Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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References

Blaschette, A., Jones, P. G., Hamann, T., Näveke, M., Schomburg, D., Cammenga, H. K., Epple, M. & Steppuhn, I. (1993). *Z. Anorg. Allg. Chem.* **619**, 912–922.

Blaschette, A., Nagel, K.-H. & Jones, P. G. (1993). *Z. Naturforsch. Teil B*, **48**, 893–897.

Blaschette, A., Nagel, K.-H. & Jones, P. G. (1994). *Z. Naturforsch. Teil B*, **49**, 36–42.

Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.

Hamann, T., Blaschette, A. & Jones, P. G. (1997). *Z. Anorg. Allg. Chem.* In the press.

Jones, P. G., Moers, O. & Blaschette, A. (1997). *Acta Cryst.* C**53**, 1809–1811.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments, Inc., Madison, USA.

Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

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Dichloro[2,3,5,6-tetra(2-pyridyl)pyrazine]-copper(II), [$CuCl_2(C_{24}H_{16}N_6)$]

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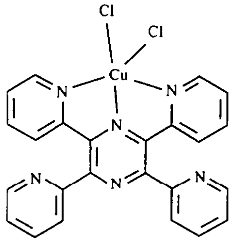
Abstract

In molecules of [$Cu(TPPZ)Cl_2$] [TPPZ is 2,3,5,6-tetra(2-pyridyl)pyrazine], the central Cu^{II} atom has a square-pyramidal coordination environment, defined by three TPPZ N atoms and by two chloro ligands, one of which is apical. The other three TPPZ N atoms remain uncoordinated. The Cu—N distances are in the range 1.975 (2)–2.058 (2) Å and the Cu—Cl bond lengths are 2.214 (1) and 2.465 (1) Å.

Comment

Tetra(2-pyridyl)pyrazine (TPPZ), known for nearly 30 years, attracts the attention of chemists because it could act as a bis-tridentate ligand. However, this would require all five aromatic rings to be coplanar. Mutual steric hindrance of neighbouring pyridine rings (due to H atoms on their β-C atoms) does not allow a coplanar arrangement and the bis-tridentate bonding mode can be achieved only by twisting the pyrazine ring (Graf, Greaves & Stoeckli-Evans, 1993; Valigura, Ondrejovič & Anderson, 1997).

Complexes with metal-to-TPPZ ratios of 1:1 and 1:2 can be obtained. The 1:1 complexes may be either mononuclear or polynuclear through the formation of infinite chains. The crystal structure of [$Cu(TPPZ)Cl_2$], (I), has been determined in order to distinguish between these two possibilities.



(I)

The crystal consists of discrete [$Cu(TPPZ)Cl_2$] molecules and is isostructural with [$Zn(TPPZ)Cl_2$], (II) (Graf, Greaves & Stoeckli-Evans, 1993) (see Table 1). The metal-coordination polyhedra of (I) and (II) are best described as tetragonal pyramids, showing trigonality τ parameters (Addison *et al.*, 1984) of 0.11 and 0.07, respectively. The basal planes are formed by three TPPZ N atoms and by one chloro ligand; deviations from the best basal plane are less than 0.030 (2) Å for (I) and less than 0.076 (2) Å for (II). The longer *M*—Cl bond in each complex involves the apical chloro ligand. The displacement of this ligand from the basal plane varies only slightly, from 2.752 (1) Å in (I) to 2.811 (2) Å in (II). The displacements of the metal atom from the basal plane are 0.327 (1) and 0.572 (2) Å for (I) and (II), respectively. The greater displacement of the Zn atom, together with the similar sizes of the coordination polyhedra of both complexes, result in the *M*—Cl(apical) distance being shorter in (II) than in (I) (see Table 1). The difference in the central-atom displacements from the basal plane may be explained by the difference in their covalent radii (r_{Cu} = 1.17 and r_{Zn} = 1.25 Å).

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The other three N atoms of the TPPZ ligand remain uncoordinated and the uncoordinated pyridine rings are turned out of the plane formed by the N atoms of the coordinated aromatic rings [dihedral angles 142.9 (1) and 57.8 (1)° in (I)]. In spite of this, twisting of the pyrazine ring is also observed [the dihedral angle between the C4—N1—C1 and C3—N2—C2 planes is 169.3 (2)°]. Similar twisting was found in (II).

