# Copper(II)-assisted Hydrolysis of 2,4,6-Tris(2-pyridyl)-1,3,5-triazine. Part 2.† Crystal Structures of [Bis(2-pyridylcarbonyl)amido](pyridine-2-carboxamide)copper(II) Trifluoromethanesulphonate and [Bis(2-pyridylcarbonyl)amido][2,4,6-tris(2-pyridyl)-1,3,5-triazine]copper(II) Trifluoromethanesulphonate‡

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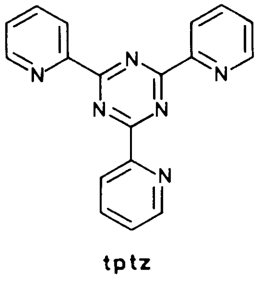
Two compounds of formula $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)][CF_3SO_3]$ (**1**) and $[Cu\{(NC_5H_4CO)_2N\}(tptz)][CF_3SO_3]$, (**2**), where $(NC_5H_4CO)_2N^-$ and $NC_5H_4CONH_2$ are bis(2-pyridylcarbonyl)amide and pyridine-2-carboxamide and tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine respectively, have been obtained from aqueous solutions of tptz and copper(II) trifluoromethanesulphonate. Crystals of complex (**1**) are monoclinic with $a$ = 9.927(4), $b$ = 26.727(5), $c$ = 8.594(4) Å, β = 98.72(2)°, space group $P2_1/n$, and $Z$ = 4. Crystals of complex (**2**) are triclinic with $a$ = 9.177(3), $b$ = 10.735(3), $c$ = 18.231(4) Å, α = 102.65(2), β = 106.60(2), γ = 93.89(3)°, space group $P\bar{1}$, and $Z$ = 2. The structure of (**1**) consists of $[Cu\{NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]^+$ mononuclear cations plus semi-co-ordinated $CF_3SO_3^-$ anions. The copper(II) ion is in a distorted octahedral environment: the three nitrogen atoms of the bis(2-pyridylcarbonyl)amido ligand and the pyridine one of the carboxamide form a distorted square plane around the copper whereas the axial positions are occupied by the oxygen atom of the carboxamide and by an oxygen atom of the $CF_3SO_3^-$ group with Cu–O bonds different from each other and significantly longer than the equatorial ones. The structure of (**2**) is made up of $[Cu\{(NC_5H_4CO)_2N\}(tptz)]^+$ mononuclear cations and non-co-ordinated $CF_3SO_3^-$ groups. The copper(II) ion is six-co-ordinated: the three nitrogen atoms of the bis(2-pyridylcarbonyl)amido ligand and one nitrogen atom of the triazine ring of tptz form a distorted square plane around the copper, while two nitrogen atoms from two pyridyl rings of tptz occupy the axial sites. The two Cu–N axial bonds are very close but significantly longer than the equatorial ones. The structure of (**1**) contains as ligands the two main products of the copper(II)-assisted tptz hydrolysis, whereas in the structure of (**2**) the co-ordination polyhedron around copper(II) is achieved by one of these products and tptz. The possibility of synthesizing copper(II) complexes containing unhydrolysed tptz is discussed in the light of the structure of complex (**2**).

2,4,6-Tris(2-pyridyl)-1,3,5-triazine, tptz, has been shown to co-ordinate to a variety of transition-metal ions through the terpyridine or bipyridine-like moieties or using both such sites simultaneously.[1–8] However, tptz and tpmtz [2,4,6-tris(2-pyrimidyl)-1,3,5-triazine] were found to undergo hydrolytic reactions in the presence of bivalent copper.[9,10] The product of these reactions are bis(arylcarbonyl)amidocopper(II) complexes and free arylamides. Very recently, the *X*-ray structure determination of [bis(2-pyridylcarbonyl)amido]-(2-pyridylformamide)copper(II) perchlorate monohydrate[11] has allowed the nature of the two main products of the copper(II)-assisted tptz hydrolysis to be established because both are present as ligands in this complex. The hydrolytic reaction probably occurs *via* nucleophilic attack at the triazine ring by $OH^-$ or $H_2O$.[12] Angular strain at the carbonyl-carbon atoms in the co-ordinated bis(2-arylcarbonyl)amido ligands[10,11] strongly supports this pathway for the metal-assisted hydrolysis of the normally stable 2,4,6-triaryl-1,3,5-triazines. A large family of copper(II) complexes containing tptz have been isolated as polycrystalline powders only recently.[8] The preparative procedures were orientated towards the formation of readily isolable solid compounds using ethanol–water mixtures as solvent and co-ordinating counter ions in order to preserve the $[Cu(tptz)]^{2+}$ unit from hydrolysis. The difficulties in growing


tptz

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† Part 1 is ref. 11.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

*Non-S.I. unit employed:* G = $10^{-4}$ T.

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

| Compound | (**1**) | (**2**) |
|---|---|---|
| Formula | $C_{19}H_{14}CuF_3N_5O_6S$ | $C_{31}H_{20}CuF_3N_9O_5S$ |
| $M$ | 560.8 | 751.1 |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 9.927(4) | 9.177(3) |
| $b$/Å | 26.727(5) | 10.735(3) |
| $c$/Å | 8.594(4) | 18.231(4) |
| $\alpha$/° | 90.0 | 102.65(2) |
| $\beta$/° | 98.72(2) | 106.60(2) |
| $\gamma$/° | 90.0 | 93.89(3) |
| $U$/Å$^3$ | 2 253.8 | 1 663.0(2) |
| $Z$ | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.652 | 1.499 |
| Crystal size/mm | 0.10 × 0.04 × 0.12 | 0.11 × 0.09 × 0.06 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 10.67 | 14.24 |
| Reflections collected | 3 952 | 5 844 |
| Independent reflections | 3 447<br>$[I \geqslant 2.0\sigma(I)]$ | 4 421<br>$[I \geqslant 1.5\sigma(I)]$ |
| No. of parameters refined | 372 | 379 |
| $R = \lVert F_0\rvert - \lvert F_c\rVert/\lvert F_0\rvert$ | 0.0531 * | 0.1153 * |

* Unit weights.

single crystals under these conditions explain the lack of structural data for such complexes. It should be noted that, taking into account the results of Gillard and Williams,[12b] the half-life of $[Cu(tptz)(H_2O)_3]^{2+}$ should be *ca.* 2 h at pH 7 and 298 K.

