted hydrolysis reaction.

The geometry of the nitrate ion is as expected. It is planar with no deviations greater than 0.003 Å from the mean plane of the four atoms. The N–O bond lengths average 1.237 Å and the intra-anion angles average 120° as reported elsewhere.[2,21] The nitrate ion contributes to the packing by forming hydrogen bonds involving its three oxygen atoms. The co-ordinated [O(2W), O(3W)] and unco-ordinated [O(4W), O(5W)] water molecules as well as the carbonyl oxygen atoms [O(1A), O(1B)] are also involved in hydrogen bonding (see Table 4). All possible hydrogen donors are utilized in the hydrogen-bond network; two of the hydrogen atoms are even bifurcated. The shortest Cu ··· Cu^{II} distance is 5.459(1) Å.

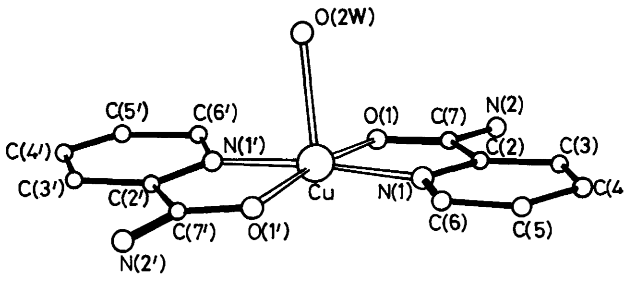

Figure 3. View of the cationic species $[Cu(NC_5H_4CONH_2)_2(H_2O)]^{2+}$ with the atom-numbering scheme. Hydrogen atoms are not included

Molecular Structure of Complex (**2**).—The structure of the cationic species $[Cu(NC_5H_4CONH_2)_2(H_2O)]^{2+}$ along with the atom-numbering scheme and a stereoscopic view of the unit cell are shown in Figures 3 and 4 respectively. Main bond lengths and non-bonded distances and angles are listed in Table 5. The structure is made up of the mononuclear cationic species $[Cu(NC_5H_4CONH_2)_2(H_2O)]^{2+}$, water of crystallization, and unco-ordinated nitrate anions.

The co-ordination geometry around copper(II) is distorted square pyramidal. The basal positions are occupied by the pyridine nitrogen [N(1), N(1′)] and carbonyl oxygen [O(1A), O(1B)] atoms of two carboxamide ligands and the apical site is occupied by one oxygen atom [O(2W)] of a water molecule. With regard to the bond lengths around the copper atom, the basal distances are very similar [1.977(3), 1.975(3), 1.955(2), and 1.956(2) Å for Cu–N(1), Cu–N(1′), Cu–O(1), and Cu–O(1′)] while the axial distance is somewhat longer [2.265(4) Å for Cu–O(2W)]. The values of the N(1)–Cu–O(1) and N(1′)–Cu–O(1′) angles [82.5(1) and 82.4(1)° respectively] are far from the ideal value of 90° because they are part, as observed for (**1**), of a five-membered planar chelate ring. The four atoms that comprise the basal co-ordination sites of the copper atom are practically coplanar. Atoms N(1) and N(1′) are 0.027 and 0.026 Å above while O(1) and O(1′) are 0.028 and 0.026 Å below the mean plane through them. The copper atom is 0.077 Å above this mean plane.

The two amide ligands are co-ordinated to copper(II) through the nitrogen atom of the pyridine ring and the oxygen atom of the amide group. The pyridine ring of each ligand is essentially planar as observed in other pyridine-2-carboxamide-containing copper(II) complexes[3,4] as well as in free carboxamide.[22] The dihedral angle between the two pyridine rings is 3.8°. The plane passing through the atoms Cu, O(1), C(7), C(2), and N(1) and the one encompassing the corresponding pyridine ring form a dihedral angle of 2.0° (0.81° for the other moiety). This angle is much smaller than that observed between the amide group and the pyridine ring in the free carboxamide. The bidentate co-ordination of this ligand to copper(II) is at the origin of such a decrease in the twisting between the amide group and the

