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Crystal and molecular structures of Cu(II) and Zn(II) complexes of 2,3,5,6-tetra(2-pyridyl)pyrazine (TPPZ): an old ligand revisited

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Abstract

Copper and zinc complexes of 2,3,5,6-tetra(2-pyridyl)pyrazine (TPPZ) have been prepared. The reaction of $Cu(ClO_4)_2$ with TPPZ leads to a dinuclear complex where the ligand is bis-tridentate (crystal data: $C_{24}H_{28}N_6O_{22}Cl_4Cu_2$, monoclinic, space group $P2_1/n$, $a=7.855(4)$, $b=16.267(6)$, $c=14.860(3)$ Å, $\beta=102.91(3)$°, $Z=2$, 2522 reflections with $I>2.5\sigma(I)$, $R=0.053$). In an acidic medium the same reaction gave a mononuclear dimeric complex where TPPZ is mono-tridentate. The Cu...Cu separation in the dimer is 3.446(3) Å and the Cu...Cl bridging bond is 2.682(2) Å. The molecules are stacked up the *a* axis with a short Cu...Cu inter-stacking distance of 3.854(4) Å. One of the non-coordinated pyridine N atoms is protonated and hydrogen bonded to a perchlorate O atom (crystal data: $C_{24}H_{17}N_6O_8Cl_3Cu$, triclinic, space group $P\bar{1}$, $a=6.873(7)$, $b=12.753(5)$, $c=16.252(7)$ Å, $\alpha=69.29(3)$, $\beta=90.10(4)$, $\gamma=83.57(4)$°, $Z=2$, 3436 reflections with $I>3\sigma(I)$, $R=0.050$). The reaction of TPPZ with an excess of $ZnCl_2$ gave a neutral mononuclear five-coordinate complex where TPPZ is mono-tridentate (crystal data: $C_{24}H_{16}N_6Cl_2Zn$, monoclinic, space group $P2_1/n$, $a=14.744(1)$, $b=7.245(1)$, $c=21.253(2)$ Å, $\beta=104.51(1)$°, $Z=4$, 3340 reflections with $I>2.5\sigma(I)$, $R=0.036$).

Introduction

The ligand tetra(2-pyridyl)pyrazine (TPPZ) was first synthesized by Goodwin and Lions in 1959 [1]. They prepared a number of transition metal complexes but on the grounds of elemental analyses and stereochemical considerations rejected the possibility of the ligand being bis-tridentate. In 1989 Escuer *et al.* [2] prepared a hexafluoroacetyl acetate copper complex of TPPZ and from the microanalytical data proposed a dinuclear complex. Ruminski *et al.* have also synthesized and characterized mono and bimetallic Ru(II) [3], Rh(II) [4] and Fe(II) [5] complexes of TPPZ. However, to our knowledge no crystal structures of any metal complex of TPPZ have been published. Here we describe the reaction of TPPZ with $Cu(ClO_4)_2$ which gives a dinuclear complex where the ligand is bis-tridentate. The same reaction in an acidic medium leads to a dimeric chlorine bridged mono-tridentate complex with one of the non-coordinated pyridine N atoms protonated and hydrogen bonded to a perchlorate O atom. The reaction of TPPZ with an excess of $ZnCl_2$ gave a neutral five-coordinate mononuclear Zn(II) complex, where the ligand is mono-tridentate. With a metal to ligand ratio of only 1:1 a small amount of the same zinc complex was formed plus crystals of a new tetragonal form of the ligand TPPZ [6]. When crystallized from $CHCl_3$ [7] or CH_2Cl_2 a monoclinic form is obtained. Their conformations differ in the orientation of one symmetrically opposed pair of pyridine rings.

Experimental

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with great care.

IR spectra were recorded on a Perkin-Elmer FT IR 1720 spectrometer using KBr pellets. UV–Vis spectra were recorded with a UVIKON 810/820; detecter: Photomultiplier R446 (standard). ^1H NMR spectra were recorded on a Bruker WM 400.

The ligand tetra(2-pyridyl)pyrazine (TPPZ) was prepared according to the method of Goodwin and Lions [1] and recrystallized from CH_2Cl_2.

Synthesis of [tetra(2-pyridyl)pyrazineCu(II)$_2$(H$_2$O)$_4$]-(ClO$_4$)$_4$·2(H$_2$O)

TTPZ (100 mg, 0.25 mmol) was dissolved in 20 ml of water in a 100 ml Erlenmeyer flask equipped with a magnetic stirrer. To the resulting mixture

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$Cu(ClO_4)_2\cdot 6H_2O$ (184 mg, 0.5 mmol) in 10 ml EtOH was added. The reaction mixture was stirred at 90 °C for 45 min. The solution was filtered and left to evaporate at room temperature. Dark green crystals were obtained (yield 66.8%).

IR (KBr, cm^{-1}): C=C, C=N; $\nu = 1630$, 1601, 1477, 1417. UV–Vis (H_2O, nm, $c = 7.6\times10^{-5}$ M): $\lambda_{max} = 300$, 362.

Anal. Calc.: C, 28.20; N, 8.22; H, 2.74. Found: C, 27.93; N, 8.18; H, 3.01%.