In this paper we report the synthesis, *X*-ray single-crystal structure determination, and spectral characterization of two new mononuclear copper(II) complexes of formulae $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)][CF_3SO_3]$ (**1**) and $[Cu\{(NC_5H_4CO)_2N\}(C_{18}H_{12}N_6)][CF_3SO_3]$ (**2**). The two main fragments resulting from the metal-assisted hydrolysis of tptz are present as ligands in the structure of (**1**). Such a situation was illustrated by some of us very recently[11] using perchlorate instead of trifluoromethanesulphonate as the copper salt. The structure determination of complex (**2**) is, as far as we know, the first of a copper(II) complex containing tptz as a ligand.

## Experimental

*Materials and Measurements.*—The compound tptz was purchased from Sigma whereas copper(II) trifluoromethanesulphonate was synthesized following a reported procedure.[13] Infrared spectra were recorded with a Philips Scientific SP 200 spectrometer as KBr pellets, electronic spectra on a u.v.–visible–near i.r. Perkin-Elmer Lambda-9 spectrophotometer as Nujol mulls on filter paper, and *X*-band e.s.r. spectra on a Brüker ER 200D spectrometer in the range 298—100 K.

*Synthesis.*—A green suspension was obtained by adding copper(II) trifluoromethanesulphonate (0.181 g, 0.5 mmol) to an aqueous suspension of tptz (0.156 g, 0.5 mmol). Heating at 90 °C with stirring for 30 min led to a dark blue solution. Dark blue prisms of complex (**1**) were obtained by slow evaporation of solvent at room temperature. This procedure yielded a mixture of green plate-like crystals of (**2**), which crystallizes first, and (**1**) when decreasing the amount of copper(II) salt. Crystals of complex (**2**) were obtained as the only product when a 1:2 $Cu^{II}$:tptz molar ratio was used [Found: C, 40.50; H, 2.55; N, 12.35. $C_{19}H_{14}CuF_3N_5O_6S$ requires C, 40.70; H, 2.50; N, 12.50%. Found: C, 49.65; H, 2.40; N, 17.05. $C_{31}H_{20}CuF_3N_9O_5S$ requires C, 49.58; H, 2.65; N, 16.75%].

*Crystallography.*—Diffraction data were collected at 293 K with a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.7107$ Å). The unit-cell parameters were derived from least-squares refinement of 25 well centred reflections ($10 \leqslant \theta \leqslant 20°$). Data collection showed systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) for (**1**) and no conditions for (**2**) which uniquely define monoclinic space group $P2_1/n$ for the former and triclinic space group $P1$ or $P\bar{1}$ for the latter. The intensities of three standard reflections measured every 50 showed no significant variations. Intensity data were collected by the $\theta$–$2\theta$ scan technique in the range $2\theta$ 4—50°. Lorentz and polarization corrections were applied, but not for absorption. 3 447 Independent reflections with $I \geqslant 2.0\sigma(I)$ for (**1**) and 4 421 independent reflections with $I \geqslant 1.5\sigma(I)$ for (**2**) were used for the structure refinements.

*Structure solution and refinement.* The structures of complexes (**1**) and (**2**) were solved by direct methods using the XM84 computer program.[14] Full-matrix least squares with the SHELX 76 system[15] was completed with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were included at the final stage of the refinement in calculated positions with an isotropic thermal parameter. The crystal data are listed in Table 1. Although the high $R$ value for complex (**2**) could be due to the poor quality of crystals (all our attempts to improve this were unsuccessful), it seems most probably due to the disorder observed in the $CF_3SO_3^-$ anion. This disorder is confirmed by the high isotropic thermal parameters of its atoms and the number of spurious peaks in the near neighbourhood (maximum 0.59 e Å$^{-3}$). The space group was assumed to be $P\bar{1}$, but according to refinement the same $R$ value was obtained by considering either a non-centrosymmetric or a centrosymmetric space group. A value of 0.1253 was obtained for $R'$ of complex (**2**) with $w = 1.6138/[\sigma^2(F) + 0.003\,604F^2]$ and a goodness of fit of 2.21.

Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 16. The final Fourier difference map showed residual maxima and minima of 1.78 and −0.52 e Å$^{-3}$ for complex (**1**) and 1.84 and −1.72 e Å$^{-3}$ for (**2**). The final atomic co-ordinates for all non-hydrogen atoms of (**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 distances and angles.

## Results and Discussion

*Molecular Structure of Complex* (**1**).—A view of complex (**1**) with the atom-numbering scheme is shown in Figure 1. The co-ordination polyhedron around the copper(II) ion can be described as a distorted octahedron (4 + 1 + 1). Selected bond distances and angles are given in Table 4. The basal plane is formed by four nitrogen atoms, N(2), N(1A), N(1B), and N(3), which are co-ordinated to copper, the copper–nitrogen distances being 1.935(4), 2.022(5), 2.016(4), and 2.000(4) Å respectively. The axial positions are filled by O(2) (the oxygen atom of the pyridine-2-carboxamide) and O(3) (one oxygen atom of the $CF_3SO_3^-$ anion) with copper–oxygen distances of 2.381(4) and 2.709(6) Å respectively. The angle N(3)–Cu–O(3) is 89.5(2)° whereas N(3)–Cu–O(2) is only 75.5(2)°. This structure is very similar to that of the analogous perchlorate complex.[11] Only few differences are observed: the deviations from the mean plane of the four nitrogen atoms comprising the equatorial co-ordinates sites of the copper atom [0.028 Å above for N(1A) and N(1B) and 0.032 and 0.025 Å below this plane for N(2) and N(3) respectively] are significantly smaller than in the analogous perchlorate compound. The copper atom lies only 0.044 Å below this same plane (0.084 Å in the perchlorate complex).

