Copper(II)-assisted Hydrolysis of 2,4,6-Tris(2-pyridyl)-1,3,5-triazine. Part 1. Crystal Structures of [bis(2-pyridylcarbonyl)amido](2-pyridylformamide)-copper(II) Perchlorate Monohydrate and [Bis(2-pyridylcarbonyl)amido]-copper(II) Perchlorate†

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2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) undergoes hydrolysis in the presence of copper(II) nitrate yielding mainly [bis(2-pyridylcarbonyl)amido]copper(II) and free 2-picolinamide (2-pyridylformamide, $NC_5H_4CONH_2$). Two new compounds of formulae $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]ClO_4{\cdot}H_2O$ (**1**) and $[Cu\{(NC_5H_4CO)_2N\}]ClO_4$ (**2**), where $(NC_5H_4CO)_2N^-$ is the bis(2-pyridylcarbonyl)amido anion, have been obtained from aqueous solutions of tptz and copper(II) perchlorate. Crystals of (**1**) are monoclinic with a = 8.443(4), b = 27.145(12), c = 9.781(5) Å, β = 100.40(6)°, space group $P2_1/n$, and Z = 4. Crystals of (**2**) are tetragonal with $a = b$ = 8.071(5), c = 21.291(8) Å, space group $P4_1$, and Z = 4. The structure of (**1**) is made up of $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]^+$ mononuclear cations plus semi-co-ordinated perchlorate anions and water of crystallization. The copper(II) ion is in a distorted octahedral environment: the three nitrogen atoms of the $(NC_5H_4CO)_2N^-$ ligand and the pyridinic one of the 2-picolinamide form a distorted square plane around the copper while the axial positions are occupied by the oxygen atom of the picolinamide and by an oxygen atom of the perchlorate anion. The structure of (**2**) consists of bis(2-pyridylcarbonyl)amido-bridged copper(II) one-dimensional chains and non-co-ordinated perchlorate anions. The copper(II) ion has a co-ordination geometry which approximates to trigonal bipyramidal: the apices and one of the equatorial positions of the bipyramid are occupied by the two nitrogen atoms of the pyridine rings and the imine-nitrogen atom respectively, whereas the two other equatorial positions are filled by the two carbonyl-oxygen atoms of another bis(2-pyridylcarbonyl)amido ligand. The structure of (**1**) allows the nature of the two main products of the copper(II)-assisted hydrolysis of tptz to be established and the structure of (**2**) shows the ability of the bis(2-pyridylcarbonyl)amido anion to act as a bridging ligand with transition metal ions.

2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) first prepared by Case and Koft,[1] has been used in spectrophotometric determination of transition metal ions.[2–4] The possibility of this ligand to co-ordinate to metals through the terpyridine- or bipyridine-like moieties and using both terpyridine- and bipyridine-like sites simultaneously has been well characterized.[5–12] However, Lerner and Lippard[13,14] reported an interesting hydrolytic reaction which occurs with tptz and the chemically similar 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpmtz) in the presence of copper(II), which promotes the hydrolysis of these triazines yielding the [bis(arylcarbonyl)amido]copper(II) complexes and free 2-picolinamide (2-pyridylformamide). It has also been pointed out that other metal ions promote the hydrolysis of these 2,4,6-trisubstituted triazines.[13] It is interesting to note that although simple triazines are known to hydrolyze under mild conditions, 2,4,6-triaryltriazines such as tptz and tpmtz are usually stable towards hydrolysis; concentrated mineral acid and temperatures above 150 °C are required to achieve it.[15] Recently reported kinetic and thermodynamic data[16,17] show that the hydrolytic reaction to yield the carboximidate ligand could be viewed as taking place *via* nucleophilic attack at the triazine ring by OH^- or H_2O. Steric considerations have been suggested to be highly significant on the basis of the structural data obtained for triaqua[bis(2-pyrimidylcarbonyl)-amido]copper(II) nitrate dihydrate.[14]

In this paper we report the synthesis, structure, and spectral characterization of two new copper(II) complexes of formulae $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]ClO_4{\cdot}H_2O$ (**1**) and $[Cu\{(NC_5H_4CO)_2N\}]ClO_4$ (**2**). The structure of (**1**) is significant because the two main fragments resulting from the hydrolytic reaction, *i.e.* 2-picolinamide ($NC_5H_4CONH_2$) and the bis(pyridylcarbonyl)amido anion [$(NC_5H_4CO)_2N$], are present as ligands in the same complex. On the other hand, the bis-chelating character of the bis(2-pyridylcarbonyl)amido ligand is illustrated by the structure of (**2**) for the first time.

Experimental

Materials and Measurements.—The reagents tptz and $[Cu(H_2O)_6][ClO_4]_2$ were purchased from Merck and Janssen respectively and used as received. I.r. spectra were taken on a Pye-Unicam SP 200 spectrometer as KBr pellets; the diffuse

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

reflectance and u.v.–visible spectra were recorded with a Pye-Unicam SP 100-8 spectrophotometer. *X*-Band e.s.r. spectra were recorded, both at room temperature and at 7 K, with a Brüker ER spectrometer equipped with a helium continuous-flow cryostat.

Synthesis.—A green coloured suspension was obtained by adding an aqueous solution of $[Cu(H_2O)_6][ClO_4]_2$ (0.370 g, 1 mmol) to an aqueous suspension of tptz (0.313 g, 1 mmol). Heating at 100 °C with stirring for 30 min yielded a dark blue solution. Evaporation of solvent at room temperature produced plate-shaped dark blue crystals and blue needles of (**1**) and (**2**) respectively [Found: C, 40.4; H, 3.15; Cl, 6.75; Cu, 11.9; N, 12.4. Calc. for $C_{18}H_{16}ClCuN_5O_8$, (**1**): C, 40.85; H, 3.05; Cl, 6.70; Cu, 12.0; N, 13.2%. Found: C, 37.3; H, 2.10; Cl, 9.35; Cu, 16.3; N, 10.6. Calc. for $C_{12}H_8ClCuN_3O_2$, (**2**): C, 37.05; H, 2.05; Cl, 9.10; Cu, 16.35; N, 10.8%].