Synthesis of [2-pyridylium-tris(2-pyridyl)pyrazineCu(II)-Cl]$_2$(ClO$_4$)$_4$

100 mg of TPPZ (0.25 mmol) were dissolved in 20 ml of water in a 100 ml Erlenmeyer flask equipped with a magnetic stirrer bar. To the resulting mixture $Cu(ClO_4)_2\cdot 6H_2O$ (95 mg, 0.25 mmol), 10 ml EtOH and 1 M HCl were added. The reaction mixture was stirred at 90 °C for 45 min. The solution was filtered and left to evaporate at room temperature. Large dark green crystals were obtained and dried over P_2O_5. m.p. (dry) = 340 °C(above).

IR (KBr, cm^{-1}): C=C, C=N; $\nu = 1404$, 1442, 1459, 1534, 1601, 1615, 1627. UV–Vis (H_2O, nm, $c = 7.6\times 10^{-5}$ M): $\lambda = 300$, 360.

Anal. Calc.: C, 41.77; N, 12.20; H, 2.79. Found: C, 41.94; N, 12.23; H, 2.49%.

This compound was also obtained by the reaction of $CuCl_2\cdot 2H_2O$ with TPPZ (molar ratio 1:1) and with 1 M $HClO_4$ under the same conditions.

Synthesis of [tetra(2-pyridyl)pyrazineZn(II)Cl$_2$]

$ZnCl_2$ (140 mg, 1.0 mmol) was dissolved in 20 ml of water in a 100 ml Erlenmeyer flask. TPPZ (200 mg, 0.52 mmol) was added and the mixture stirred in a 70 °C water bath for 30 min. EtOH (5 ml) was added to dissolve the remaining solid TPPZ. The resulting yellow solution was stirred at 70 °C for 4 h, cooled to room temperature and filtered into a 100 ml Erlenmeyer flask. After standing one day pale yellow crystals were formed.

IR (KBr, cm^{-1}): C=C, C=N; $\nu = 1636$, 1588, 1466, 1402. UV–Vis (H_2O, nm, $c = 7.6\times10^{-5}$ M): $\lambda_{max} = 295$, 315.

Anal. Calc.: C, 54.88; N, 16.00; H, 3.07. Found: C, 53.51; N, 15.52; H, 3.54%.

^1H NMR (d in ppm, CD_2Cl_2): d1 = 7.30(d) *J*(H–H) = 7 Hz; d2 = 7.56(m); d3 = 7.63(m); d4 = 7.76(m); d5 = 8.06(m); d6 = 8.25(d) *J*(H–H) = 7 Hz; d7 = 8.67(s); d8 = 9.11(s).

X-ray data collection, structure solution and refinement

Intensity data were collected at room temperature on a Stoe AED2 4-circle diffractometer using Mo Kα graphite monochromated radiation. A numerical absorption correction was applied to the zinc complex using SHELX-76 [8]. Transmission factors were max. 0.816 and min. 0.658. The structures were solved by Patterson and difference Fourier syntheses using the NRCVAX [9] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [9] are from the International Tables for X-ray Crystallography [10]. The majority of the H atoms were located from difference maps, the rest were included in calculated positions. They were refined isotropically while the non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares. Crystal data, details of data collection and structure refinement for the copper and the zinc complexes are given in Table 1. Atomic parameters and equivalent isotropic thermal parameters for the three complexes are given in Table 2. The numbering schemes used are illustrated in the ORTEP-II [11] and PLUTO [12] plots of the cations, Figs. 1, 2, 3 and 4; see also 'Supplementary material'.

Results and discussion

Selected distances and angles in the three cations are given in Table 3. In Table 4 selected distances in the three complexes are compared with similar values for copper [13–15], bridged copper chloride [16, 17] and zinc [18] complexes of 2,2′:6′2″-terpyridine (terpy). The metal–nitrogen bond lengths show the expected pattern of short contacts to the central pyrazine ring and longer contacts to the terminal pyridine rings. In general however, as can be seen in Table 4, the metal–N(pyrazine) distances are longer than the central metal–N(pyridine) distances, while the terminal metal–N(pyridine) distances are shorter than the same distances in the terpy complexes. In Table 5 the dihedral angles between the different pyridine rings (A, B, D, E) and the pyrazine ring (C) in the three complexes and the two forms of the ligand are compared.