The pyridine-2-carboxamide ligand is co-ordinated to the

**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 | 0.473 4(1) | 0.110 8(1) | 0.267 0(1) | N(2) | 0.654 9(5) | 0.082 7(2) | 0.290 6(5) |
| O(1A) | 0.810 8(5) | 0.045 5(2) | 0.150 3(6) | N(3) | 0.285 9(5) | 0.140 1(2) | 0.234 9(5) |
| N(1A) | 0.466 4(5) | 0.082 7(2) | 0.047 5(5) | N(4) | 0.117 0(7) | 0.036 2(2) | 0.388 8(10) |
| C(2A) | 0.584 2(6) | 0.060 8(2) | 0.023 5(7) | C(8) | 0.180 6(5) | 0.114 7(2) | 0.280 1(6) |
| C(3A) | 0.598 5(8) | 0.039 0(2) | −0.118 8(8) | C(9) | 0.051 8(7) | 0.135 2(3) | 0.259 0(10) |
| C(4A) | 0.509 6(8) | −0.038 8(2) | 0.240 9(8) | C(10) | 0.029 8(8) | 0.182 1(3) | 0.190 6(10) |
| C(5A) | 0.372 1(9) | 0.060 6(3) | −0.216 3(8) | C(11) | 0.134 9(7) | 0.206 4(2) | 0.141 9(8) |
| C(6A) | 0.362 6(8) | 0.082 4(3) | −0.071 2(8) | C(12) | 0.262 3(7) | 0.184 9(2) | 0.165 8(7) |
| C(7A) | 0.697 9(6) | 0.061 6(2) | 0.162 6(7) | C(13) | 0.216 3(6) | 0.063 3(2) | 0.348 2(7) |
| O(1B) | 0.845 5(4) | 0.068 1(2) | 0.478 9(5) | O(3) | 0.568 0(6) | 0.195 2(2) | 0.146 4(7) |
| N(1B) | 0.538 2(5) | 0.135 2(2) | 0.487 6(5) | O(4) | 0.743 9(5) | 0.247 5(2) | 0.069 8(7) |
| C(2B) | 0.665 2(6) | 0.119 0(2) | 0.543 9(6) | O(5) | 0.734 9(7) | 0.233 6(3) | 0.345 7(7) |
| C(3B) | 0.728 7(8) | 0.132 2(3) | 0.694 1(8) | S(1) | 0.663 6(2) | 0.235 6(1) | 0.190 7(2) |
| C(4B) | 0.661 1(8) | 0.161 5(3) | 0.788 4(8) | C(14) | 0.553 3(9) | 0.289 9(3) | 0.193 6(9) |
| C(5B) | 0.529 9(8) | 0.177 5(2) | 0.731 6(8) | F(1) | 0.469 7(5) | 0.284 1(2) | 0.298 8(6) |
| C(6B) | 0.473 5(7) | 0.163 9(2) | 0.580 5(8) | F(2) | 0.477 3(6) | 0.297 2(2) | 0.057 6(6) |
| C(7B) | 0.733 4(6) | 0.087 0(2) | 0.433 7(7) | F(3) | 0.624 8(7) | 0.330 1(2) | 0.234 4(9) |
| O(2) | 0.335 7(4) | 0.048 9(1) | 0.365 5(5) | | | | |

**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 | 0.072 0(1) | 0.261 4(1) | 0.188 0(1) | C(12) | 0.218 7(15) | 0.608 2(10) | 0.114 3(7) |
| O(1A) | −0.190 0(9) | −0.054 4(6) | 0.026 6(5) | C(13) | 0.222 2(16) | 0.571 0(11) | 0.038 0(7) |
| N(1A) | −0.157 9(9) | 0.264 9(7) | 0.139 8(5) | C(14) | 0.183 4(15) | 0.446 4(11) | −0.002 4(7) |
| C(2A) | −0.227 7(12) | 0.156 9(9) | 0.081 9(6) | C(15) | 0.141 2(12) | 0.354 9(9) | 0.034 9(6) |
| C(3A) | −0.378 2(13) | 0.148 0(11) | 0.035 4(7) | N(4) | 0.138 3(9) | 0.388 8(7) | 0.108 4(4) |
| C(4A) | −0.464 3(13) | 0.241 1(12) | 0.051 0(9) | C(16) | 0.082 9(11) | 0.369 6(9) | 0.364 6(6) |
| C(5A) | −0.397 8(13) | 0.349 2(11) | 0.110 1(8) | C(17) | 0.079 4(14) | 0.387 6(10) | 0.440 9(7) |
| C(6A) | −0.243 9(13) | 0.358 2(10) | 0.152 1(6) | C(18) | 0.023 6(17) | 0.285 8(14) | 0.463 9(8) |
| C(7A) | −0.130 3(12) | 0.048 7(9) | 0.072 4(6) | C(19) | −0.018 8(14) | 0.165 9(12) | 0.410 0(8) |
| O(1B) | 0.118 2(10) | −0.107 4(6) | 0.091 9(5) | C(20) | −0.010 3(12) | 0.154 6(10) | 0.335 7(7) |
| N(1B) | 0.285 4(9) | 0.202 9(7) | 0.214 7(5) | N(5) | 0.037 8(9) | 0.252 7(7) | 0.311 5(5) |
| C(2B) | 0.282 5(12) | 0.079 8(9) | 0.178 3(6) | C(21) | 0.254 9(12) | 0.822 3(9) | 0.396 3(7) |
| C(3B) | 0.415 7(15) | 0.023 3(11) | 0.189 2(8) | C(22) | 0.281 9(13) | 0.919 4(9) | 0.360 8(7) |
| C(4B) | 0.551 5(15) | 0.095 7(15) | 0.237 3(10) | C(23) | 0.318 3(14) | 1.045 6(10) | 0.408 4(8) |
| C(5B) | 0.554 1(14) | 0.220 7(12) | 0.274 7(8) | C(24) | 0.328 0(14) | 1.068 1(10) | 0.485 3(8) |
| C(6B) | 0.418 4(14) | 0.272 4(11) | 0.262 5(7) | C(25) | 0.303 5(13) | 0.964 4(12) | 0.514 6(7) |
| C(7B) | 0.130 3(13) | 0.007 3(9) | 0.124 8(7) | N(8) | 0.266 0(12) | 0.843 5(9) | 0.470 3(6) |
| N(2) | 0.016 0(9) | 0.084 9(6) | 0.121 7(5) | O(2) | −0.117 7(21) | −0.159 6(18) | 0.352 9(11) |
| N(3) | 0.131 8(9) | 0.446 1(7) | 0.258 2(4) | O(3) | −0.279 8(27) | −0.386 8(24) | 0.315 1(14) |
| C(9) | 0.174 8(11) | 0.545 3(8) | 0.230 6(5) | O(4) | −0.415 8(24) | −0.213 1(19) | 0.289 9(12) |
| N(6) | 0.215 9(9) | 0.666 2(7) | 0.273 7(5) | S(1) | 0.771 5(9) | 0.733 5(8) | 0.298 4(5) |
| C(10) | 0.210 9(11) | 0.686 3(10) | 0.347 1(6) | C(26) | −0.317 7(88) | −0.201 5(76) | 0.204 7(44) |
| N(7) | 0.170 0(10) | 0.594 5(7) | 0.380 8(5) | F(1) | −0.374 4(29) | −0.309 1(26) | 0.156 4(16) |
| C(8) | 0.132 2(11) | 0.476 8(8) | 0.333 9(6) | F(2) | −0.219 2(44) | −0.140 1(36) | 0.195 4(22) |
| C(11) | 0.177 8(11) | 0.515 3(9) | 0.147 6(5) | F(3) | −0.133 5(28) | −0.313 1(23) | 0.210 9(14) |

