Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Dipotassium aquabis(pyrazine-2,3-dicarboxylato-κ^2N,O)cuprate(II) hexahydrate

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Received 7 July 2003
Accepted 5 August 2003
Online 30 August 2003

The crystal structure of the title compound, $K_2[Cu(C_6H_2N_2O_4)_2(H_2O)]\cdot 6H_2O$, consists of mononuclear $[Cu(pzdc)_2(H_2O)]^{2-}$ complex anions (pzdc is pyrazine-2,3-dicarboxylate), K^+ cations and water molecules, held together by means of K—O/*OW* bonds and an extended *OW*—H···O/*OW* and *OW*—H···N hydrogen-bond network. The distorted square-pyramidal coordination of the Cu atom is achieved by two N and two O donor atoms from two bidentate pzdc ligands in the basal plane, while a water molecule occupies the apical position with a longer metal–O distance.

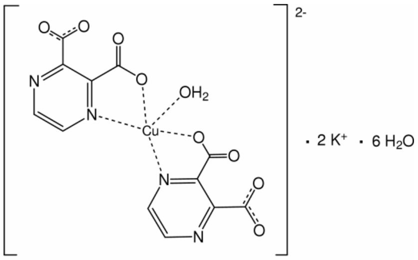
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.054
wR factor = 0.158
Data-to-parameter ratio = 19.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Pyrazine-2,3-dicarboxylic acid (H_2pzdc; Takusagawa & Shimada, 1973) and its dianion (Richard *et al.*, 1973; Nepveu *et al.*, 1993) have proved to be well suited for the construction of multidimensional frameworks (nD, n = 1–3), due to the presence of two adjacent carboxylate groups (O donor atoms) as substituents on the *N*-heterocyclic pyrazine ring (N donor atoms). This permits multiple coordination modes and the usual non-coplanarity of these carboxylate groups, which favours the construction of high-dimensional covalent networks (O'Connor *et al.*, 1982; Kondo *et al.*, 1999; Zou *et al.*, 1999; Kitaura *et al.*, 2002). One approach to the design of extended homo- and heterometallic coordination polymers is to use mononuclear transition metal complexes possessing multidentate terminal ligands with free coordination sites, which can further connect a second metal centre, thus increasing the dimensionality of the coordination network (Pilkington *et al.*, 2001; Ciurtin *et al.*, 2003). This paper reports the synthesis and crystal structure of the potassium salt of one of these complexes, namely, $K_2[Cu(C_6H_2N_2O_4)_2(H_2O)]\cdot 6H_2O$, (I). This compound is a potential building block in the design of extended metal–organic networks, by replacing the K^+ cations with transition metal ions.



(I)

As shown in Fig. 1, the Cu^{II} atom of (I) is located on a general position and is surrounded by two *N*,*O*-bidentate pzdc

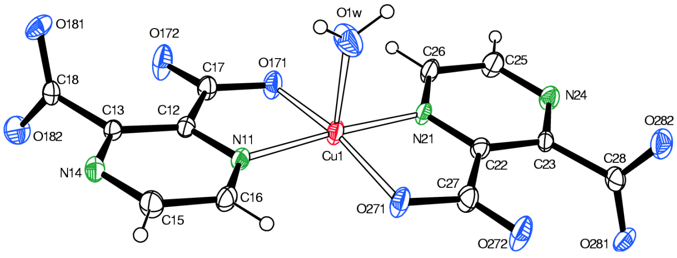


Figure 1
A view of the *trans*-$[Cu(C_6H_2N_2O_4)_2(H_2O)]^{2-}$ complex anion in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