Structures

[Cu$_2$(TPPZ)(H$_2$O)$_4$](ClO$_4$)$_4\cdot$2H$_2$O

The reaction of $Cu(ClO_4)_2$ with TPPZ gave large green square rods whose crystal structure analysis showed that it is indeed a dinuclear complex and the ligand is bis-tridentate. The complex posses crystallographic C_i symmetry and the central pyrazine ring is planar, Fig. 1. The pyridine rings A and B are inclined to one another by 34.3(2)°, and by 21.3(3) and 21.7(3)°, respectively, to the central pyrazine ring C. The shortest C…C intramolecular distance is that between atoms C(4) and C(9a), at 3.089 Å. Protons H(4) and H(9a) are separated by 2.316 Å. The coordination of the copper atom can be described as skew-trigonal bypyr-

TABLE 1. Crystal data, details of data collection and structure refinement for $[Cu_2(TPPZ)(H_2O)_4](ClO_4)_4 \cdot 2H_2O$, $[Cu(TPPZH)Cl]_2(ClO_4)_4$ and $[Zn(TPPZ)Cl_2]$

Formula	$C_{24}H_{24}N_6O_4Cu_2(ClO_4)_4 \cdot 2H_2O$	$C_{24}H_{17}N_6ClCu(ClO_4)_2$	$C_{24}H_{16}N_6Cl_2Zn$
Molecular weight	1021.4	687.3	524.7
Crystal colour/habit	green rod	yellow rod	yellow block
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Z	2	2	4
D_{calc} (g/cm^3)	1.833	1.726	1.586
μ(Mo Kα) (cm^{-1})	15.4	11.9	14.1
Crystal size (mm)	0.76	0.42	0.57
	0.36	0.38	0.49
	0.34	0.28	0.17
Cell parameters: least-squares fit of N reflections	18	21	17
2θ Range (°)	28–37	28–37	30–37
a (Å)	7.855(4)	6.873(7)	14.744(1)
b (Å)	16.267(6)	12.753(5)	7.245(1)
c (Å)	14.860(5)	16.252(7)	21.253(2)
α (°)		69.29(3)	
β (°)	102.91(3)	90.10(4)	104.51(1)
γ (°)		83.57(4)	
V (Å^3)	1850.8	1322.8	2197.8
Scan method	$\omega/2\theta$	$\omega/2\theta$	ω/θ
θ_{max} (°)	25	25	27.5
h, k, l Range	± 9, $+19$, $+17$	± 8, $+15$, ± 19	± 19, $+9$, $+27$
No. reference reflections	3	2	3
variation (%)	5	3	3
No. unique reflections	3246	4656	4514
No. reflections in refinement	2522	3436	3340
$I > x\sigma(I)$, x	2.5	3.0	2.5
No. parameters refined	294	447	362
R_f[a]	0.053	0.050	0.036
R_w[b]	0.082	0.070	0.056
k[c]	0.002	0.0025	0.0022
Max. shift/sigma ratio	0.047	0.074	0.037
Residual density (e/Å^2)	+0.59(max)	+0.88(max)	+0.34(max)
	−0.59(min)	−1.00(min)	−0.44(min)

[a] $R_f = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma F_o^2]^{1/2}$. [c] $w^{-1} = \sigma^2(F_o) + k(F_o)^2$.

amid; the copper atom being displaced by −0.008(3) Å from the plane through atoms N(1), OW(1) and OW(2), with atoms N(2) and N(3) displaced by −1.982(5) and 1.953(5) Å, respectively, and the N(2)–Cu–N(3) angle equal to 158.57(15)°. The central Cu–N(pyrazine) distance is slightly longer than the central Cu–N(pyridine) distance in the copper terpy complexes [13–15], while the Cu–N(pyridine) distances are significantly shorter (*c.* 0.04 Å), see Table 4. The Cu...Cu separation in the dinuclear complex is 6.497(2) Å (symmetry operation: $2-x$, $1-y$, $-z$).

[Cu(TPPZH)Cl]$_2$(ClO$_4$)$_4$

The reaction of TPPZ with $Cu(ClO_4)_2$ in the presence of HCl gave large thick green lozenge type crystals. X-ray analysis showed that the complex is mononuclear. The copper atom is five-coordinate and the complex forms a dimer with a bridging Cu...Cl[a] distance of 2.682(3) Å, a Cu...Cu[a] bridging separation of 3.446(3) Å and a bridging angle Cu–Cl(1)...Cu[a] of 88.49(7)°, Fig. 2. In the crystal the dimers are stacked up the *a* axis with a short Cu...Cu[b] inter-stacking distance of only 3.854(4) Å, see Table 3 and Fig. 3. The coordinated part of the ligand is less planar than that found in Cu(terpy) complexes [13–17]. The torsion angles N(1)–C(1)–C(3)–N(2) and N(1)–C(2)–C(8)–N(3) are 2.3 and 13.7°, respectively; compared to a maximum value of 8.93° and a minimum value of 0.03° in the Cu(terpy) complexes considered. It is, however, more planar than in the zinc complex described below where the same torsion angles are −5.8 and −17.8°, respectively. The pyrazine ring is considerably distorted. The dihedral angle between planes C′[C(1), N(1), C(4)] and C″[C(2), N(2), C(3)] is 8.0(2)°. Larger and smaller twist angles have been observed in the pyrazine rings of a rhodium complex (12.3 and 15.3°) [19], a ruthenium complex (12.8°) [20] and a copper complex (3.9 and 8.0°) [21] of the similar ligand 2,3-bis(2-pyridyl)-