copper(II) ion in a bidentate fashion *via* the N(3) and O(2) atoms [Cu–N(3) and Cu–O(2) 2.000(4) and 2.381(4) Å respectively].

The average length of the carbon–carbon bonds within the pyridine rings (1.38 Å) and the average intra-ring carbon–nitrogen bond length (1.35 Å) compare favourably with values reported for similar systems.[4,10,11,17,18]

The pyridine ring of the co-ordinated pyridinecarboxamide is essentially planar as observed for the free amide[19] and in the structure of the perchlorate complex. The dihedral angle between this plane and the one passing through the atoms Cu, O(2), C(13), C(8), and N(3) is 1.7° (2.7° in the perchlorate complex).

The structure of complex (**1**) contains a semi-co-ordinated $CF_3SO_3^-$ group. Although several transition-metal complexes containing co-ordinated $CF_3SO_3^-$ have been synthesized in recent years,[20] there are few structural data on such compounds.[21] In complex (**1**) one of the axial positions is occupied by an oxygen atom O(3) of $CF_3SO_3^-$ at a longer distance [2.709(6) Å] than the equatorial ones. This bond length is very close to that reported for the analogous perchlorate compound [2.726(25) Å] which may reflect a similar low basicity for trifluoromethanesulphonate and perchlorate anions. The bonding parameters for $CF_3SO_3^-$ are similar to those found in other complexes. For example, this anion adopts a staggered-ethane configuration about the S–C bond and the O–S–O angles are greater than the C–S–O angles. The S–O(3) bond involving the oxygen bound to copper [1.449(5) Å] is longer than those involving the terminally bound oxygen atoms, mean 1.425 Å.

The shorter Cu $\cdots$ Cu$^{I}$ distance is 7.124(1) Å where I refers to the equivalent position $1-x,-y,-z$ relative to the reference molecule at *x*,*y*,*z*.

*Molecular Structure of Complex* (**2**).—A perspective view of the cationic part of complex (**2**) is depicted in Figure 2. The co-ordination polyhedron around the copper(II) ion can be