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

Compound	(**1**)	(**2**)
Formula	$C_{18}H_{16}ClCuN_5O_8$	$C_{12}H_8ClCuN_3O_6$
M	511.36	389.11
Space group	$P2_1/n$	$P4_1$
a/Å	8.443(4)	8.071(5)
b/Å	27.145(12)	8.071(5)
c/Å	9.781(5)	21.291(8)
β/°	100.40(6)	90
U/Å^3	2 205(3)	1 387.0(1)
Z	4	4
D_c/g cm^{-3}	1.54	1.86
D_m/g cm^{-3}	1.53[a]	1.84[a]
F(000)	932	888
Crystal size (mm)	0.5 × 0.2 × 0.5	0.5 × 0.5 × 0.2
μ(Mo-K_α)/cm^{-1}	10.80	17.49
Max., min. transmission factors	0.80, 0.58	0.70, 0.42
Standard reflections	800, 040, 004	008, 040, 400
Reflections collected	3 835	1 464
Independent reflections[b]	3 167	1 261
No. of parameters refined	354	239
$R\ (=\Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert)$	0.0549	0.0509
$R'(=[\Sigma w\lVert F_o\rvert - \lvert F_c\rVert^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}})$	0.0576[c]	0.0509[d]

[a] Measured by flotation in n-C_6H_{14}–$BrCH_2CH_2Br$. [b] $I > 2.5\ \sigma(I)$ for (**1**); $I > 1.5\sigma(I)$ for (**2**). [c] Weighting scheme $w = 1/[\sigma^2|F_o| + 0.000\,51|F_o|^2]$. [d] Unit weights.

Collection of Diffraction Data.—Diffraction data were collected at 293 K with a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 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 ($00l; l = 4n$) for (**2**) which uniquely define monoclinic space group $P2_1/n$ for the former and tetragonal space groups $P4_1$ and $P4_3$ for the latter. The intensities of three standard reflections measured every 50 reflections showed no significant variations. Intensity data were collected by the θ–2θ scan technique in the 2θ range 4—50°. Lorentz and polarization corrections were applied, but not for absorption. Independent reflections with $I > 2.5\sigma(I)$ for (**1**) and $I > 1.5\sigma(I)$ 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.[18] Full-matrix least-squares refinement with the SHELX 76 system[19] 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. A water hydrogen atom was placed at a calculated position with an O–H distance of 1.0 Å, but it could not be well refined and was therefore excluded. For (**2**), space groups $P4_1$ and $P4_3$ were probable; we refined the structure in both space groups with the same number of parameters and reflections. As the *R* values obtained are 0.0509 and 0.0547 for $P4_1$ and $P4_3$ respectively, the former was chosen. The crystal data are listed in Table 1.

Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 20. The final difference-Fourier map showed residual maxima and minima of 1.42 and −0.64 e Å^{-3} for (**1**) and 0.54 and −0.97 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 H-bonding distances for (**1**).

Results and Discussion

Molecular Structure of (**1**).—Figure 1 shows a perspective drawing of complex (**1**) with the atom-numbering scheme. The

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

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.782 3(1)	0.108 9(0)	0.467 7(1)	O(2)	0.872 4(4)	0.048 9(1)	0.331 7(3)
O(1A)	1.021 7(4)	0.075 6(1)	0.850 4(3)	N(2)	0.823 4(4)	0.082 5(1)	0.653 9(4)
N(1A)	1.004 6(5)	0.137 5(1)	0.529 1(4)	N(3)	0.736 6(4)	0.137 4(1)	0.275 9(4)
C(2A)	1.070 2(6)	0.124 4(2)	0.660 4(5)	N(4)	0.878 7(7)	0.032 9(2)	0.107 6(5)
C(3A)	1.220 2(7)	0.140 9(2)	0.725 3(6)	C(8)	0.776 8(6)	0.112 6 (2)	0.170 3(4)
C(4A)	1.305 8(8)	0.170 7(3)	0.649 8(8)	C(9)	0.755 3(8)	0.131 6(2)	0.038 9(6)
C(5A)	1.240 6(7)	0.183 1(2)	0.515 1(7)	C(10)	0.685 9(10)	0.177 1(3)	0.013 1(7)
C(6A)	1.089 7(6)	0.165 9(2)	0.458 6(6)	C(11)	0.637 3(7)	0.202 7(2)	0.120 5(6)
C(7A)	0.968 5(6)	0.091 4(2)	0.733 4(5)	C(12)	0.667 0(7)	0.181 6(2)	0.250 1(6)
O(1B)	0.703 4(5)	0.039 8(2)	0.813 1(4)	C(13)	0.847 2(6)	0.062 1(2)	0.209 4(5)
N(1B)	0.560 6(4)	0.081 9(1)	0.470 7(4)	Cl(1)	0.224 1(2)	0.264 7(1)	0.137 7(2)
C(2B)	0.549 1(6)	0.059 7(2)	0.592 0(5)	O(3)	0.164 2(6)	0.311 5(2)	0.086 0(6)
C(3B)	0.407 6(6)	0.038 5(2)	0.615 2(6)	O(4)	0.264 2(8)	0.236 9(2)	0.027 4(6)
C(4B)	0.272 9(7)	0.039 8(2)	0.509 5(7)	O(5)	0.105 7(7)	0.241 5(2)	0.201 6(7)
C(5B)	0.285 4(6)	0.062 1(2)	0.385 8(6)	O(6)	0.364 0(7)	0.271 2(3)	0.238 9(6)
C(6B)	0.430 6(6)	0.082 9(2)	0.371 0(6)	O(w1)	0.197 3(11)	0.126 0(3)	0.102 8(9)
C(7B)	0.700 8(6)	0.059 2(2)	0.700 6(5)				