TABLE 2. Atomic parameters and equivalent isotropic thermal parameters

Atom	x	y	z	B_{iso}[a]
$[Cu_2(TPPZ)(H_2O)_4](ClO_4)_4 \cdot 2H_2O$				
Cu	0.90135(7)	0.44424(3)	0.19202(3)	2.78(3)
N(1)	0.9876(5)	0.4759(2)	0.0828(2)	2.49(13)
N(2)	0.9132(5)	0.3329(2)	0.1355(2)	2.73(14)
N(3)	0.9576(5)	0.5624(2)	0.2216(3)	2.85(16)
O(W1)	0.8378(5)	0.4121(3)	0.3070(2)	4.34(17)
O(W2)	0.6244(6)	0.4645(3)	0.1242(4)	6.40(23)
C(1)	0.9823(5)	0.4170(2)	0.0183(3)	2.16(15)
C(2)	1.0089(6)	0.5563(2)	0.0710(3)	2.34(16)
C(3)	0.9727(5)	0.3331(3)	0.0566(3)	2.36(15)
C(4)	1.0272(6)	0.2615(3)	0.0214(3)	3.04(18)
C(5)	1.0118(7)	0.1878(3)	0.0660(4)	3.61(22)
C(6)	0.9460(7)	0.1878(3)	0.1436(4)	3.85(22)
C(7)	0.8990(7)	0.2610(3)	0.1776(3)	3.64(20)
C(8)	1.0245(5)	0.6031(3)	0.1582(3)	2.52(16)
C(9)	1.1095(6)	0.6777(3)	0.1787(3)	2.97(18)
C(10)	1.1111(7)	0.7137(3)	0.2629(3)	3.62(20)
C(11)	1.0318(8)	0.6752(3)	0.3249(4)	4.02(23)
C(12)	0.9595(7)	0.5985(3)	0.3020(3)	3.65(23)
Cl(1)	0.36361(18)	0.44485(8)	0.32414(11)	4.33(6)
O(11)	0.2117(6)	0.4002(3)	0.2821(4)	7.59(27)
O(12)	0.5084(6)	0.3900(4)	0.3477(4)	7.03(27)
O(13)	0.3935(10)	0.5065(4)	0.2645(6)	9.96(41)
O(14)	0.3332(8)	0.4838(4)	0.4054(4)	9.01(36)
Cl(2)	0.45933(18)	0.31810(10)	−0.06119(9)	4.61(6)
O(21)	0.3903(8)	0.3538(4)	0.0103(4)	9.08(34)
O(22)	0.5904(8)	0.2644(5)	−0.0252(6)	10.92(43)
O(23)	0.3189(8)	0.2833(6)	−0.1209(4)	12.34(52)
O(24)	0.5360(13)	0.3753(5)	−0.1087(7)	14.48(62)
O(W3)	1.0577(8)	0.4085(4)	0.4707(3)	8.01(33)
$[Cu(TPPZH)Cl]_2(ClO_4)_4$				
Cu(1)	0.76826(7)	0.48883(4)	0.04001(3)	2.258(22)
Cl(1)	0.85631(16)	0.57962(9)	−0.09694(7)	2.77(4)
N(1)	0.6479(5)	0.4182(3)	0.1511(2)	2.21(14)
N(2)	0.7174(5)	0.3426(3)	0.0277(2)	2.30(15)
N(3)	0.7368(5)	0.6187(3)	0.0846(2)	2.50(16)
N(4)	0.4575(5)	0.3254(3)	0.2993(2)	2.51(16)
N(5)	0.2779(7)	0.6034(4)	0.2671(3)	3.76(20)
N(6)	0.3690(7)	0.1084(4)	0.3472(3)	3.33(18)
C(1)	0.6118(6)	0.3102(3)	0.1727(3)	2.25(18)
C(2)	0.5959(6)	0.4803(3)	0.2000(3)	2.21(17)
C(3)	0.6483(6)	0.2673(3)	0.1001(3)	2.17(17)
C(4)	0.6080(7)	0.1624(4)	0.1006(3)	3.00(21)
C(5)	0.6401(8)	0.1354(4)	0.0260(3)	3.28(22)
C(6)	0.7069(7)	0.2131(4)	−0.0472(3)	3.04(21)
C(7)	0.7435(7)	0.3160(4)	−0.0451(3)	2.71(18)
C(8)	0.6703(6)	0.5919(4)	0.1664(3)	2.59(19)
C(9)	0.6777(8)	0.6622(4)	0.2156(4)	3.52(24)
C(10)	0.7455(8)	0.7670(4)	0.1735(4)	4.12(27)
C(11)	0.8030(8)	0.7960(4)	0.0893(4)	3.70(25)
C(12)	0.7992(7)	0.7201(4)	0.0455(4)	3.07(21)
C(13)	0.4761(6)	0.4357(4)	0.2706(3)	2.53(18)
C(14)	0.5329(6)	0.2614(3)	0.2551(3)	2.26(16)