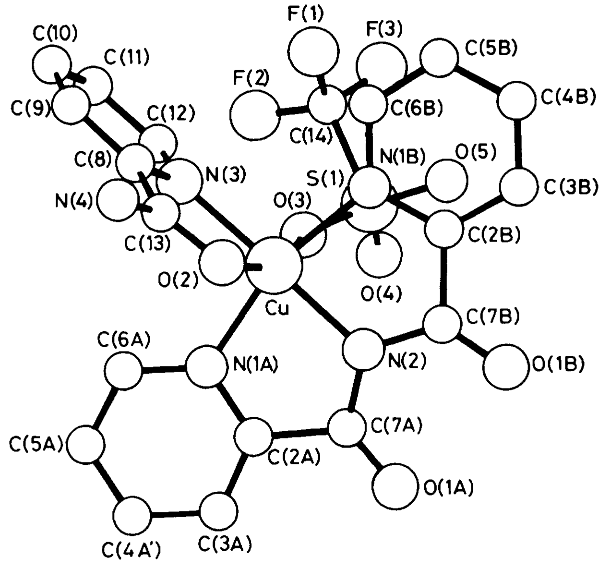


**Figure 1.** View of the structure of complex (**1**) with the atom-numbering scheme. Hydrogen atoms are not included

**Table 4.** Bond distances (Å) and angles (°) for non-hydrogen atoms of complex (**1**)

| | | | |
|---|---|---|---|
| Copper environment | | | |
| Cu–N(1A) | 2.022(5) | Cu–N(3) | 2.000(4) |
| Cu–N(2) | 1.935(4) | Cu–O(2) | 2.381(4) |
| Cu–N(1B) | 2.016(4) | Cu–O(3) | 2.709(6) |
| N(2)–Cu–N(1A) | 81.5(2) | N(2)–Cu–N(1B) | 82.4(2) |
| N(2)–Cu–N(3) | 178.1(2) | N(2)–Cu–O(2) | 105.6(2) |
| N(2)–Cu–O(3) | 89.5(2) | N(3)–Cu–O(2) | 75.5(2) |
| N(3)–Cu–N(1A) | 96.7(2) | N(3)–Cu–N(1B) | 99.2(2) |
| N(3)–Cu–O(3) | 89.5(2) | N(1B)–Cu–N(1A) | 163.5(2) |
| N(1A)–Cu–O(2) | 97.7(2) | N(1B)–Cu–O(2) | 98.8(1) |
| N(1A)–Cu–O(3) | 85.3(2) | N(1B)–Cu–O(3) | 90.6(2) |
| O(2)–Cu–O(3) | 164.8(2) | | |
| Bis(2-pyridylcarbonyl)amido ligand | | | |
| N(1A)–C(2A) | 1.352(7) | N(1B)–C(2B) | 1.352(7) |
| C(2A)–C(3A) | 1.381(8) | C(2B)–C(3B) | 1.394(8) |
| C(3A)–C(4A$^{\mathrm{I}}$) | 1.382(10) | C(3B)–C(4B) | 1.372(10) |
| C(4A$^{\mathrm{I}}$)–C(5A) | 1.356(10) | C(4B)–C(5B) | 1.388(10) |
| C(5A)–C(6A) | 1.393(10) | C(5B)–C(6B) | 1.382(9) |
| C(6A)–N(1A) | 1.336(8) | C(6B)–N(1B) | 1.338(7) |
| C(2A)–C(7A) | 1.514(8) | C(2B)–C(7B) | 1.511(8) |
| C(7A)–O(1A) | 1.220(7) | C(7B)–O(1B) | 1.229(7) |
| C(7A)–N(2) | 1.361(7) | C(7B)–N(2) | 1.358(7) |
| Cu–N(1A)–C(2A) | 113.3(4) | Cu–N(1B)–C(2B) | 112.3(4) |
| Cu–N(1A)–C(6A) | 128.9(5) | Cu–N(1B)–C(6B) | 129.3(4) |
| C(2A)–N(1A)–C(6A) | 117.8(5) | C(2B)–N(1B)–C(6B) | 118.4(3) |
| N(1A)–C(2A)–C(7A) | 115.6(5) | N(1B)–C(2B)–C(7B) | 116.1(5) |
| N(1A)–C(2A)–C(3A) | 121.7(6) | N(1B)–C(2B)–C(3B) | 121.1(6) |
| C(7A)–C(2A)–C(3A) | 122.8(6) | C(7B)–C(2B)–C(3B) | 122.8(6) |
| C(2A)–C(3A)–C(4A$^{\mathrm{I}}$) | 120.0(6) | C(2B)–C(3B)–C(4B) | 119.9(7) |
| C(3A)–C(4A$^{\mathrm{I}}$)–C(5A) | 118.1(7) | C(3B)–C(4B)–C(5B) | 119.0(6) |
| C(4A$^{\mathrm{I}}$)–C(5A)–C(6A) | 119.7(7) | C(4B)–C(5B)–C(6B) | 118.3(6) |
| C(5A)–C(6A)–N(1A) | 122.4(7) | C(5B)–C(6B)–N(1B) | 123.2(7) |
| C(2A)–C(7A)–O(1A) | 120.7(5) | C(2B)–C(7B)–O(1B) | 120.3(5) |
| C(2A)–C(7A)–N(2) | 110.9(5) | C(2B)–C(7B)–N(2) | 111.4(5) |
| O(1A)–C(7A)–N(2) | 128.3(6) | O(1B)–C(7B)–N(2) | 128.3(5) |
| Cu–N(2)–C(7A) | 118.5(4) | Cu–N(2)–C(7B) | 117.3(4) |

$^{\mathrm{I}}$ denotes atoms at position $1 - x, -y, -z$.

described as a tetragonally elongated octahedron (4 + 2). Main bond distances and angles are listed in Table 5. The basal plane is comprised of the three nitrogen atoms of the tridentate bis(2-pyridylcarbonyl)amido ligand [N(1A), N(1B), and N(2)] and one of the nitrogen atoms of the triazine ring [N(3)], the copper–nitrogen bond distances being 2.047(8), 2.055(8), 1.956(6), and 2.052(7) Å respectively. The two apical positions are occupied by nitrogen atoms of two pyridyl rings of tptz at greater distances: 2.369(9) and 2.379(10) Å for Cu–N(4) and Cu–N(5) respectively. It should be pointed out that copper–nitrogen distances of 2.2—2.4 Å are commonly taken as typical for 'long' Cu–N bonds in Jahn–Teller distorted complexes of copper(II).[22,23] The values of the angles N(3)–Cu–N(4) and N(3)–Cu–N(5) [74.4(3) and 73.6(3)° respectively] illustrate the distortion of the octahedron surrounding copper. The four nitrogen atoms comprising the equatorial co-ordination sites fall on a plane and the copper atom does not deviate significantly from this mean plane. The angles in this square-planar array are distorted from the ideal angles, due mainly to the constrained geometry of the chelating bis(2-pyridylcarbonyl)amido ligand. The values of the angles N(1A)–Cu–N(2) and N(1B)–Cu–N(2) are nearly identical [81.5(3) and 81.3(3)° respectively] and very close to those reported for the same ligand in other copper(II) complexes.[11,24] These values illustrate the typical small 'bite' possible for this type of chelating ligand. The structural features of the bis(2-pyridylcarbonyl)amido ligand are very similar to those observed in complex (**1**).

The tptz ligand co-ordinates to copper(II) ion in an asymmetrically tridentate fashion *via* N(3), N(4), and N(5). A comparison between the structural features of the co-ordination of bis(2-pyridylcarbonyl)amide and tptz to the copper atom in cpmplex (**2**) can be made by means of Figure 3. The three copper–nitrogen bond lengths are different and those of the co-ordinated tptz are significantly larger. The longer the metal–nitrogen bonds the lesser is the angular strain. This effect can be seen by comparing the angles at the sp$^2$-hybridized carbonyl-carbon atoms C(7A) and C(7B) of unit C with the corresponding ones at the carbon atoms C(9) and C(8) of unit D. The angles around C(7A) are 129.6(10), 119.0(9), and 111.4(7)° for O(1A)–C(7A)–N(2), C(2A)–C(7A)–O(1A), and C(2A)–C(7A)–N(2) respectively, whereas the corresponding angles around C(7B) are 128.0(9), 120.7(10), and 111.2(8)°. However, the angles around C(8) and C(9) are closer to the ideal values of 120°. For instance, within the chelate rings the angles are 117.5(7) and 116.4(7)° for N(3)–C(9)–C(11) and N(3)–C(8)–C(16) respectively. The larger deviations from the expected value of 120° which are exhibited by the former unit are clearly caused by the binding of the copper atom. Short metal–nitrogen bonds induce this angular strain.

The three pyridyl rings of tptz show no significant deviation from planarity. Nevertheless, the central triazine ring shows some significant deviations from planarity [N(3) and C(10) are 0.041 and 0.037 Å below and above the mean plane respectively] adopting a chair conformation. The non-co-ordinated pyridyl ring of tptz forms an angle of 10.7° with the main plane containing the triazine ring and the two co-ordinated pyridyl rings. The dihedral angle between this last plane and the one containing the bis(2-pyridylcarbonyl)amidocopper(II) unit is 88.7°.