An interesting feature of both crystal structures is the impairment of π-electron delocalization in the aromatic pyrazine ring due to the stress that is caused by forming three M—N bonds [in (I), C—C bond lengths are 1.410 (3) and 1.414 (3) Å, and C—N bond lengths are in the range 1.333 (3)–1.337 (3) Å; in (II), corresponding distances are 1.411 and 1.415 Å (C—C), and 1.329–1.343 Å (C—N)].

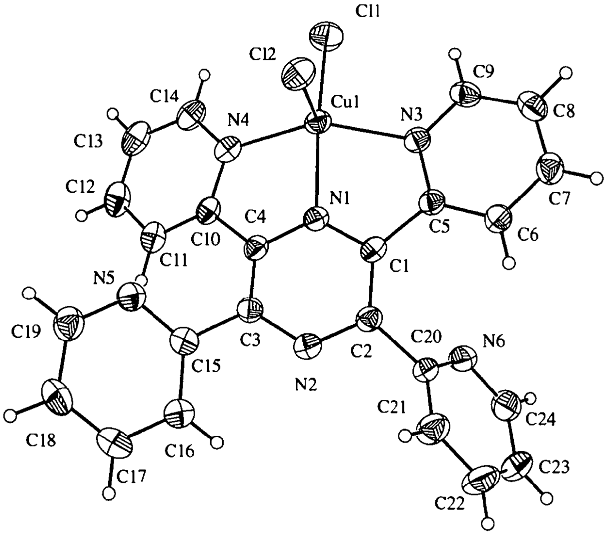

Fig. 1. The molecular structure of the title compound (*ORTEP*II; Johnson, 1971), with displacement ellipsoids at 50% probability.

Experimental

$[Cu(TPPZ)Cl_2]$ was prepared by mixing solutions of 2 mmol of TPPZ in 150 ml of dimethylformamide (DMF) and 2 mmol of $CuCl_2.2H_2O$ in 15 ml of DMF. The resulting dark green solution was filtered and allowed to stand at room temperature.

Crystal data

$[CuCl_2(C_{24}H_{16}N_6)]$
$M_r = 522.87$
Monoclinic
$P2_1/n$
$a = 14.5643\ (11)$ Å
$b = 7.1338\ (11)$ Å
$c = 21.231\ (2)$ Å
$\beta = 105.021\ (8)°$
$V = 2130.5\ (4)$ Å^3
$Z = 4$
$D_x = 1.630$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 6.6$–$11.5°$
$\mu = 1.303$ mm^{-1}
$T = 291\ (2)$ K
Block
0.80 × 0.60 × 0.40 mm
Deep green

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.501$, $T_{max} = 0.594$
3720 measured reflections
3569 independent reflections
3088 reflections with $I > 2\sigma(I)$

$R_{int} = 0.020$
$\theta_{max} = 25.1°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 8$
$l = -25 \rightarrow 24$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.093$
$S = 1.084$
3569 reflections
299 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 1.3329P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0041 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for $[Cu(TPPZ)Cl_2]$ and $[Zn(TPPZ)Cl_2]$*

	(I)[a]	(II)[b]
M—N1	1.975 (2)	2.156 (3)
M—N3	2.058 (2)	2.204 (3)
M—N4	2.031 (2)	2.175 (3)
M—Cl1	2.214 (1)	2.237 (1)
M—Cl2	2.465 (1)	2.276 (1)
Cl1—M—Cl2	106.26 (3)	115.08 (4)
Cl1—M—N1	160.84 (7)	146.35 (8)
Cl1—M—N3	100.08 (6)	101.36 (7)
Cl1—M—N4	97.14 (6)	96.53 (7)
Cl2—M—N1	92.89 (6)	98.56 (8)
Cl2—M—N3	90.89 (6)	95.93 (7)
Cl2—M—N4	103.07 (6)	106.60 (8)
N1—M—N3	78.56 (8)	73.11 (9)
N1—M—N4	78.70 (8)	73.31 (9)
N3—M—N4	153.81 (8)	141.8 (1)

Notes: (*a*) $[Cu(TPPZ)Cl_2]$ (this work); (*b*) $[Zn(TPPZ)Cl_2]$ (Graf, Greaves & Stoeckli-Evans, 1993).

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1342). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Graf, M., Greaves, B. & Stoeckli-Evans, H. (1993). *Inorg. Chim. Acta*, **204**, 239–246.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Valigura, D., Ondrejovič, G. & Anderson, O. P. (1997). In preparation.