C(15)	0.3659(7)	0.5015(4)	0.3182(3)	2.77(19)
C(16)	0.3552(9)	0.4584(5)	0.4086(3)	3.79(26)
C(17)	0.2495(10)	0.5242(6)	0.4485(4)	5.13(33)
C(18)	0.1590(10)	0.6286(6)	0.3978(4)	4.87(32)
C(19)	0.1772(9)	0.6652(5)	0.3073(4)	4.44(27)
C(20)	0.5297(6)	0.1385(3)	0.3040(3)	2.44(17)
C(21)	0.6862(9)	0.0583(4)	0.3122(3)	3.09(22)
C(22)	0.6729(10)	−0.0533(4)	0.3674(4)	4.28(27)
C(23)	0.5060(10)	−0.0802(5)	0.4100(4)	4.72(28)
C(24)	0.3512(9)	0.0016(5)	0.3996(4)	4.36(26)
Cl(2)	0.15167(19)	0.00286(10)	0.17835(9)	3.57(5)
O(21)	0.1321(9)	0.1156(4)	0.1752(4)	6.6(3)
O(22)	0.0833(14)	0.0000(7)	0.0985(6)	12.6(6)
O(23)	0.3443(8)	−0.0477(5)	0.1937(5)	8.5(4)
O(24)	0.0333(11)	−0.0590(5)	0.2414(6)	12.6(5)
Cl(3)	0.94254(18)	0.26152(12)	0.40792(8)	3.75(6)
O(31)	0.7830(8)	0.2071(5)	0.4479(3)	7.6(3)
O(32)	1.1101(7)	0.2383(5)	0.4654(3)	6.0(3)
O(33)	0.8813(9)	0.3800(4)	0.3801(4)	7.8(3)
O(34)	0.9907(7)	0.2358(5)	0.3321(3)	6.0(3)
$[Zn(TPPZ)Cl_2]$				
Zn(1)	0.24165(2)	0.11462(5)	0.01368(2)	2.600(15)
Cl(1)	0.28054(6)	0.41224(12)	−0.00174(4)	3.37(3)
Cl(2)	0.26890(7)	0.02627(15)	0.11757(4)	4.12(4)
N(1)	0.1887(2)	0.0363(4)	−0.0867(1)	2.42(10)
N(2)	0.0890(2)	0.1601(4)	−0.0109(1)	2.57(10)
N(3)	0.3483(2)	−0.0579(4)	−0.0112(1)	2.73(10)
N(4)	0.1397(2)	0.0284(4)	−0.2174(1)	2.65(10)
N(5)	0.3847(2)	0.0808(4)	−0.1959(1)	3.36(12)
N(6)	−0.0738(2)	−0.1005(4)	−0.1958(1)	3.06(11)
C(1)	0.1004(2)	0.0780(4)	−0.1174(1)	2.38(11)
C(2)	0.2522(2)	−0.0136(4)	−0.1181(1)	2.44(11)
C(3)	0.0442(2)	0.1586(4)	−0.0745(1)	2.41(11)
C(4)	−0.0459(2)	0.2280(5)	−0.0964(2)	2.89(12)
C(5)	−0.0911(2)	0.2971(5)	−0.0514(2)	3.24(14)
C(6)	−0.0459(2)	0.2943(5)	0.0134(2)	3.18(14)
C(7)	0.0446(2)	0.2256(5)	0.0314(2)	2.95(13)
C(8)	0.3381(2)	−0.0954(4)	−0.0744(2)	2.54(11)
C(9)	0.3985(2)	−0.2128(5)	−0.0956(2)	3.02(14)
C(10)	0.4734(2)	−0.2875(5)	−0.0500(2)	3.51(15)
C(11)	0.4858(2)	−0.2450(5)	0.0144(2)	3.61(14)
C(12)	0.4205(2)	−0.1326(5)	0.0320(2)	3.36(13)
C(13)	0.2297(2)	0.0108(4)	−0.1863(1)	2.42(11)
C(14)	0.0728(2)	0.0461(4)	−0.1850(1)	2.43(11)
C(15)	0.2986(2)	0.0228(4)	−0.2265(1)	2.56(11)
C(16)	0.2710(2)	−0.0156(5)	−0.2926(2)	2.90(13)
C(17)	0.3379(3)	0.0037(5)	−0.3285(2)	3.51(15)
C(18)	0.4267(3)	0.0582(6)	−0.2976(2)	3.70(16)
C(19)	0.4472(3)	0.0954(5)	−0.2314(2)	3.60(16)
C(20)	−0.0243(2)	0.0127(4)	−0.2240(1)	2.46(11)
C(21)	−0.0567(3)	0.0805(6)	−0.2866(2)	3.75(16)
C(22)	−0.1445(3)	0.0251(7)	−0.3219(2)	5.04(20)
C(23)	−0.1943(3)	−0.0962(7)	−0.2946(2)	4.45(17)
C(24)	−0.1579(3)	−0.1510(6)	−0.2318(2)	3.76(16)