The shortest Cu $\cdots$ Cu$^{\mathrm{II}}$ distance is 7.563(2) Å where II refers to the equivalent position $-x, -y, -z$ relative to the reference molecule at $x,y,z$.

*Infrared, Electronic, and E.S.R. Spectra.*—The strong band at 1 710 cm$^{-1}$ present in the i.r. spectrum of both complexes, which corresponds to an imide group, is diagnostic of the presence of the bis(2-pyridylcarbonyl)amido ligand in such compounds. The i.r. spectrum of complex (**1**) displays bands of

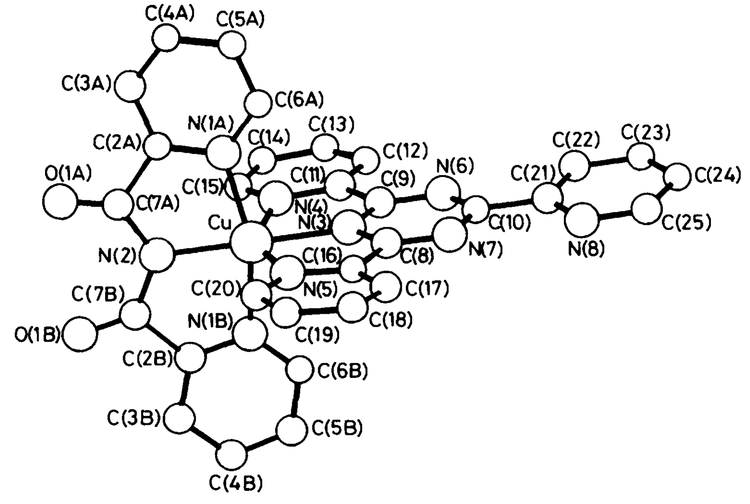


**Figure 2.** View of the structure of complex (**2**) with the atom-numbering scheme. Hydrogen atoms and the $CF_3SO_3^-$ group are not included

**Table 5.** Bond distances (Å) and angles (°) for non-hydrogen atoms of complex (**2**)

Copper environment

| | | | |
|---|---|---|---|
| Cu–N(1A) | 2.047(8) | Cu–N(3) | 2.052(7) |
| Cu–N(1B) | 2.055(8) | Cu–N(4) | 2.369(9) |
| Cu–N(2) | 1.956(6) | Cu–N(5) | 2.379(10) |
| N(1A)–Cu–N(2) | 81.5(3) | N(1B)–Cu–N(2) | 81.3(3) |
| N(1A)–Cu–N(3) | 98.8(3) | N(1B)–Cu–N(3) | 98.4(3) |
| N(1A)–Cu–N(4) | 92.5(3) | N(1B)–Cu–N(4) | 91.7(3) |
| N(1A)–Cu–N(5) | 91.1(3) | N(1B)–Cu–N(5) | 94.2(3) |
| N(1A)–Cu–N(1B) | 162.8(3) | | |
| N(2)–Cu–N(3) | 179.6(2) | N(4)–Cu–N(5) | 147.9(2) |
| N(2)–Cu–N(4) | 105.8(3) | N(2)–Cu–N(5) | 106.2(3) |
| N(3)–Cu–N(4) | 74.4(3) | N(3)–Cu–N(5) | 73.6(3) |

Bis(2-pyridylcarbonyl)amido ligand

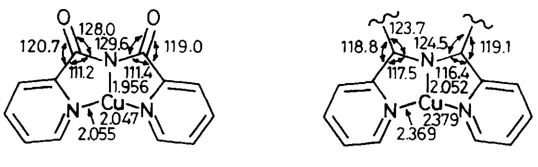
| | | | |
|---|---|---|---|
| N(1A)–C(2A) | 1.358(11) | N(1B)–C(2B) | 1.337(12) |
| C(2A)–C(3A) | 1.383(14) | C(2B)–C(3B) | 1.385(17) |
| C(3A)–C(4A) | 1.347(18) | C(3B)–C(4B) | 1.368(16) |
| C(4A)–C(5A) | 1.364(16) | C(4B)–C(5B) | 1.361(20) |
| C(5A)–C(6A) | 1.386(15) | C(5B)–C(6B) | 1.378(18) |
| C(6A)–N(1A) | 1.336(14) | C(6B)–N(1B) | 1.337(12) |
| C(2A)–C(7A) | 1.523(15) | C(2B)–C(7B) | 1.500(13) |
| C(7A)–O(1A) | 1.214(10) | C(7B)–O(1B) | 1.227(11) |
| C(7A)–N(2) | 1.359(12) | C(7B)–N(2) | 1.380(14) |
| Cu–N(1A)–C(2A) | 112.4(7) | Cu–N(1B)–C(2B) | 112.5(6) |
| N(1A)–C(2A)–C(3A) | 121.0(10) | N(1B)–C(2B)–C(3B) | 120.8(9) |
| C(2A)–C(3A)–C(4A) | 120.9(9) | C(2B)–C(3B)–C(4B) | 119.0(11) |
| C(3A)–C(4A)–C(5A) | 118.9(11) | C(3B)–C(4B)–C(5B) | 120.1(13) |
| C(4A)–C(5A)–C(6A) | 118.4(11) | C(4B)–C(5B)–C(6B) | 118.7(10) |
| C(5A)–C(6A)–N(1A) | 123.7(7) | C(5B)–C(6B)–N(1B) | 121.6(10) |
| C(6A)–N(1A)–Cu | 130.6(6) | C(6B)–N(1B)–Cu | 127.7(7) |
| C(6A)–N(1A)–C(2A) | 116.8(8) | C(6B)–N(1B)–C(2B) | 119.7(9) |
| N(1A)–C(2A)–C(7A) | 115.9(8) | N(1B)–C(2B)–C(7B) | 117.3(9) |
| C(2A)–C(7A)–O(1A) | 119.0(9) | C(2B)–C(7B)–O(1B) | 120.7(10) |
| C(2A)–C(7A)–N(2) | 111.4(7) | C(2B)–C(7B)–N(2) | 111.2(8) |
| O(1A)–C(7A)–N(2) | 129.6(10) | O(1B)–C(7B)–N(2) | 128.0(9) |
| C(7A)–N(2)–Cu | 118.2(6) | C(7B)–N(2)–Cu | 117.6(6) |
| C(7A)–N(2)–C(7B) | 124.1(7) | | |