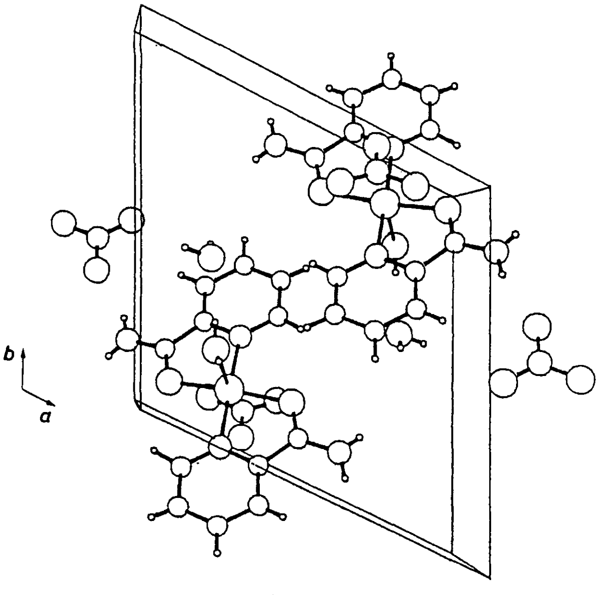

Figure 4. Stereoscopic view of the unit cell of complex (2) down the c axis

pyridine ring as shown recently.[3] The average carbon–carbon and carbon–nitrogen bond distances within the pyridyl rings are very close to those of the free and asymmetrically bidentate carboxamide.

The nitrate ions have their expected trigonal geometry. They are planar with no deviations greater than 0.003 Å from their individual mean planes. Average nitrogen–oxygen bond lengths and oxygen–nitrogen–oxygen angles are identical to those of the preceding structure. The non-bonding contacts involving nitrate ions, water molecules, and oxygen and nitrogen atoms of the carboxamide are listed in Table 5.

The shortest $Cu \cdots Cu^{V}$ distance is 6.361(1) Å.

Infrared and E.S.R. Spectra.—The i.r. spectra of complexes (**1**) and (**2**) exhibit bands for ionic nitrate[23] at 2 430w, 1 390s, and 830w cm^{-1}. A continuous absorption at 3 600—3 270 cm^{-1} with a relatively sharp maximum at 3 460 cm^{-1} for both complexes is attributable to the simultaneous presence of aqua ligand[24] and lattice water.[25] The most relevant feature of the i.r. spectrum of (**1**) is the appearance of a sharp intense band located at *ca.* 1 710 cm^{-1} which is assigned to the ν(C=O) vibration of the imide group of the bis(2-pyridylcarbonyl)amido ligand.[1—4,26] The presence of such a band provides evidence that hydrolysis of tptz has occurred. The i.r. spectrum of complex (**2**) displays bands of co-ordinated pyridine-2-carboxamide at 3 410w, 3 260w, 3 100w, 3 030w, 1 660s, 1 560m, 780m, and 760 cm^{-1}. In the far-i.r. region new bands due to ν(Cu–O) [490w and 420w cm^{-1} for (**1**) and 470w cm^{-1} for (**2**)] are clearly detectable. The absorptions at 280w cm^{-1} for (**1**) and 270w cm^{-1} for (**2**) may be assigned to ν[$Cu(OH_2)$].

X-Band e.s.r. spectra of both complexes recorded on polycrystalline samples do not exhibit any hyperfine structure; the $g_{\parallel}$ values [2.25 and 2.27 for (**1**) and (**2**) respectively], being higher than $g_{\perp}$ [2.08 and 2.07 for (**1**) and (**2**)], are indicative of a copper(II) $d_{x^2-y^2}$ orbital ground state, in accord with the observed square-pyramidal geometry for both complexes. In addition, both spectra show a weak half-field transition both at room and liquid-nitrogen temperatures. This feature is assigned to a $\Delta M_s = 2$ forbidden transition within the triplet for binuclear copper(II) complexes. In our case, as we are dealing with mononuclear copper(II) units, it could arise from dipolar interactions or hydrogen bonds between them.

Acid-Base Properties of the Complex [Bis(2-pyridylcarbonyl)amido]copper(II).—A previous study of the formation of complexes between [bis(2-pyridylcarbonyl)amido]copper(II) and oxalic acid revealed the existence of the protonated species $[Cu\{(NC_5H_4CO)_2NH\}]^{2+}$ at low pH values.[6a] On the other hand, we have isolated two hydroxo-complexes of formulae [CuL(OH)] and $[Cu_2L_2(OH)]ClO_4 \cdot H_2O$ which show the acidic character of the basal co-ordinated water molecule as observed in complex (**1**). The presumed structure of these hydroxo complexes is one in which the hydroxo group and three nitrogen donor atoms occupy the four positions of a square plane. Unfortunately, we were not able to grow single crystals of these complexes.