(*continued*)

TABLE 2. (*continued*)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoids.

quinoxaline BPQ, and the zinc complex described below. The coordinated pyridine rings (A and B) are inclined to one another by 1.9(2)° and to plane C′ by 13.7(3) and 13.0(3)°, respectively. The uncoordinated pyridine rings (D and E) are inclined to one another by 49.8(2)° and to plane C″ by 38.2(4) and 41.8(3)°, respectively. The copper coordination is best described as square

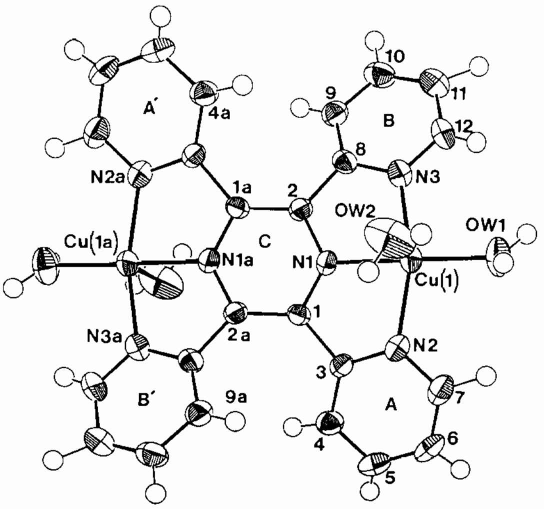

Fig. 1. An ORTEP plot of the cation $[Cu_2(TPPZ)(H_2O)_4]^{4+}$, showing the numbering scheme (ellipsoids at 50% probability level).

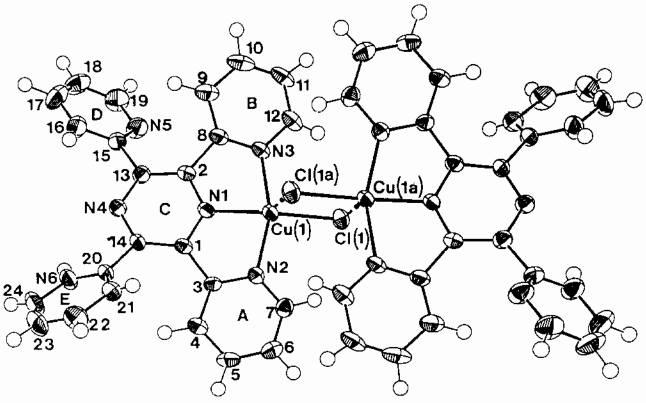

Fig. 2. An ORTEP plot of the dimer $[Cu(TPPZH)Cl_2]^{4+}$, showing the numbering scheme (ellipsoids at 50% probability level).

pyramidal; the copper atom being displaced by 0.172(2) Å from the best plane through atoms N(1), N(2), N(3) and Cl(1) (planar to within 0.002(2) Å). Atom Cl(1^a) occupies the apical position at 2.682(3) Å from atom Cu(1), showing a typical Jahn–Teller distortion. The central Cu–N(pyrazine) distance (1.943(4) Å) is similar to the central Cu–N(pyridine) distance observed in a number of mononuclear Cu(terpy) complexes (13–15) and in two dimeric Cl bridged Cu(terpy) complexes [16, 17] and a NCO bridged Cu(terpy) complex [15]. The lateral Cu–N(pyridine) distances are also similar to those observed in the above mentioned compounds, see Table 4. The pyridine ring involving atom N(6) is protonated and hydrogen bonded to a perchlorate O atom, see Table 3 for details.

[Zn(TPPZ)Cl$_2$]

The reaction of TPPZ with an excess of $ZnCl_2$ (ligand to metal ratio = 1:2 at least) in H_2O/EtOH at 70 °C

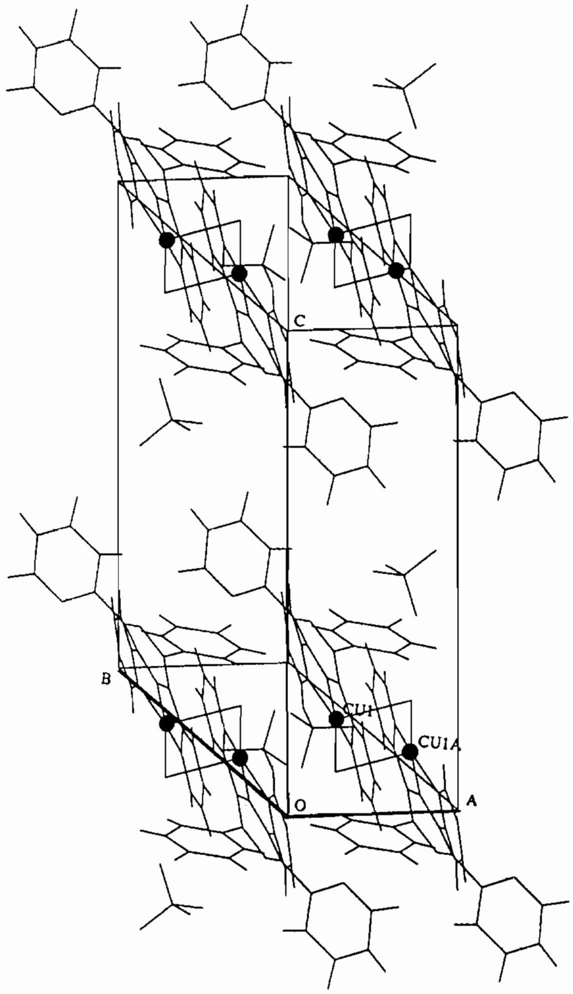

Fig. 3. A PLUTO packing diagram of $[Cu(TPPZH)Cl_2](ClO_4)_4$ showing the short inter-stacking Cu...Cu distances.