2,4,6-Tris(2-pyridyl)-1,3,5-triazine ligand

| | | | |
|---|---|---|---|
| N(3)–C(9) | 1.355(13) | N(3)–C(8) | 1.346(13) |
| C(9)–C(11) | 1.484(14) | C(8)–C(16) | 1.483(15) |
| C(11)–C(12) | 1.360(17) | C(16)–C(17) | 1.372(17) |
| C(12)–C(13) | 1.371(19) | C(17)–C(18) | 1.370(21) |
| C(13)–C(14) | 1.346(15) | C(18)–C(19) | 1.391(17) |
| C(14)–C(15) | 1.403(18) | C(19)–C(20) | 1.359(20) |
| C(15)–N(4) | 1.317(14) | C(20)–N(5) | 1.323(15) |
| N(4)–C(11) | 1.359(11) | N(5)–C(16) | 1.361(11) |
| C(9)–N(6) | 1.320(11) | C(8)–N(7) | 1.321(11) |
| N(6)–C(10) | 1.322(15) | N(7)–C(10) | 1.354(15) |
| C(10)–C(21) | 1.496(13) | | |
| C(21)–C(22) | 1.385(17) | C(21)–N(8) | 1.290(16) |
| C(22)–C(23) | 1.399(14) | N(8)–C(25) | 1.329(16) |
| C(23)–C(24) | 1.345(22) | C(25)–C(24) | 1.367(20) |
| Cu–N(3)–C(9) | 121.4(6) | Cu–N(3)–C(8) | 122.9(7) |
| N(3)–C(9)–C(11) | 117.5(7) | N(3)–C(8)–C(16) | 116.4(7) |
| C(9)–C(11)–C(12) | 122.0(8) | C(8)–C(16)–C(17) | 122.2(8) |
| C(11)–C(12)–C(13) | 117.9(9) | C(16)–C(17)–C(18) | 119.1(10) |
| C(12)–C(13)–C(14) | 120.4(13) | C(17)–C(18)–C(19) | 118.4(14) |
| C(13)–C(14)–C(15) | 119.2(12) | C(18)–C(19)–C(20) | 119.3(13) |
| C(14)–C(15)–N(4) | 121.2(9) | C(19)–C(20)–N(5) | 123.2(9) |
| C(15)–N(4)–Cu | 130.0(6) | C(20)–C(5)–Cu | 130.8(6) |
| C(15)–N(4)–C(11) | 118.3(9) | C(20)–N(5)–C(16) | 117.7(10) |
| N(4)–C(11)–C(12) | 123.0(9) | N(5)–C(16)–C(17) | 122.3(10) |
| N(4)–C(11)–C(9) | 115.0(9) | N(5)–C(16)–C(8) | 115.5(9) |
| C(11)–C(9)–N(6) | 118.8(9) | C(16)–C(8)–N(7) | 119.1(9) |
| N(3)–C(9)–N(6) | 123.7(9) | N(3)–C(8)–N(7) | 124.5(10) |
| C(9)–N(6)–C(10) | 115.8(9) | C(8)–N(7)–C(10) | 114.8(9) |
| N(6)–C(10)–N(7) | 125.5(8) | | |
| N(6)–C(10)–C(21) | 116.5(10) | N(7)–C(10)–C(21) | 118.0(10) |
| C(10)–C(21)–C(22) | 118.9(10) | C(10)–C(21)–N(8) | 118.1(10) |
| C(22)–C(21)–N(8) | 123.0(9) | | |
| C(21)–C(22)–C(23) | 117.0(12) | C(21)–N(8)–C(25) | 118.7(11) |
| C(22)–C(23)–C(24) | 120.1(12) | N(8)–C(25)–C(24) | 123.3(12) |
| C(23)–C(24)–C(25) | 117.9(10) | | |

co-ordinated pyridine-2-carboxamide (3 410m, 3 195w, 1 660s, and 1 590w cm$^{-1}$) whereas strong bands centred at 1 520 and 1 560 cm$^{-1}$ present in the i.r. spectrum of complex (**2**) correspond to the co-ordinated tptz ligand. Strong bands at 1 270, 1 250, 1 170, 1 150, 1 040, 640, and 630 cm$^{-1}$ in the i.r. spectra of both complexes are due to the triflate groups.

The reflectance electronic spectra of both complexes show relevant differences: complex (**1**) displays a shoulder at 770 nm



C D

**Figure 3.** Schematic drawing showing the relevant structural features exhibited by [bis(2-pyridylcarbonyl)amido]copper(II) (C) and [2,4,6-tris(2-pyridyl)-1,3,5-triazine]copper(II) (D) fragments of complex (**2**)