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Cadmium Glutamate Dihydrate

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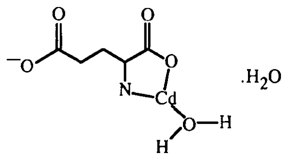
Abstract

Crystals of aqua(glutamato)cadmium hydrate, $[Cd(C_5H_7O_4)(H_2O)].H_2O$, are orthorhombic, space group $P2_12_12_1$. The compound is nearly isostructural with the corresponding zinc and copper complexes. The coordination about the cadmium is a distorted octahedron, with Cd—O1 2.282 (3), Cd—O2 2.254 (3), Cd—O3 2.303 (2), Cd—O4 2.449 (2), Cd—O5 2.255 (2) and Cd—N 2.290 (2) Å.

Comment

In our laboratories, we have been investigating the optical properties of metal–glutamate complexes. By performing the Kurtz test (Kurtz & Perry, 1968; Kurtz & Dougherty, 1978), we have found that Zn, Cu and Cd glutamate complexes have excellent second-order nonlinearity. Upon irradiation at 1064 nm, the powders show intense green light at 532 nm. Also, large single crystals can be grown from these materials, making them possible candidates for non-linear optical materials. Second-order non-linear optical materials have numerous applications as second-harmonic generators, optical parametric oscillators and electro-optic modulators.

The coordination about the Cd atom in the title compound, (I), is very similar to the square pyramid found in the corresponding Zn adduct (Gramaccioli, 1966). The additional glutamate O atom (O4) at 2.449 Å completes the distorted octahedron exhibited by both the Zn and Cu complexes (Gramaccioli & Marsh, 1966; Gramaccioli, 1966). The Cd atom lies 0.22 Å from the base of the pyramid and is approximately equidistant from all five atoms. The average distance from the Cd atom to the five nearest neighbors is 2.277 Å, which is at least 0.2 Å larger than those reported in the Cu and Zn studies (2.047 and 2.069 Å, respectively; Gramaccioli & Marsh, 1966; Gramaccioli, 1966). However, the O4 atom is at least 0.12 Å closer in the Cd complex.



(I)

There are six H atoms available for hydrogen bonding [four from the two water molecules (H8—H11) and two from the nitrogen (H6 and H7)], however, only five actively participate in hydrogen bonding. The four O—H···O distances of 2.717 (3)–2.786 (3) Å and the N—H6···O1 distance of 2.967 (3) Å are typical values indicative of moderately strong interactions. The second H atom on the nitrogen (H7) does not participate in hydrogen bonding.

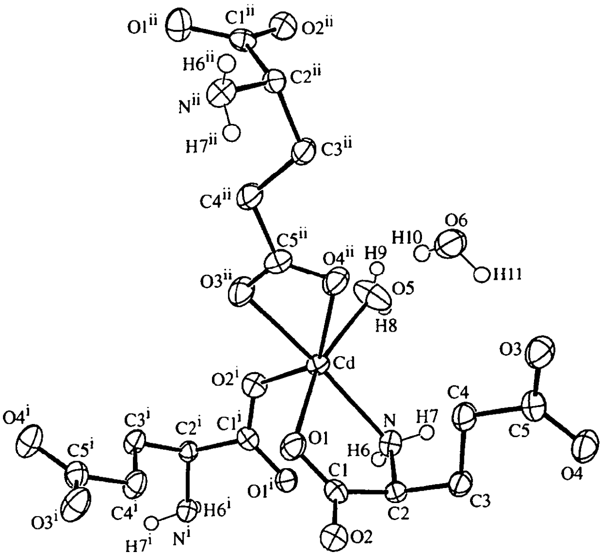


Fig. 1. The molecular structure of cadmium glutamate dihydrate along with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

A one liter solution of 0.34 *M* L-glutamic acid was heated to 373 K with gentle stirring and the pH was adjusted to 7.0 with 6 *M* NaOH. A one liter solution of 0.34 *M* cadmium acetate was added dropwise to the glutamic acid solution over a period of 1 h. The solution was removed from the heat. Cadmium glutamate was precipitated by adjusting the pH to 10.0 (10 *M* NaOH). The precipitate was then washed with ethanol and ether and dried for 48 h at 323 K. Cadmium glutamate was

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