Table 3. Final atomic co-ordinates with estimated standard deviations in parentheses for (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.969 4(1)	−0.010 5(2)	0.262 1(0)
O(1B)	1.143 0(8)	0.082 7(9)	0.334 5(3)
N(1B)	1.074 5(1)	−0.231 4(10)	0.248 1(4)
C(5B)	1.196 3(14)	−0.494 9(14)	0.273 8(6)
C(2B)	1.110 6(11)	−0.259 0(11)	0.186 2(5)
C(7A)	0.860 5(11)	−0.070 2(10)	0.394 1(4)
C(4B)	1.231 0(14)	−0.521 5(13)	0.209 6(7)
C(7B)	1.126 5(11)	0.062 8(10)	0.390 9(5)
N(1A)	0.869 8(9)	0.215 9(10)	0.251 8(3)
O(1A)	0.832 4(8)	−0.085 8(10)	0.337 5(3)
C(2A)	0.862 0(12)	0.261 3(10)	0.190 9(4)
C(6B)	1.117 7(15)	−0.345 6(15)	0.289 7(6)
N(2)	0.998 5(8)	0.008 2(8)	0.171 7(3)
C(4A)	0.728 9(15)	0.515 6(13)	0.218 2(7)
C(3A)	0.789 9(14)	0.410 0(14)	0.170 9(6)
C(3B)	1.185 5(14)	−0.404 1(14)	0.166 0(6)
C(5A)	0.740 9(16)	0.468 9(16)	0.279 2(6)
C(6A)	0.813 8(15)	0.315 4(15)	0.295 2(6)
Cl(1)	0.504 4(3)	0.023 7(3)	0.723 8(1)
O(2)	0.554 3(10)	0.150 0(13)	0.766 0(5)
O(3)	0.493 5(12)	−0.129 6(14)	0.757 3(7)
O(4)	0.341 9(9)	0.061 9(10)	0.698 7(4)
O(5)	0.618 7(13)	0.015 0(17)	0.672 6(6)

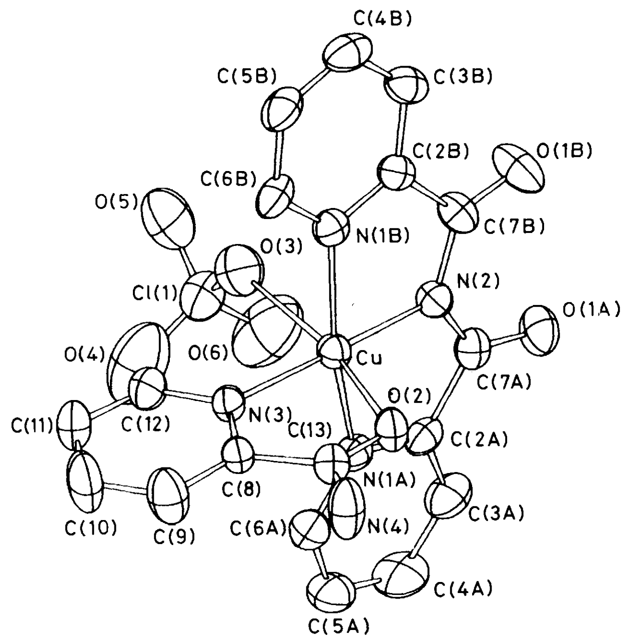


Figure 1. ORTEP drawing of complex (**1**) showing 50% probability ellipsoids. Hydrogen atoms and water molecule are omitted

geometry around the copper(II) ion can be described as a distorted octahedron. Selected bond distances and angles are given in Table 4. By comparing the geometries of the A and B halves of the bis(2-pyridylcarbonyl)amido ligand it is inferred that an approximate mirror plane passes through atoms Cu, N(3), O(2), O(3), and N(2). The basal plane is formed by four nitrogen atoms, N(2), N(1A), N(3), and N(1B), which are co-ordinated to copper(II) [Cu–N 1.931(4), 2.018(4), 2.001(4), and 2.017(4) Å respectively]. The axial positions are occupied by O(2) (the oxygen atom of the 2-picolinamide) and O(3) (one oxygen atom of the perchlorate group) with Cu–O distances of 2.316(3) and 2.726(25) Å respectively. The angle N(3)–Cu–O(3) is 93.85(3)° whereas N(3)–Cu–O(2) is only 76.1(1)°.

The four nitrogen atoms that comprise the equatorial co-ordination sites of the copper atom show significant deviations from the mean plane through them. Atoms N(1A) and N(1B) are 0.065 Å above while atoms N(2) and N(3) are 0.075 and 0.055 Å below this plane. The copper atom lies 0.084 Å below this same plane. The angles N(1B)–Cu–N(2) and N(1A)–Cu–N(2) are 82.0(2) and 82.1(2)° respectively. Their deviations from the ideal value of 90° can be easily understood as these angles are part of a five-membered planar chelate ring. The individual pyridine rings of the bis(2-pyridylcarbonyl)amido ligand show no deviations from planarity greater than 0.0119 Å. However the ligand is not planar. Best-plane calculations through the ligand and copper show several atoms with quite large deviations: Cu, O(1A), C(7A), N(1A), N(2), N(1B), C(6B), and C(6A) atoms are 0.225, 0.099, 0.084, 0.137, 0.069, 0.035 and 0.034 Å below while C(4B), C(3B), C(5B), C(5A), C(3A), and C(4A) atoms are 0.149, 0.125, 0.059, 0.084, 0.139, and 0.182 Å above this plane. The ligand can be described by two halves A and B; the A half shows no deviations from planarity greater than 0.059 Å while the B half shows no deviations greater than 0.012 Å. The dihedral angle between these two planes is 8.6°. In the related complex triaqua[bis(2-pyrimidylcarbonyl)amido]-copper(II) nitrate dihydrate[14] this angle is 2.9°.

The 2-picolinamide ligand is co-ordinated to copper(II) *via* the nitrogen atom N(3) of the pyridine ring and the oxygen atom O(2) of the amide group, with bond distances of 2.001(4) and 2.316(3) Å respectively. The dihedral angle between the mean plane of the 2-picolinamide and copper atom and that comprising the bis(2-pyridylcarbonyl)amido ligand and copper atom is 87.9°.