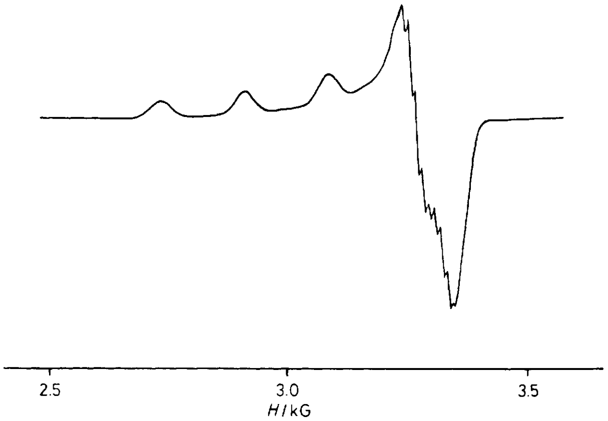


**Figure 4.** E.s.r. spectrum of complex (**2**) in nitromethane at 100 K

and two maxima centred at 600 and 420 nm, the former showing a greater intensity than the latter; (**2**) also exhibits two maxima but centred at 1 120 and 640 nm. In this case, the first one is very broad and less intense than the second one. Intense charge-transfer bands are observed below 370 and 420 nm for complexes (**1**) and (**2**) respectively. These spectral features are related to the presence of two different chromophores around copper(II), $CuN_4O_2$ and $CuN_6$ for complexes (**1**) and (**2**). The absorptions exhibited by complex (**2**) are in accord with those reported for $Cu(terpy)_2X_2$ (terpy = 2,2′:6′,2″-terpyridyl) by Reinen and co-workers.[25,26] Highly distorted octahedral $CuN_6$ chromophores are present in such compounds. The band at 1 120 nm can be assigned to the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition whereas the band at 640 nm would correspond to the overlap of $d_{xy} \longrightarrow d_{x^2-y^2}$ and $d_{xz}d_{yz} \longrightarrow d_{x^2-y^2}$. For complex (**1**) the weaker interaction with the axial $CF_3SO_3^-$ ligand stabilizes the $d_{z^2}$ orbital resulting in a more energetic $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition (770 nm) and in the resolution of the $d_{xy} \longrightarrow d_{x^2-y^2}$ and $d_{xz}d_{yz} \longrightarrow d_{x^2-y^2}$ transition into two separate absorption bands.

*X*-Band e.s.r. spectra of both complexes recorded on micro-crystalline powders at room temperature show sites of axial symmetry around copper(II) with $g_{\parallel} = 2.23$ and $g_{\perp} = 2.06$ for (**1**) and $g_{\parallel} = 2.25$ and $g_{\perp} = 2.06$ for (**2**). These values point toward a mainly copper(II) $d_{x^2-y^2}$ ground-state electron configuration, a result which is fully in accord with their structures. In addition a weak half-field transition is observed in both spectra which is generally associated with the $\Delta M_s = 2$ forbidden transition in binuclear copper(II) complexes. However this interpretation is not valid in the structurally characterized mononuclear complexes (**1**) and (**2**).[27] This transition could arise from dipolar interactions between copper(II) ions of different mononuclear units. The e.s.r. spectrum of complex (**1**) does not show any significant variation in the temperature range studied (from room temperature to 100 K) whereas a splitting of the parallel component of complex (**2**) appears when cooling down. We have recorded the e.s.r. spectra of samples of (**2**) dissolved in nitromethane and Figure 4 shows the well resolved spectrum obtained at 100 K. This spectrum is characterized by $g_{\parallel} = 2.24$ and $g_{\perp} = 2.04$ with hyperfine couplings on the parallel and perpendicular components respectively. The value of $A_{\parallel}(Cu)$ (170 G) is easily inferred from the uniform signal splitting of three peaks (four peaks were expected) which arise from the hyperfine coupling with the copper nucleus ($I = \frac{3}{2}$). The parallel component is split into nine peaks because of superhyperfine coupling with the nucleus of the four equatorial nitrogen atoms [$A_{\perp}(N) = 12$ G]. The $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}(Cu)$ values are consistent with those expected for a $CuN_6$ elongated tetragonal octahedron and the $A_{\perp}(N)$ value lies within the range of those previously observed.[28]

*Hydrolysis Reaction of tptz.*—The ion $Cu^{2+}_{(aq.)}$ promotes the partial hydrolysis of tptz, leading to the formation of bis(2-pyridylcarbonyl)amido anions which remain co-ordinated to the metal ion, and free pyridine-2-carboxamide. The main species in solution is the complex $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_3]^+$ which has been isolated as a nitrate salt.[9,10] The complex $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]^+$, which contains the two fragments resulting from the $Cu^{II}$-assisted hydrolysis of tptz, has been isolated as a perchlorate or trifluoromethanesulphonate salt. In the case of perchlorate, a compound of formula $[Cu\{(NC_5H_4CO)_2N\}]ClO_4$ in which the bis(2-pyridylcarbonyl)amide acts as a bridging ligand has also been isolated and characterized.[11]

Our results clearly show that this hydrolysis reaction has a 1:1 $Cu^{II}$:tptz molar ratio. Each copper(II) ion binds and hydrolyses one tptz molecule. Once the bis(2-pyridylcarbonyl)-amide is bound to copper(II) the metal ion loses its ability to promote the hydrolysis of any more tptz. When an excess of tptz is present in solution it binds unaltered to the metal ion yielding a stable green complex that we have isolated as $[Cu\{(NC_5H_4CO)_2N\}(tptz)][CF_3SO_3]$ (**2**) and characterized by *X*-ray diffraction. This compound is very interesting because, as far as we are aware, it is the first copper(II) complex with a tptz ligand whose structure has been determined. Structural parameters of $(NC_5H_4CO)_2N^-$ and tptz as ligands are compared in Figure 3. Both ligands are tridentate but whereas the former is bound to the metal ion through three short copper–nitrogen bonds the latter has only one short and two longer copper–nitrogen bonds. Significant differences in bond angles are associated with these different bond lengths: the angles at the carbonyl-carbon atoms inside the chelate ring of the bis(2-pyridylcarbonyl)amido ligand are about 110°, whereas the corresponding angles in tptz are greater and closer to the ideal value of 120°. Thus the molecular structure of (**2**) affords definitive evidence of how copper(II) ion promotes the hydrolysis of tptz supporting Lippard's suggestion.[10] Co-ordination of tptz to the metal ion induces an angular strain allowing the nucleophilic attack by the solvent.

If the copper–nitrogen (pyridyl ring) bond distances increase the strain decreases and the hydrolysis reaction does not occur. Apparently, the Jahn–Teller effect is the cause of the asymmetric co-ordination of the tptz molecule.

Therefore, compound (**2**) exemplifies also the required condition for synthesis of $Cu^{II}$–tptz complexes which are stable towards hydrolysis. Copper(II) ion should be previously bound to a strong ligand preventing the formation of three short bonds with tptz. A strong bidentate ligand may be sufficient, if it is not displaced by tptz, but a tridentate ligand such as terpy would be more effective. Indeed, addition of tptz to a water–ethanol solution of $[Cu(terpy)]^{2+}$ leads to a green solution whose colour does not change on heating, evidencing the formation of the mixed-ligand complex $[Cu(terpy)(tptz)]^{2+}$.

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