In order to characterize the acid–base behaviour of the complex [bis(2-pyridylcarbonyl)amido]copper(II), we have investigated its protonation and hydroxo-complex formation in aqueous solution. Series of aqueous solutions of complex (**1**) previously acidified with dilute nitric acid to pH 2 were titrated with NaOH. The initial concentration of complex (**1**), c_M, was varied in the range (1.25—2.50) × 10^{-3} mol dm^{-3}. Data treatment by SUPERQUAD of 239 experimental points from three different experiments carried out in the range pH 2.0—10.4 allowed us to determine the constants of the equilibria [equations (1) and (2)]. The values obtained for log K_1 and log K_2 are 1.83(1) and −8.80(1). Since equilibrium (2) may be written in terms of equilibrium (3) and K_w for water, K_2 may be expressed as in, equation (4). From this equation a value of 4.96 for log K_3 was calculated. The distribution diagram for the species existing in solution is depicted in Figure 5. The protonated species $[Cu(HL)(H_2O)]^{2+}$ and the $[CuL(H_2O)]^+$ complex co-exist at low pH values whereas the latter is the only species existing in the pH range 3—7. At higher pH values the neutral hydroxo-complex is formed, and is the only species

$$[CuL(H_2O)]^+ + H^+ \overset{K_1}{\rightleftharpoons} [Cu(HL)(H_2O)]^{2+} \qquad (1)$$

$$[CuL(H_2O)]^+ \overset{K_2}{\rightleftharpoons} [CuL(OH)] + H^+ \qquad (2)$$

$$[CuL(H_2O)]^+ + OH^- \overset{K_3}{\rightleftharpoons} [CuL(OH)] + H_2O \qquad (3)$$

$$K_2 = K_3K_w \qquad (4)$$

Table 5. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex (**2**)

Copper environment

Cu–N(1)	1.977(3)	Cu–N(1′)	1.975(3)
Cu–O(1)	1.955(2)	Cu–O(1′)	1.956(2)
Cu–O(2W)	2.265(4)		
O(1)–Cu–O(1′)	171.3(1)	N(1)–Cu–N(1′)	174.5(1)
O(1)–Cu–N(1)	82.5(1)	O(1′)–Cu–N(1′)	82.4(1)
N(1′)–Cu–O(1)	97.7(1)	N(1)–Cu–O(1′)	96.5(1)
O(2W)–Cu–O(1)	92.8(1)	O(2W)–Cu–O(1′)	95.8(1)
O(2W)–Cu–N(1)	95.6(1)	O(2W)–Cu–N(1′)	89.5(1)

Pyridine-2-carboxamide ligand

N(1)–C(2)	1.348(4)	N(1′)–C(2′)	1.344(4)
C(2)–C(3)	1.372(4)	C(2′)–C(3′)	1.374(4)
C(3)–C(4)	1.389(5)	C(3′)–C(4′)	1.380(5)
C(4)–C(5)	1.366(5)	C(4′)–C(5′)	1.367(5)
C(5)–C(6)	1.374(5)	C(5′)–C(6′)	1.376(5)
C(6)–N(1)	1.332(4)	C(6′)–N(1′)	1.339(4)
C(2)–C(7)	1.495(4)	C(2′)–C(7′)	1.495(4)
C(7)–N(2)	1.305(4)	C(7′)–N(2′)	1.305(4)
C(7)–O(1)	1.260(4)	C(7′)–O(1′)	1.261(4)
Cu–N(1)–C(2)	113.4(2)	Cu–N(1′)–C(2′)	113.5(2)
N(1)–C(2)–C(3)	122.0(3)	N(1′)–C(2′)–C(3′)	122.8(3)
C(2)–C(3)–C(4)	118.5(3)	C(2′)–C(3′)–C(4′)	118.4(3)
C(3)–C(4)–C(5)	119.3(3)	C(3′)–C(4′)–C(5′)	119.5(3)
C(4)–C(5)–C(6)	119.2(3)	C(4′)–C(5′)–C(6′)	119.7(3)
C(5)–C(6)–N(1)	122.2(3)	C(5′)–C(6′)–N(1′)	121.2(3)
C(6)–N(1)–Cu	127.9(2)	C(6′)–N(1′)–Cu	127.0(2)
C(6)–N(1)–C(2)	118.7(3)	C(6′)–N(1′)–C(2′)	119.3(3)
N(1)–C(2)–C(7)	111.9(3)	N(1′)–C(2′)–C(7′)	112.0(3)
C(2)–C(7)–O(1)	118.1(3)	C(2′)–C(7′)–O(1′)	117.7(3)
C(2)–C(7)–N(2)	119.8(3)	C(2′)–C(7′)–N(2′)	120.1(3)
C(7)–O(1)–Cu	114.1(2)	C(7′)–O(1′)–Cu	114.2(2)