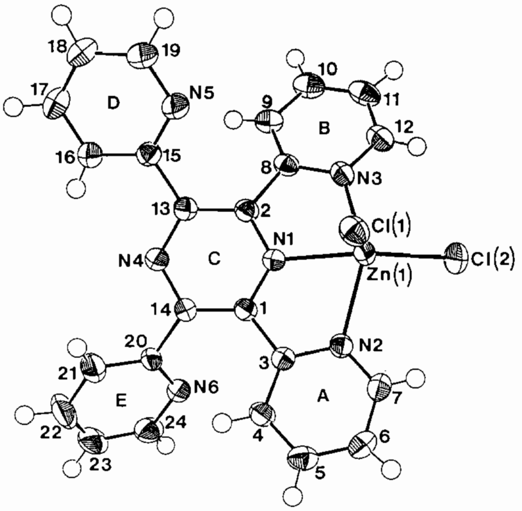

Fig. 4. An ORTEP plot of $[Zn(TPPZ)Cl_2]$, showing the numbering scheme (ellipsoids at 50% probability level).

TABLE 3. Selected distances (Å) and angles (°) in the Cu(II) and Zn(II) complexes of TPPZ

[Cu_2(TPPZ)(H_2O)$_4$]			
Cu(1)–N(1)	1.962(3)	Cu(1)–OW(1)	1.955(3)
Cu(1)–N(2)	2.007(4)	Cu(1)–OW(2)	2.209(4)
Cu(1)–N(3)	1.999(4)	Cu(1)...Cu(1^a)	6.497(2)
N(1)–Cu(1)–N(2)	80.42(15)	N(2)–Cu(1)–OW(1)	99.71(16)
N(1)–Cu(1)–N(3)	80.18(15)	N(2)–Cu(1)–OW(2)	94.42(16)
N(1)–Cu(1)–OW(1)	174.74(15)	N(3)–Cu(1)–OW(1)	98.77(17)
N(1)–Cu(1)–OW(2)	94.04(19)	N(3)–Cu(1)–OW(2)	95.95(18)
N(2)–Cu(1)–N(3)	158.57(15)	OW(1)–Cu(1)–OW(2)	91.20(19)
[Cu(TPPZH)Cl]$_2$			
Cu(1)–Cl(1)	2.2359(16)	Cu(1)–N(2)	2.013(4)
Cu(1)–Cl(1^a)	2.682(3)	Cu(1)–N(3)	2.022(4)
Cu(1)–N(1)	1.943(4)	Cu(1)...Cu(1^a)	3.446(3)
N(6)–H(6N)	0.71(6)	Cu(1)...Cu(1^b)	3.854(4)
H(6N)...O(34^c)	2.18(6)	N(6)...O(34^c)	2.869(7)
Cl(1)–Cu(1)–Cl(1^a)	91.51(7)	Cl(1^a)–Cu(1)–N(3)	95.48(11)
Cl(1)–Cu(1)–N(1)	170.59(11)	N(1)–Cu(1)–N(2)	79.82(14)
Cl(1)–Cu(1)–N(2)	99.11(11)	N(1)–Cu(1)–N(3)	79.86(15)
Cl(1)–Cu(1)–N(3)	99.58(11)	N(2)–Cu(1)–N(3)	158.05(14)
Cl(1^a)–Cu(1)–N(1)	97.90(12)	Cu(1)–Cl(1)–Cu(1^a)	88.49(7)
Cl(1^a)–Cu(1)–N(2)	95.43(11)	N(6)–H(6N)...O(34^c)	163(6)
[Zn(TPPZ)Cl_2]			
Zn(1)–Cl(1)	2.2759(10)	Zn(1)–N(2)	2.204(3)
Zn(1)–Cl(2)	2.2365(9)	Zn(1)–N(3)	2.175(3)
Zn(1)–N(1)	2.1561(24)		
Cl(1)–Zn(1)–Cl(2)	115.08(4)	Cl(2)–Zn(1)–N(2)	101.36(7)
Cl(1)–Zn(1)–N(1)	98.56(8)	Cl(2)–Zn(1)–N(3)	96.53(7)
Cl(1)–Zn(1)–N(2)	95.93(7)	N(1)–Zn(1)–N(2)	73.11(9)
Cl(1)–Zn(1)–N(3)	106.60(8)	N(1)–Zn(1)–N(3)	73.31(9)
Cl(2)–Zn(1)–N(1)	146.35(8)	N(2)–Zn(1)–N(3)	141.80(10)

Symmetry operation: ^{a}2−x, 1−y, −z; ^{b}1−x, 1−y, −z; ^{c}−1+x, y, z.

goes to completion and gives large pale yellow crystals of a neutral five-coordinate Zn(II) mononuclear complex where TPPZ is mono-tridentate, Fig. 4. The coordination of the zinc atom is best described as a trigonal bypyramid. The zinc atom lies in the plane through atoms N(1), Cl(1) and Cl(2) while atoms N(2) and N(3) are displaced by −2.097(3) and 2.024(3) Å either side of this plane. The central Zn–N(pyrazine) distance 2.156(2) Å is longer than the central Zn–N(pyridine) distance of 2.112 Å in the complex Zn(terpy)Cl_2 [18]. The lateral Zn–N(pyridine) and the Zn–Cl distances are similar in the two complexes, Table 4. As in the above copper complex the ligand is considerably distorted. Here the pyrazine ring has a twist conformation with a dihedral angle between planes C′ and C″ of 10.6(2)°. The coordinated pyridine rings A and B are inclined to one another by 13.5(1)°. The dihedral angles between the various pyridine rings are given in Table 5.