The average carbon–carbon bond length within the pyridyl rings is 1.37 Å and the average intra-ring carbon–nitrogen distance is 1.34 Å. These values compare favourably with those reported for similar systems (see ref. 8 and refs. therein). The distances between the carbonyl-carbon atoms and their respective ring-carbon atom in the bis(2-pyridylcarbonyl)amido ligand are 1.509(7) and 1.513(7) Å. These values are close to those of the free picolinamide[21] [1.515(8) Å] and the bidentate picolinamide ligand in (**1**) [1.514(6) Å, see Table 4]. The angles around C(7A) are 120.1(5), 111.7(4), and 128.1(5)° for C(2A)–C(7A)–O(1A), C(2A)–C(7A)–N(2), and O(1A)–C(7A)–N(2) respectively. The corresponding angles around C(7B) are 120.9(4), 111.0(4), and 128.1(5)°. The deviations of these angles from the expected value of 120° which would correspond to the sp^2-hybridized carbonyl carbon atoms C(7A) and C(7B) are caused by the co-ordination of the copper(II) to the bis(2-pyridylcarbonyl)amido ligand. As it has been recently pointed out, the need for a short metal–nitrogen bond introduces this angular strain: the larger the metal–nitrogen distances are, the smaller the angular strain.[14,22,23] It has been suggested that the angular strain could be responsible for the copper-promoted hydrolysis reaction.[14]

The pyridine ring of the co-ordinated picolinamide is essentially planar as observed for the free picolinamide. This plane and the plane passing through the atoms Cu, O(2), C(13), C(8), and N(3) make an angle of 2.5° while in free picolinamide the angle between the plane of the pyridine ring and that of the amide group is 19°. The bidentate co-ordination of the 2-picolinamide to copper causes this remarkable decreasing of the twisting between the amide group and the pyridine ring.

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

Copper environment			
Cu–N(1A)	2.018(4)	Cu–N(3)	2.001(4)
Cu–N(2)	1.931(4)	Cu–O(2)	2.316(3)
Cu–N(1B)	2.017(4)	Cu–O(3)	2.726(25)
N(2)–Cu–N(1A)	82.1(2)	N(2)–Cu–N(1B)	82.0(2)
N(2)–Cu–N(3)	178.9(2)	N(2)–Cu–O(2)	104.9(1)
N(2)–Cu–O(3)	85.06(3)	N(3)–Cu–O(2)	76.1(1)
N(3)–Cu–N(1A)	98.2(2)	N(3)–Cu–N(1B)	97.6(2)
N(3)–Cu–O(3)	93.85(3)	N(1B)–Cu–N(1A)	162.0(2)
N(1A)–Cu–O(2)	93.3(1)	N(1B)–Cu–O(2)	98.8(1)
N(1A)–Cu–O(3)	87.65(3)	N(1B)–Cu–O(3)	82.58(2)
O(2)–Cu–O(3)	170.0(0)		
Bis(2-pyridylcarbonyl)amido ligand			
N(1A)–C(2A)	1.349(6)	N(1B)–C(2B)	1.352(6)
C(2A)–C(3A)	1.383(7)	C(2B)–C(3B)	1.377(7)
C(3A)–C(4A)	1.380(9)	C(3B)–C(4B)	1.393(8)
C(4A)–C(5A)	1.374(9)	C(4B)–C(5B)	1.374(8)
C(5A)–C(6A)	1.375(6)	C(5B)–C(6B)	1.388(7)
C(6A)–N(1A)	1.329(6)	C(6B)–N(1B)	1.336(6)
C(2A)–C(7A)	1.509(7)	C(2B)–C(7B)	1.513(7)
C(7A–O(1A)	1.230(6)	C(7B)–O(1B)	1.217(6)
C(7A)–N(2)	1.346(6)	C(7B)–N(2)	1.361(6)
Cu–N(1A)–C(2A)	112.5(3)	Cu–N(1B)–C(2B)	112.9(3)
Cu–N(1A)–C(6A)	129.0(4)	Cu–N(1B)–C(6B)	128.2(3)
C(2A)–N(1A)–C(6A)	118.5(4)	C(2B)–N(1B)–C(6B)	119.0(4)
N(1A)–C(2A)–C(7A)	115.7(4)	N(1B)–C(2B)–C(7B)	115.9(4)
N(1A)–C(2A)–C(3A)	122.3(5)	N(1B)–C(2B)–C(3B)	122.0(5)
C(7A)–C(2A)–C(3A)	121.9(5)	C(7B)–C(2B)–C(3B)	122.1(4)
C(2A)–C(3A)–C(4A)	118.0(6)	C(2B)–C(3B)–C(4B)	119.1(5)
C(3A)–C(4A)–C(5A)	119.8(6)	C(3B)–C(4B)–C(5B)	118.6(5)
C(4A)–C(5A)–C(6A)	118.8(6)	C(4B)–C(5B)–C(6B)	119.6(5)
C(5A)–C(6A)–N(1A)	122.6(6)	C(5B)–C(6B)–N(1B)	121.7(5)
C(2A)–C(7A)–O(1A)	120.1(5)	C(2B)–C(7B)–O(1B)	120.9(4)
C(2A)–C(7A)–N(2)	111.7(4)	C(2B)–C(7B)–N(2)	110.0(4)
O(1A)–C(7A)–N(2)	128.1(5)	O(1B)–C(7B)–N(2)	128.1(5)
Cu–N(2)–C(7A)	117.8(3)	Cu–N(2)–C(7B)	118.2(3)
2-Picolinamide ligand			
N(3)–C(8)	1.327(6)	C(12)–N(3)	1.340(6)
C(8)–C(9)	1.366(7)	C(8)–C(13)	1.514(6)
C(9)–C(10)	1.371(9)	C(13)–O(2)	1.229(5)
C(10)–C(11)	1.381(9)	C(13)–N(4)	1.336(6)
C(11)–C(12)	1.378(8)		
Cu–N(3)–C(8)	120.0(3)	C(9)–C(10)–C(11)	118.9(6)
Cu–N(3)–C(12)	121.7(3)	C(10)–C(11)–C(12)	117.9(6)
C(8)–N(3)–C(12)	118.3(4)	C(11)–C(12)–N(3)	123.1(5)
N(3)–C(8)–C(13)	114.0(4)	C(8)–C(13)–N(4)	118.0(4)
N(3)–C(8)–C(9)	122.0(5)	C(8)–C(13)–O(2)	120.0(4)
C(13)–C(8)–C(9)	124.0(5)	N(4)–C(13)–O(2)	122.0(5)
C(8)–C(9)–C(10)	119.8(6)	Cu–O(2)–C(13)	109.7(3)
Perchlorate anion			
Cl(1)–O(3)	1.424(5)	Cl(1)–O(5)	1.421(5)
Cl(1)–O(4)	1.408(6)	Cl(1)–O(6)	1.408(6)
O(4)–Cl(1)–O(3)	108.9(4)	O(6)–Cl(1)–O(3)	109.6(4)
O(5)–Cl(1)–O(3)	108.6(3)	O(6)–Cl(1)–O(4)	108.6(4)
O(5)–Cl(1)–O(4)	112.5(4)	O(6)–Cl(1)–O(5)	108.6(4)