Hydrogen bonds

A[a]	D[b]	H	A···D	A···H–D
N(1′)	O(2W)	H(2W1)	2.993(6)	107(6)
O(43^{I})[c]	N(2′)	H(2′1)	2.856(6)	168(5)
O(32^{II})	N(2′)	H(2′2)	3.154(4)	137(4)
O(33^{II})	N(2′)	H(2′2)	2.931(5)	170(5)
N(3^{II})	N(2′)	H(2′2)	3.487(4)	163(4)
O(42^{III})	O(2W)	H(2W1)	2.810(5)	167(8)
O($3\mathrm{W}^{\mathrm{IV}}$)	O(2W)	H(2W2)	2.706(7)	177(4)

[a] Acceptor atom. [b] Donor atom. [c] Symmetry translations: I $1 - x, 1 - y, -z$; II $1 + x, 1 + y, z$; III $x, 1 + y, z$; IV $x, y, 1 + z$.

existing at pH ⩾ 10.5. Introduction of constants corresponding to the formation of species $[Cu_2L_2(OH)]^+$ and $[CuL(OH)_2]^-$ as parameters to be refined improved the fit; however, they were not considered in the calculation of K_1 and K_2 because of the negligible concentrations of these complexes under our experimental conditions.

The bis(2-pyridylcarbonyl)amido ligand protonates easily in aqueous solution yielding the neutral monoprotic acid which has only very recently been isolated.[15] The proton is bound to the imide nitrogen atom according to n.m.r. and i.r. data. Equimolar aqueous solutions of complex (**1**) at pH values of 7 and 1.5 display nearly identical u.v.–visible spectra,[3] revealing that the CuN_3 chromophore is retained in the protonated species. This rules out protonation of the pyridyl groups. The imine-nitrogen atom and the carbonyl-carbon atoms which are involved in electronic delocalization through O(1A), C(7A), N(2), C(7B), and O(1B) could be protonated. Taking into account that the protonation of N(2) would lead to lengthening[27] or to the breaking of the Cu–N(2) bond, it can be concluded that the proton is most probably linked to the carbonyl groups. All our attempts to isolate such a species from acidic aqueous solutions were however unsuccessful. Summarizing, the co-ordination of the imide group to copper(II) decreases its basicity as shown by the low value of the protonation constant that we have measured.

As far as the hydroxo stability constant is concerned, its value is close to those reported for the related complex $[Cu(dien)(OH)]^+$ (4.86 and 5.17)[28] and smaller than that for $[Cu(terpy)(OH)]^+$ (5.64),[29] where dien and terpy are diethylenetriamine and 2,2′:6′,2″-terpyridyl respectively. Both dien and terpyridyl ligands are bound to copper(II) through a σ-donor bond giving cationic species with the same charge and five-membered chelate rings. The greater stability of the hydroxo-complex with terpyridyl is due to the π-acceptor character of this ligand which enhances the Lewis acid character of the metal ion. In the case of the [bis(2-pyridylcarbonyl)amido]copper(II) complex, although five-membered chelate rings are present, the lower charge, the presence of only two pyridyl rings, and the more basic character of the imide-nitrogen atom make the in-plane aqua ligand less acidic. Consequently, its hydroxo stability constant is smaller than that observed for $[Cu(terpy)(OH)]^+$.

On the Nature of the Isolated Products of the Hydrolytic Reaction of tptz.—Copper(II) promotes partial hydrolysis of tptz yielding the anionic bis(2-pyridylcarbonyl)amido species, which remains co-ordinated to the metal ion, and pyridine-2-carboxamide. We have found that the nature of the compounds which can be isolated from the hydrolysed solutions is very dependent on the copper(II): tptz molar ratio, *x*, and to a lesser extent on the anion which is present in solution, *i.e.* on the copper(II) salt used. Thus we have reported the synthesis and crystal structure of six different complexes (see Table 6). The nature of these complexes, as well as their structural features, allows us to establish a clear picture of the course of this reaction.

Complex (**1**) is the only compound isolated when the hydrolysis is carried out with sufficient excess of Cu^{2+}(aq) ($x \geqslant 2$). Although this complex was obtained previously by Lerner and Lippard,[1,2] they were unable to grow suitable single crystals for an *X*-ray diffraction study. The formation of three short Cu–N bonds when tptz is co-ordinated to the metal ion produces an angular strain which facilitates attack at the triazine ring by water molecules, promoting a hydrolytic reaction. The excess of Cu^{2+}(aq) in the solution allows the formation of a 1:1 copper(II)–pyridine-2-carboxamide complex with the ligand generated by the hydrolysis of tptz. This complex has not been isolated, probably due to a high solubility in water. When copper(II) perchlorate is substituted for copper(II) nitrate, a different complex, (**3**) was obtained. In this compound the $(NC_5H_4CO)_2N^-$ anion acts as a bridge co-ordinating a second metal ion *via* the two carbonyl-oxygen atoms. Aqua ligands are displaced and a polymeric one-dimensional copper(II) chain results.[3]