Tetragonal form of TPPZ

With a ligand to metal ratio of only 1:1, at room temperature, no zinc complex was formed. EtOH was added to completely dissolve the ligand and the solution kept at 50 °C for 4 h. On cooling a small quantity of the mononuclear Zn(II) complex was formed and a large number of transparent block-like crystals. The X-ray crystal structure analysis of the latter indicated that it was a tetragonal form of TPPZ [6]. When TPPZ was recrystallized from $CHCl_3$ [7] or CH_2Cl_2 (this work) a monoclinic modification was obtained. Both forms possess C_i symmetry with planar central pyrazine rings.

Supplementary material

Further data (atomic fractional coordinates, complete distances and angles, etc.) can be obtained on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Other details are available from the author H.St.-E.

Acknowledgement

We wish to thank the Swiss National Science Foundation for financial support.

TABLE 4. Selected distances (Å) in Cu(II) and Zn(II) complexes of TPPZ and terpy

	$[Cu_2(TPPZ)(H_2O)_4]$	$[Cu(terpy)Cl_2]$ [13]	$[Cu(terpy)Cl_2](H_2O)$ [14]	$[Cu(terpy)(NCO)(H_2O)](NO_3^-)$ [15]
Cu–N(1)	1.962(3)	1.952	1.952	1.942
Cu–N(2)	2.007(4)	2.056	2.044	2.047
Cu–N(3)	1.999(4)	2.052	2.039	2.043
Cu–Cl(1)		2.252	2.221	
Cu–Cl(2)		2.469	2.554	
Cu–OW(1)	1.955(3)			
Cu–NCO				1.893
Cu–OW(2)	2.209(4)			2.210
Cu...Cu	6.497(2)^{a}	5.54	4.01	3.950
	$[Cu(TPPZH)Cl]_2$	$[Cu(terpy)Cl]_2$ [16]	$[Cu(terpy)(NCO)(H_2O)]_2(PF_6^-)_2$ [15]	$[\{Cu(terpy)Cl_2\}CuCl_2]_2$ [17]
Cu–N(1)	1.943(4)	1.909	1.933	1.938
Cu–N(2)	2.013(4)	2.021	2.038	2.021
Cu–N(3)	2.022(4)	2.017	2.028	2.014
Cu–Cl(1)	2.236(2)	2.218		2.221
Cu–Cl(1)	2.682(3)^{b}	2.723		2.613
Cu–NCO			1.906	
Cu–Ow			2.298	
Cu...Cu	3.446^{b}	3.510	3.678	3.595
	$[Zn(TPPZ)Cl_2]$	$[Zn(terpy)Cl_2]$ [18]		
Zn–N(1)	2.156(2)	2.112		
Zn–N(2)	2.204(3)	2.196		
Zn–N(3)	2.178(3)	2.196		
Zn–Cl(1)	2.276(1)	2.274		
Zn–Cl(2)	2.237(1)	2.274		

Symmetry operations: $^{a}={}^{b}2-x,\ 1-y,\ -z$.

TABLE 5. Dihedral angles (°) between the pyrazine ring (C) and the coordinated pyridine rings (A and B) and the uncoordinated pyridine rings (D and E)

Angle	$[Cu_2(TPPZ)(H_2O)_4]$	$[Cu(TPPZH)Cl]_2$	$[Zn(TPPZ)Cl_2]$	TPPZ	
				monoclinic	tetragonal
A^B	34.3(2)	1.9(2)	13.5(1)	62.4	60.4
A^C(C′)	21.3(3)	13.7(3)	7.8(2)	48.9	59.0
B^C(C′)	21.7(3)	13.0(3)	21.0(1)	51.7	46.4
D^E		49.8(2)	37.0(1)		
D^C″		38.2(4)	22.8(2)		
E^C″		41.8(3)	43.9(2)		
A^D		46.8(2)	37.6(1)		
A^E		62.4(2)	61.9(1)		
B^D		48.1(2)	50.9(1)		
B^E		61.9(2)	74.1(1)		
C′^C″	0	8.0(2)	10.6(2)	0	0

Ring A = N(2), C(3–7); Ring B = N(3), C(8–12); Ring C = N(1), C(1), C(2), and N(1a), C(1a), C(2a) or N(4), C(13), C(14); Ring C′ = N(1), C(1), C(2); Ring C″ = N(4), C(13), C(14); Ring D = N(5), C(15–19); Ring E = N(6), C(20–24).

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