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

Copper environment			
Cu–N(1A)	2.009(9)	Cu–O(1A)	2.042(7)
Cu–N(2)	1.944(7)	Cu–O(1B)	2.215(7)
Cu–N(1B)	1.998(9)		
N(2)–Cu–N(1A)	82.5(3)	N(2)–Cu–N(1B)	82.5(3)
N(1A)–Cu–O(1A)	98.1(3)	N(1B)–Cu–O(1A)	94.7(3)
N(1A)–Cu–O(1B)	91.2(3)	N(1B)–Cu–O(1B)	97.9(3)
N(2)–Cu–O(1B)	125.9(3)	O(1A)–Cu–O(1B)	84.1(3)
N(2)–Cu–O(1A)	150.1(3)	N(1B)–Cu–N(1A)	165.0(3)
Bis(2-pyridylcarbonyl)amido ligand			
N(1A)–C(2A)	1.348(12)	N(1B)–C(2B)	1.368(13)
C(2A)–C(3A)	1.400(15)	C(2B)–C(3B)	1.386(16)
C(3A)–C(4A)	1.408(17)	C(3B)–C(4B)	1.377(17)
C(4A)–C(5A)	1.356(20)	C(4B)–C(5B)	1.413(20)
C(5A)–C(6A)	1.413(18)	C(5B)–C(6B)	1.403(18)
C(6A)–N(1A)	1.305(14)	C(6B)–N(1B)	1.324(14)
C(2A)–C(7A′)	1.503(15)	C(2B)–C(7B′)	1.490(16)
C(7A)–O(1A)	1.234(12)	C(7B)–O(1B)	1.219(13)
C(7A′)–N(2)	1.332(15)	C(7B)–N(2′)	1.372(16)
Cu–O(1A)–C(7A)	129.7(6)	Cu–O(1B)–C(7B)	124.9(6)
Cu–N(1A)–C(2A)	111.8(6)	Cu–N(1B)–C(2B)	112.3(6)
Cu–N(1A)–C(6A)	128.4(8)	Cu–N(1B)–C(6B)	129.3(8)
C(2A)–N(1A)–C(6A)	119.8(10)	C(2B)–N(1B)–C(6B)	118.4(10)
N(1A)–C(2A)–C(7A′)	116.2(10)	N(1B)–C(2B)–C(7B′)	116.9(10)
N(1A)–C(2A)–C(3A)	123.1(9)	N(1B)–C(2B)–C(3B)	121.9(10)
C(7A′)–C(2A)–C(3A)	120.7(10)	C(7B′)–C(2B)–C(3B)	121.2(10)
C(2A)–C(3A)–C(4A)	116.5(12)	C(2B)–C(3B)–C(4B)	119.2(12)
C(3A)–C(4A)–C(5A)	119.5(11)	C(3B)–C(4B)–C(5B)	119.7(11)
C(4A)–C(5A)–C(6A)	120.3(12)	C(4B)–C(5B)–C(6B)	116.9(11)
C(5A)–C(6A)–N(1A)	120.8(13)	C(5B)–C(6B)–N(1B)	123.8(12)
C(2A)–C(7A′)–O(1A′)	119.4(10)	C(2B)–C(7B′)–O(1B′)	121.6(10)
O(2A)–C(7A′)–N(2)	112.3(10)	C(2B)–C(7B′)–N(2)	110.9(10)
O(1A′)–C(7A′)–N(2)	128.3(10)	O(1B′)–C(7B′)–N(2)	127.4(10)
Cu–N(2)–C(7A′)	116.6(10)	Cu–N(2)–C(7B′)	117.2(10)
Perchlorate anion			
Cl(1)–O(2)	1.417(10)	Cl(1)–O(4)	1.449(8)
Cl(1)–O(3)	1.430(11)	Cl(1)–O(5)	1.431(10)
O(3)–Cl(1)–O(2)	108.9(8)	O(3)–Cl(1)–O(5)	112.2(9)
O(5)–Cl(1)–O(2)	109.6(6)	O(3)–Cl(1)–O(4)	108.2(5)
O(4)–Cl(1)–O(2)	109.7(6)	O(4)–Cl(1)–O(5)	108.2(7)

* Primes denote atoms at position 1 + *x*, 1 + *y*, *z* − 1.

The geometry of the perchlorate group is as expected. The bond lengths are all within 0.016 Å and the angles are very close to tetrahedral except for O(5)–Cl(1)–O(4) which is 112.5(4)°.

The shortest Cu(1) ··· Cu^i distance is 6.930(4) Å where i refers to the equivalent position 1 − *x*, −*y*, 1 − *z* relative to the reference molecule at *x*, *y*, *z*. The packing of the molecules is shown in Figure 2.

The structural characterization of complex **(1)** by *X*-ray diffraction reveals that the structure of this bis(2-pyridylcarbonyl)amido complex is very similar to that of the corresponding bis(2-pyrimidylcarbonyl)amido complex[14] (Figure 3). The three copper–nitrogen bond lengths are practically identical in both structures. The binding of these ligands to the copper atom in a tridentate fashion causes relevant angular strain, as can be seen in the deviations of the angles at the sp^2-hybridized carbonyl-carbon atoms C(7A) and C(7B) from the expected value of 120°. Angles are also very similar in both complexes and although both ligands are nearly planar, the planarity is more rigorous for the pyrimidyl derivative (see above).