When the reaction is carried out in presence of only a slight excess of Cu^{2+}(aq) ($1 < x < 1.5$), the concentration of pyridine-2-carboxamide, which is formed in the hydrolysis of tptz, is greater than the remaining Cu^{2+}(aq) (double when $x = 1.5$) allowing the formation of a 1:2 complex $[Cu(NC_5H_4CONH_2)_2(H_2O)]^+$ (**2**), which crystallizes as a nitrate together with complex (**1**). Thus, two copper(II) complexes, each containing one of the fragments of the hydrolysis of tptz, are obtained under these conditions.

For $x = 1$, there is no free Cu^{2+}(aq) to bind the pyridine-2-carboxamide which will be co-ordinated to the metal ion of the complex $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_2]^+$ displacing the two water molecules. The main product of the reaction is $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]^+$ which has been isolated

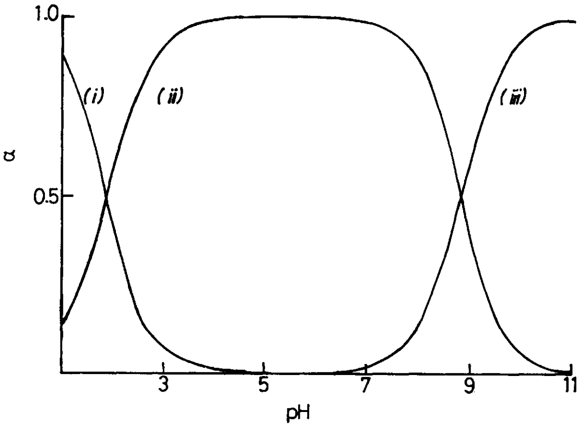

Figure 5. Distribution diagram for species in an aqueous solution of $[CuL(H_2O)]^+$ as a function of pH; α is the ratio between the concentration of each species and the initial concentration of $[CuL(H_2O)]^+$. Complexes: $[Cu(HL)(H_2O)]^{2+}$ (*i*), $[CuL(H_2O)]^+$ (*ii*), and $[CuL(OH)]$ (*iii*)

Table 6. Isolated products of the copper(II)-assisted hydrolysis reaction of tptz

Cu(II) : tptz molar ratio (x)	Compound(s) isolated[a]	Ref.[b]
$x \geqslant 2$	(**1**)	This work
	(**3**)	3
$1.5 > x > 1$	(**1**) and (**2**)	This work
$x = 1$	(**4**) and low amounts of (**3**)	3.4
	(**5**)	
$1 > x > 0.5$	(**5**) and (**6**)	4
$x = 0.5$	(**6**)	4

[a] $[Cu\{(NC_5H_4CO)_2N\}]ClO_4$ (**3**), $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]ClO_4{\cdot}H_2O$ (**4**), $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)][CF_3SO_3]$ (**5**), and $[Cu\{(NC_5H_4CO)_2N\}(tptz)][CF_3SO_3]$ (**6**). [b] Reports of the structures of the complexes.

as its perchlorate (**4**)[3] and trifluoromethanesulphonate (**5**)[4] salts. Only one copper(II) complex which contains the two fragments of the hydrolysis of tptz is obtained under these conditions. Moreover, a small amount of complex (**3**) is obtained together with complex (**4**) probably arising from further hydrolysis of a small amount of the carboxamide to the carboxylic acid.

Finally, a further complex (**6**), which contains one unhydrolysed tptz molecule as ligand, is obtained when $x < 1$, and is the only product of the reaction when $x = 0.5$. Once complex (**1**) has been formed, the excess tptz in solution can only be coordinated *via* displacement of the aqua ligands. However, owing to the Jahn–Teller effect, the copper(II) ion can form only one additional short Cu–N bond as evidenced by the structural results.[4] Consequently, there is no angular strain in the triazine ring in this case, and a complex containing unhydrolysed tptz as ligand becomes stable.

Acknowledgements

We are grateful to the Comisión Interministerial de Ciencia y Tecnología (Spain) for financial support (Proyecto PB85-0190). One of us (I. C.) thanks the Conselleria de Cultura, Educació i Ciència de la Generalitat Valenciana for a grant. Thanks are also extended to the Alexander von Humboldt Foundation for support to J. M. A. during his stay in Ulm.

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Received 2nd *June* 1989; *Paper* 9/02313E