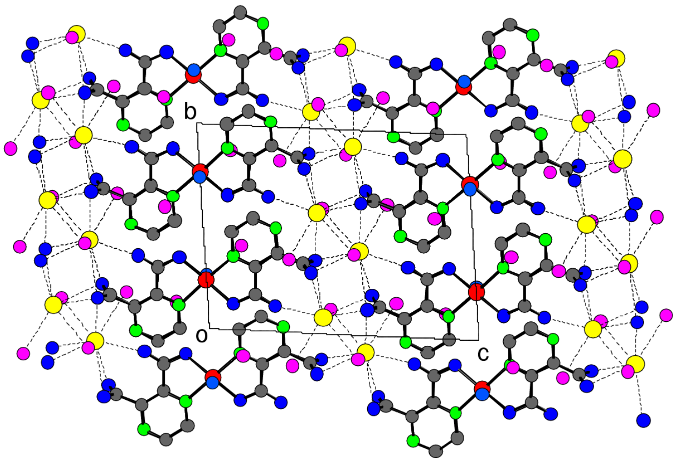


Figure 2
The crystal structure of (I), viewed along the *a* axis. H atoms have been omitted for clarity. The coordination environment of the K^+ cations is shown by dotted lines.

ligands and a water molecule, which impose a distorted square-pyramidal CuN_2O_3 environment. The two pzdc anions coordinate to the metal centre *via* one pyrazine N atom and one O atom from the adjacent carboxylate group, forming a five-membered ring. These four donor atoms form the basal plane [maximum deviation from the mean plane 0.074 (3) Å, for atom N21], while the Cu atom is displaced by 0.1612 (4) Å from this plane towards the apical position, which is occupied by a water molecule. The Cu—O1*W* bond distance of 2.203 (3) Å is substantially longer than the equatorial Cu—O/N distances (<2.00 Å). The coordination distances (Table 1) are similar to those reported for analogous Cu^{II} complexes containing the pzdc ligand (Kondo *et al.*, 1999; Kitaura *et al.*, 2002; Wang *et al.*, 2003). The remaining O atoms of the carboxylate groups are connected to K^+ cations (Fig. 2). The C—O bond distances of the K-bound O atoms are somewhat shorter (<1.25 Å) than those involving the O atoms attached to the Cu centres (>1.28 Å).

For both pzdc ligands, the carboxylate group coordinated to the Cu atoms is nearly coplanar with the pyrazine ring [dihedral angles 5.5 (1) and 4.5 (1)°], while the remaining one is twisted by 85.0 (1) and 82.5 (1)°, respectively. Both K^+ cations are surrounded by nine O atoms, six from four carboxylate groups and three from water molecules, with K—O distances ranging from 2.688 (3) to 3.221 (3) Å. An extensive O*W*—H···O, O*W*—H···N and O*W*—H···O*W* hydrogen-bond network involving the water molecules and the heteroatoms of the pzdc ligands further stabilizes the crystal packing (Table 2).

Experimental

Blue crystals of (I) suitable for X-ray analysis were obtained by slow diffusion of a water–methanol mixture of pyrazine-2,3-dicarboxylic acid (84 mg, 0.5 mmol), adjusted to pH ~7 with 1 *N* KOH, into an aqueous solution containing $Cu(NO_3)_2\cdot 3H_2O$ (60 mg, 0.25 mmol) (yield 60–70%, based on Cu). Elemental analysis (C/H/N/Cu), found: 24.32, 3.08, 9.28, 10.50%; calculated for $C_{12}H_{18}Cu\ K_2N_4O_{15}$: 24.02, 3.02, 9.34, 10.59%.

Crystal data

$K_2[Cu(C_6H_2N_2O_4)_2(H_2O)]\cdot 6H_2O$
$M_r = 600.05$
Triclinic, $P\overline{1}$
$a = 6.830$ (1) Å
$b = 11.339$ (2) Å
$c = 14.627$ (2) Å
$\alpha = 94.58$ (1)°
$\beta = 95.92$ (1)°
$\gamma = 102.54$ (2)°
$V = 1093.8$ (3) Å^3
$Z = 2$
$D_x = 1.822$ Mg m^{-3}
$D_m = 1.82$ (1) Mg m^{-3}
Density measured by flotation in a mixture of carbon tetrachoride and bromoform
Mo *Kα* radiation
Cell parameters from 6673 reflections
$\theta = 3.2$–30.6°
$\mu = 1.46$ mm^{-1}
$T = 294$ (1) K
Hexagonal plate, blue
0.4 × 0.4 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
Absorption correction: analytical (*CrysAlisRED*; Oxford Diffraction, 2002)
$T_{min} = 0.572$, $T_{max} = 0.854$
11 367 measured reflections
6673 independent reflections
3580 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 30.6°$
$h = -9 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.158$
$S = 0.94$
6673 reflections
349 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O171	1.953 (3)	K1—O2W^{iii}	2.994 (3)
Cu1—O271	1.953 (2)	K1—O3W^{iii}	3.179 (4)
Cu1—N11	1.994 (3)	K2—O172	2.785 (3)
Cu1—N21	1.990 (2)	K2—O181	2.884 (3)
Cu1—O1*W*	2.203 (3)	K2—O182	3.221 (3)
K1—O181	2.866 (3)	K2—O281^{ii}	2.860 (2)
K1—O182	3.148 (3)	K2—O282^{iv}	3.067 (3)
K1—O182^{i}	2.836 (3)	K2—O282^{ii}	3.153 (3)
K1—O272^{ii}	2.688 (3)	K2—O4*W*	2.783 (3)
K1—O281^{ii}	2.941 (3)	K2—O4W^{v}	3.067 (3)
K1—O282^{ii}	3.108 (3)	K2—O5*W*	3.008 (4)
K1—O2*W*	2.762 (3)		