Molecular Structure of **(2)**.—A partial ORTEP drawing of complex **(2)** is depicted in Figure 4 and a projection of the chain packing along the *a* axis is shown in Figure 5. The geometry

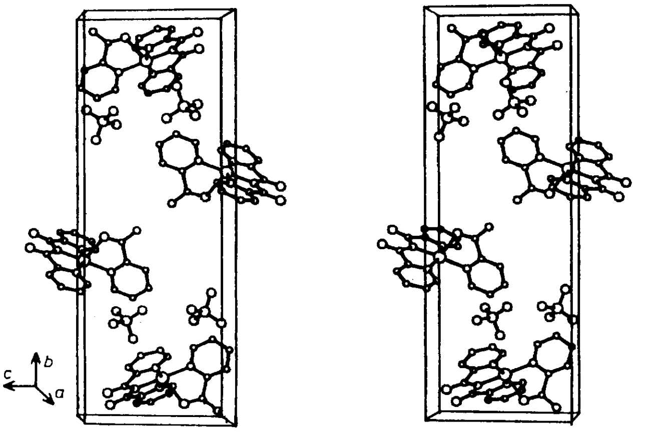


Figure 2. Stereoscopic view of the unit cell of complex (**1**) down the *a* axis

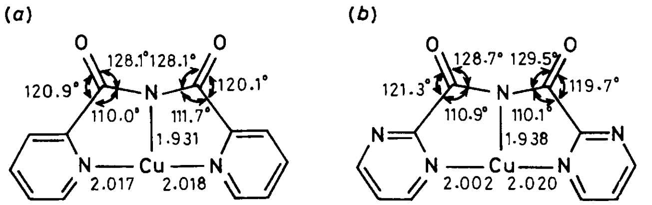


Figure 3. Schematic drawings of [bis(2-arylcarbonyl)amido]copper(II) fragments (distances in Å): (*a*) $[Cu\{(NC_5H_4CO)_2N\}]^+$, (*b*) $[Cu\{(N_2C_4H_3CO)_2N\}]^+$

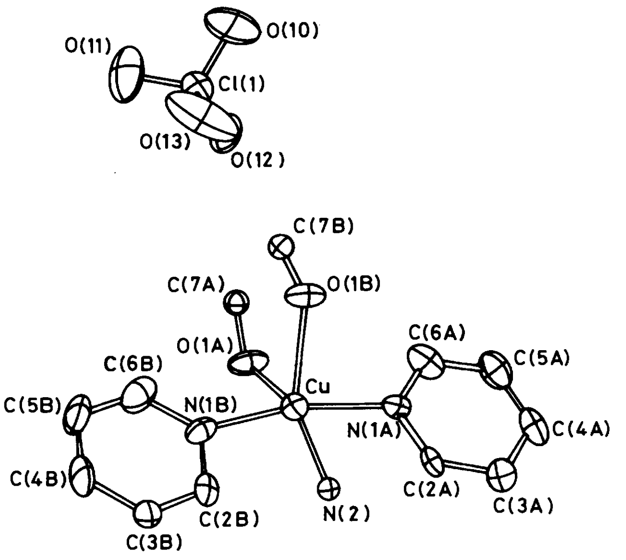


Figure 4. ORTEP drawing of the copper(II) environment in complex (**2**) with the atom-numbering scheme. Thermal ellipsoids are plotted at the 50% probability level, and hydrogen atoms are not included

around the copper atom is best described as a distorted trigonal bipyramid. The trigonal plane is formed by atoms O(1A), O(1B), and N(2) and the trigonal axis lies along the N(1A)–Cu–N(1B) bond. Bond distances and angles are listed in Table 5.

Valency angles at the copper atom show significant distortion from an ideal trigonal-bipyramidal arrangement. One of the three angles subtended at the copper atom by adjacent equatorial atoms is smaller than the ideal value of 120° [84.1(3)° for O(1A)–Cu–O(1B)], while the other two are larger [125.9(3) and 150.1(3)° for N(2)–Cu–O(1B) and N(2)–Cu–O(1A)]. The range of the equatorial to axial angles is 82.5(3)—97.9(3)°; the interaxial angle is reduced from a theoretical 180 to 165.0(3)°.

The copper atom lies 0.006 Å above the equatorial plane defined by the O(1A), O(1B), and N(2) set of atoms in the direction of the N(1B) atom.

With regard to the bond lengths around the copper atom, the two axial distances are practically identical [2.009(9) and 1.998(9) Å for Cu–N(1A) and Cu–N(1B)], while the equatorial distances are significantly different [1.944(7), 2.042(7), and 2.215(7) Å for Cu–N(2), Cu–O(1A), and Cu–O(1B)].

The individual pyridine rings of the bis(2-pyridylcarbonyl)amido ligand show no deviations from planarity greater than 0.011 Å. Best-plane calculations through the ligand show few atoms with large deviations: O(1B′), C(2B), C(7A), C(4B), C(7B), N(1A), C(2A), N(2), C(3B), C(5A), and C(6A) atoms are 0.027, 0.010, 0.001, 0.018, 0.041, 0.024, 0.015, 0.096, 0.015, 0.013, and 0.040 Å above while Cu, N(1B), C(5B), O(1A′), C(6B), C(4A), and C(3A) atoms are 0.018, 0.041, 0.027, 0.116, 0.052, 0.022, and 0.029 Å below this plane. As in (**1**), the ligand can be described by two halves denoted A and B; the A half shows no deviations from planarity greater than 0.059 Å while the B half shows no deviations greater than 0.036 Å. The dihedral angle between these two planes is 3.7° which is smaller by *ca.* 5° than that observed for this ligand in (**1**). On the other hand, the dihedral angle between the main plane of the bis(2-pyridylcarbonyl)amido ligand and the copper atom and that comprising Cu, O(1A), O(1B), C(7A), and C(7B) is 90°.

A comparison of the bond distances of the A half with the related ones of the B half shows that the bis(2-pyridylcarbonyl)amido ligand is less symmetrical in (**2**) than in (**1**) (*cf.* Tables 4 and 5). This fact can be attributed to the asymmetrically bridging co-ordination of this ligand in (**2**). To our knowledge the structure of (**2**) is the first one to illustrate the possibility of this ligand co-ordinating to a metal ion through the terpyridine-like site and the carbonyl-oxygen atoms simultaneously in a bis-chelating mode. In our case this mode of co-ordination leads to a one-dimensional copper(II) chain shown in Figure 4(*b*). The relevant angular strain reported for the bis(2-pyridylcarbonyl)amido ligand in (**1**) is also observed in (**2**): the related angles at the sp^2-hybridized carbonyl-carbon atoms of both structures are very similar.

The geometry of the non-co-ordinated perchlorate anion is as expected. The mean Cl–O bond distance is 1.43 Å and the angles are very close to tetrahedral except for O(3)–Cl(1)–O(5) which is 112.2(9)°.

The shortest intra-chain Cu ··· Cu^{ii} and inter-chain Cu ··· Cu^{iii} distances are 5.32(1) and 8.07(0) Å respectively, where ii and iii refer to the equivalent positions $x, y, z + \frac{1}{4}$ and $x, y + 1, z$, respectively, relative to the reference molecule at x, y, z.

Infrared, Electronic and E.S.R. Spectra.—The i.r. spectra of complexes (**1**) and (**2**) exhibit bands for the bis(2-pyridylcarbonyl)amido ligand at 3 100w, 1 710s, 1 645m, 1 600s, 1 570m, 1 460m, 1 440m, 1 360s, br, 1 290m, 1 250w, 1 045w, 1 025m, 1 000w, 820w, 800w, 760s, 700m, 650w, 610w, 495w, 410w, and 350w cm^{-1} and for the perchlorate groups at 1 150s, 1 115s, 1 090s, 940w, and 625m cm^{-1}. The strong band at 1 710 cm^{-1} present in the i.r. spectrum of both complexes, which corresponds to an imide group, indicates that hydrolysis of tptz has occurred. The i.r. spectrum of complex (**1**) displays bands for water (3 500m, br, 1 620w, and 610w cm^{-1}) and co-ordinated 2-picolinamide (3 410m, 3 195w, 1 660s, and 1 590w cm^{-1}).

Both compounds exhibit similar electronic reflectance spectra consisting of a broad *d–d* band centred at 600 nm for (**1**) and at 650 nm for (**2**), a small peak at 415 nm for (**1**) and a shoulder at 425 nm for (**2**), and intense charge-transfer bands for (**1**) and (**2**) at lower wavelengths. Their spectra in aqueous solution are

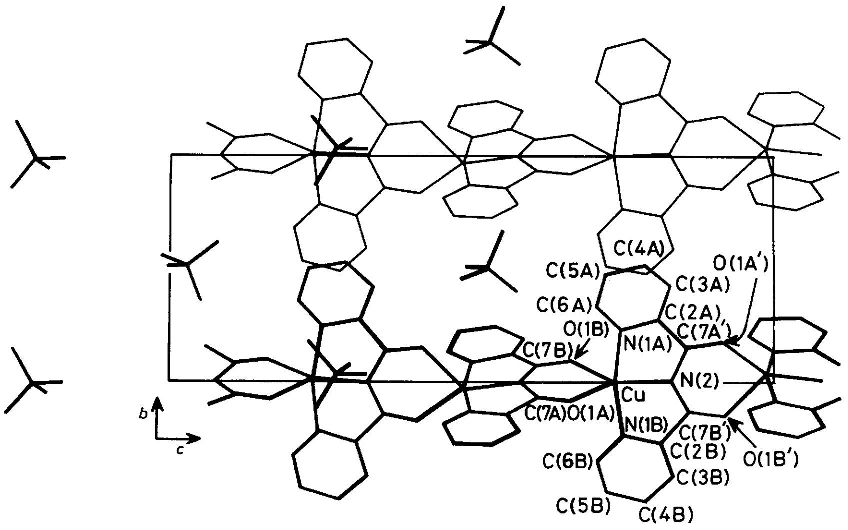
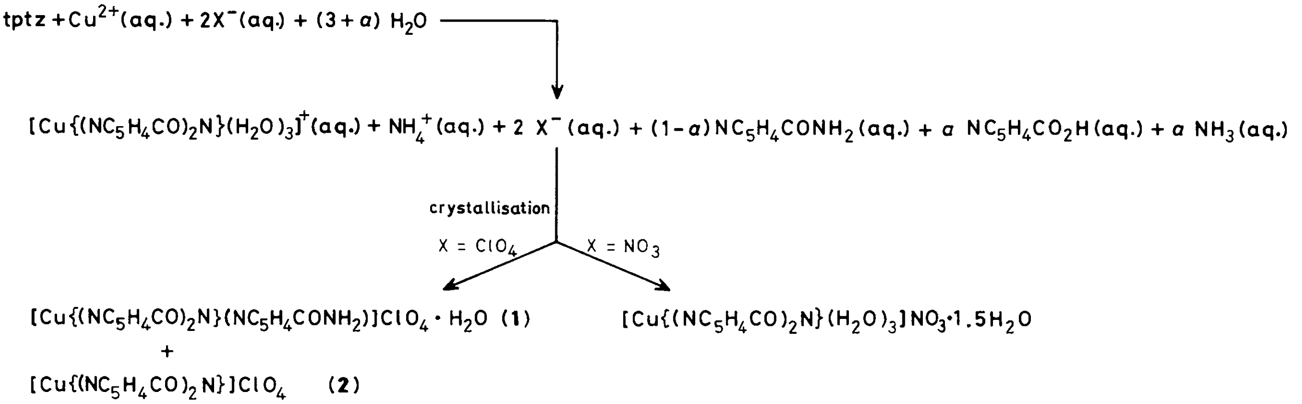