Symmetry codes: (i) $2-x, 2-y, 1-z$; (ii) $x, y, 1+z$; (iii) $1-x, 2-y, 1-z$; (iv) $1-x, 1-y, -z$; (v) $2-x, 1-y, 1-z$.

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O6*W*	0.85 (3)	1.89 (3)	2.714 (4)	163 (3)
O1*W*—H12*W*···O7*W*$^{\mathrm{iv}}$	0.85 (3)	1.81 (4)	2.639 (4)	165 (4)
O2*W*—H21*W*···O182$^{\mathrm{vi}}$	0.85 (3)	2.20 (3)	2.866 (4)	136 (4)
O2*W*—H22*W*···N14$^{\mathrm{iii}}$	0.85 (1)	2.15 (2)	2.894 (4)	146 (4)
O3*W*—H31*W*···O6*W*	0.85 (1)	2.11 (3)	2.743 (4)	132 (4)
O3*W*—H32*W*···O181	0.86 (4)	1.90 (3)	2.708 (4)	158 (4)
O4*W*—H41*W*···N24$^{\mathrm{vii}}$	0.85 (1)	2.20 (3)	2.964 (4)	149 (4)
O4*W*—H42*W*···O282$^{\mathrm{viii}}$	0.85 (3)	2.32 (3)	2.956 (4)	132 (3)
O5*W*—H51*W*···O281$^{\mathrm{vii}}$	0.85 (3)	1.87 (3)	2.715 (4)	168 (4)
O5*W*—H52*W*···O282$^{\mathrm{iv}}$	0.85 (3)	2.02 (3)	2.779 (4)	149 (4)
O6*W*—H61*W*···O271$^{\mathrm{ix}}$	0.85 (1)	2.10 (3)	2.873 (4)	152 (4)
O6*W*—H61*W*···O272$^{\mathrm{ix}}$	0.85 (1)	2.48 (2)	3.228 (4)	147 (3)
O6*W*—H62*W*···N11$^{\mathrm{vi}}$	0.85 (1)	2.52 (1)	3.279 (5)	149 (3)
O7*W*—H71*W*···O5*W*	0.85 (1)	1.85 (2)	2.692 (4)	175 (5)
O7*W*—H72*W*···O171	0.85 (3)	2.13 (3)	2.953 (4)	161 (4)
O7*W*—H72*W*···O172	0.85 (3)	2.39 (3)	3.087 (5)	139 (4)

Symmetry codes: (iv) $1-x, 1-y, -z$; (vi) $x-1, y, z$; (iii) $1-x, 2-y, 1-z$; (vii) $2-x, 1-y, -z$; (viii) $1+x, y, 1+z$; (ix) $1-x, 2-y, -z$.

The water H atoms were located and refined subject to the restraints O—H = 0.85 (3) Å and H···H = 1.35 (3) Å, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{O})$. The C-bound H atoms were positioned geometrically, with C—H = 0.93 Å, and were included in the refinement in the riding-model approximation, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the Ministerio de Ciencia y Tecnología (project MAT2002-03166). GB thanks Gobierno Vasco for a Doctoral Fellowship.

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