Figure 5. Projection of the cell contents of complex (2) along the *a* axis



Scheme. $(NC_5H_4CO)_2N^-$ = bis(2-pyridylcarbonyl)amido anion, $NC_5H_4CONH_2$ = 2-picolinamide, $NC_5H_4CO_2H$ = 2-picolinic acid (2-pyridinecarboxylic acid)

identical, consisting of a broad *d–d* band centred at 638 (ε *ca.* 87), a shoulder at 425 (ε *ca.* 37), and an intense charge-transfer absorption at 273 nm (ε *ca.* 20 000 dm^3 mol^{-1} cm^{-1}). The results reveal that in aqueous solution both complexes yield the same hydrated species. Therefore, perchlorate anion and 2-picolinamide would be substituted by water molecules in (**1**) and the polymeric nature of (**2**) would be broken leading probably to the hydrated [bis(2-pyridylcarbonyl)amido]copper(II) cationic species. In order to confirm this assumption, we have synthesized the parent compound [bis(2-pyridylcarbonyl)amido]copper(II) nitrate tetrahydrate[13] and recorded its u.v.–visible spectrum in aqueous solution and as a solid. The two spectra are very similar and identical to that observed in aqueous solution for compounds (**1**) and (**2**). These results lead to the conclusion that under our experimental conditions [25 °C, 2×10^{-3} mol dm^{-3} (**1**) and (**2**) in water], both complexes give the [bis(2-pyridylcarbonyl)amido]copper(II) cationic species.

X-Band e.s.r. spectra of both complexes recorded on microcrystalline powders show an absorption band of axial symmetry. The spectrum of (**1**) remains unchanged in the temperature range investigated, whereas the spectrum of (**2**) shows greater resolution at lower temperatures. The axial spectrum of (**1**) has features at $g_{\parallel} = 2.23$ and $g_{\perp} = 2.07$, which clearly indicates a mainly copper(II) $d_{x^2-y^2}$ orbital ground state, as confirmed by its structure. For complex (**2**), the $g_{\parallel} = 2.08$ signal occurs at higher field than the $g_{\perp} = 2.17$ signal, in agreement with the trigonal-bipyramidal geometry around the copper(II) ion. Both complexes show a weak half-field forbidden transition at room temperature and at 7 K. In binuclear copper(II) complexes this transition can be interpreted as the $\Delta M_s = 2$ forbidden transition in the triplet, but in our compounds (**1**) and (**2**) this interpretation is no longer valid. In (**1**) it could be due to dipolar interactions or hydrogen bonds between mononuclear units.[24]

Hydrolysis Reaction of tptz.—Free tptz undergoes hydrolysis only in concentrated mineral acids at high temperatures yielding 2-pyridinecarboxylic acid and ammonium ions. However, copper(II) ion promotes partial hydrolysis of tptz in neutral aqueous solutions yielding the anionic bis(2-pyridylcarbonyl)amido species which is stabilized by co-ordination to the metal ion (see Scheme). This reaction was described for the first time by Lerner and Lippard,[13,14] who isolated the complexes $[Cu\{(NC_5H_4CO)_2N\}]NO_3{\cdot}4.5H_2O$ and $[Cu\{(N_2C_4H_3CO)_2N\}(H_2O)_3]NO_3{\cdot}2H_2O$ by the copper(II)-assisted hydrolysis of tptz and tpmtz respectively. The crystal structure of the latter compound shows that the co-ordination sphere of the metal ion is formed by three nitrogen atoms of the bis(2-pyrimidylcarbonyl)amido ligand and three oxygen atoms of three water molecules. The structure of the former compound is unknown but our spectrophotometric data suggest that in this compound the nitrate ion is not co-ordinated to the metal ion. The other product of the hydrolysis reaction of tptz, 2-picolinamide, was isolated as a white powder and identified by i.r. and mass spectra.

The reaction of tptz with copper(II) perchlorate instead of nitrate yields complexes (**1**) and (**2**). A very interesting feature of the structure of (**1**), which is the main product of the metal-assisted hydrolysis of tptz, is that it contains bis(2-pyridylcarbonyl)amido and 2-picolinamide as ligands enabling us to elucidate directly the nature of the other major product of the hydrolysis reaction.

Complexes (**1**) and (**2**) crystallize simultaneously but only small amounts of (**2**) are obtained. As this complex contains neither picolinamide nor water, oxygen atoms of the bis(2-pyridylcarbonyl)amido ligand and/or of the perchlorate group should be involved in the co-ordination sphere of the copper(II) ion. Our *X*-ray study on a single crystal of (**2**) reveals the presence of one-dimensional copper(II) chains in which the bis(2-pyridylcarbonyl)amido anion acts as both tridentate and bidentate ligands through nitrogen atoms and carbonyl-oxygen atoms respectively.

The above mentioned spectrophotometric study of aqueous solutions of complexes (**1**) and (**2**) enable us to conclude that the cationic complex $[Cu\{(NC_5H_4CO)_2N\}(H_2O)_3]^+$ is the main species in this medium. However, only crystals of compound (**1**) are obtained by slow evaporation of aqueous solutions of this complex. The addition of variable amounts of sodium perchlorate does not modify this result. Thus, if the hydrolysis reaction of tptz yielded exclusively bis(2-pyridylcarbonyl)amido anion and 2-picolinamide, complex (**1**) would be the only product. We think that under the conditions in which the hydrolysis reaction takes place, part of the 2-picolinamide is further hydrolyzed to the corresponding carboxylic acid (see Scheme).

It seems evident that the nature of the isolated products from the copper(II)-assisted hydrolysis of tptz is strongly dependent on the nature of the anion present in solution. Copper(II) salts other than nitrate or perchlorate could be used in order to isolate different compounds which could contribute to elucidating the pathway of this hydrolysis reaction: we have obtained dark blue and green crystals when using a trifluoromethanesulphonate salt. Chemical analyses and preliminary spectral studies indicate that the former are analogous to (**1**) and the latter contain bis(2-pyridylcarbonyl)amido and unhydrolyzed tptz ligands.[25]

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