Aqua(di-2-pyridylamine-$\kappa^2N^2,N^{2\prime}$)(D-gluconato-$\kappa^2O,O^\prime$)copper(II) trihydrate

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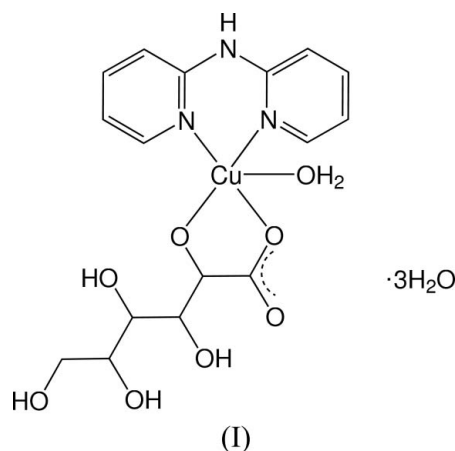In the title complex, [Cu($C_6H_{10}O_7$)($C_{10}H_9N_3$)(H_2O)]·$3H_2O$, the Cu atom has a distorted square-pyramidal geometry coordinated by two O atoms of a D-gluconate ligand, two N atoms of a bidentate di-2-pyridylamine ligand and a water O atom. The deprotonated α-hydroxyl and carbonate O atoms of the D-gluconate ligand form a five-membered chelate ring with the Cu atom. The crystal structure is stabilized both by all of the available hydrogen bonds and by π–π stacking interactions between di-2-pyridylamine ligands.

Comment

The interaction of a sugar with metal ions is very important for the biological properties of carbohydrates, such as the interaction of D-gluconic acid or D-glucono-1,5-lactone with metal ions (Escandar *et al.*, 1996; Tajmir-Riahi, 1990). The crystal structures of metal complexes of D-gluconic acid have been reported, for example of Mn[II], Pb[II] (Lis, 1979, 1984a), Na[I], K[I] and Rb[I] (Lis, 1984b; Littleton, 1953; Jeffrey & Fasiska, 1972). In the present study, the crystal structure of the copper(II) complex, (I), of D-gluconic acid with di-2-pyridylamine (BPA) is reported.

(I)

The molecular structure of (I) (Fig. 1) shows the Cu atom to have a distorted square-pyramidal geometry in which the basal plane is defined by two O atoms of the D-gluconate ligand and two N atoms of the bidentate BPA ligand; a water O atom occupies the apical site of the pyramid. A five-membered chelate ring, Cu1/O1/C11/C12/O3, is formed between the Cu atom and the D-gluconate ligand, and a six-membered chelate ring, Cu1/N1/C5/N2/C6/N3, between the Cu atom and the BPA ligand.

The two pyridyl rings in the BPA ligand are nearly coplanar, with the interplanar angle being 14.5 (2)°. The dihedral angle
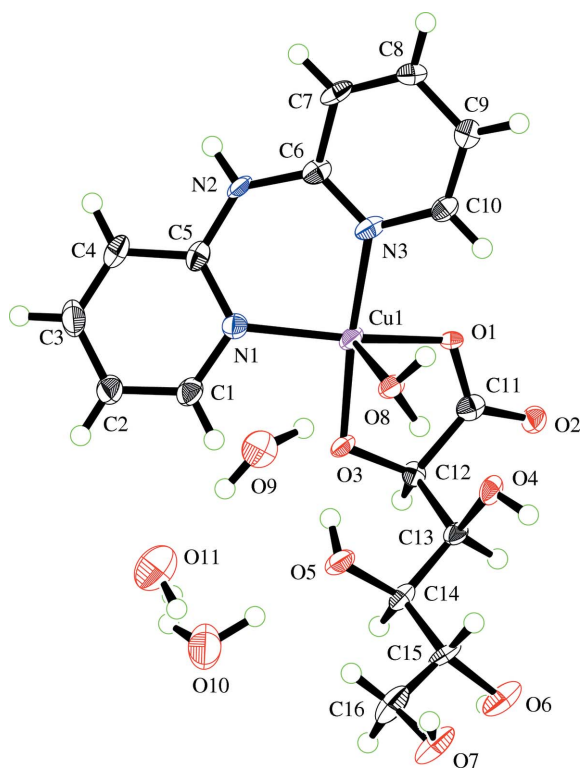
Figure 1
The asymmetric unit of (I) with the the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.
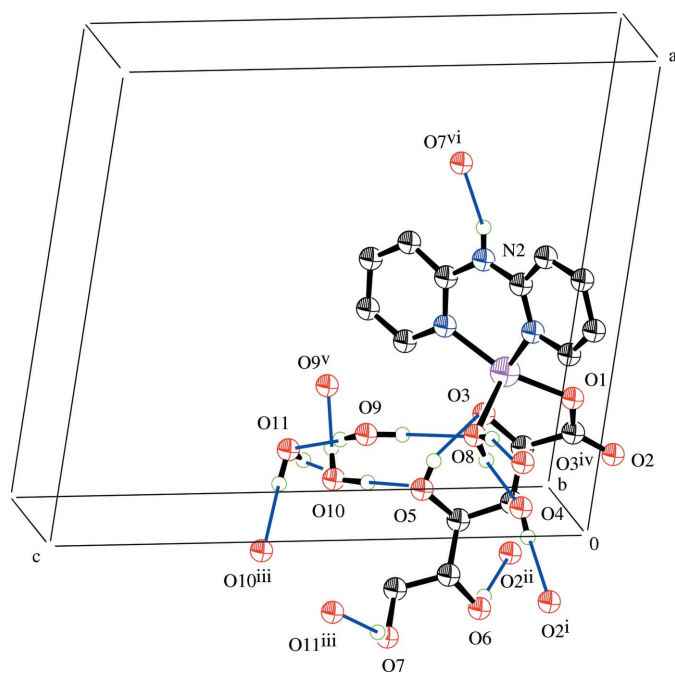

Figure 2
A view of the hydrogen bonding (blue lines) in (I). [Symmetry codes: (i) $-x, y - \frac{1}{2}, -z$; (ii) $-x, y + \frac{1}{2}, -z + 1$; (iii) $-x, y - \frac{1}{2}, -z + 1$; (iv) $x, y - 1, z$; (v) $x, y + 1, z$; (vi) $x + 1, y, z$.]

between the planes formed by N1/Cu1/N3 and O1/Cu1/O3 is 22.3 (2)°. The atoms N1, N3, O1 and O3 deviate by 0.180 (4), −0.185 (4), 0.203 (3) and −0.197 (3) Å, respectively, from their least-squares plane and the Cu atom lies above this plane

by 0.1923 (5) Å in the direction of the coordinated water molecule.

The Cu1—O1, Cu1—O3 and Cu1—O8 bond lengths (Table 1) are slightly longer than the respective distances of the square-pyramidal copper(II) complex of lactic acid with 1,10-phenanthroline [1.947 (4), 1.904 (4) and 2.299 (4) Å; Carballo *et al.*, 2001]. The Cu1—N1 and Cu1—N3 bond lengths are also longer than those in dichloro(BPA)copper(II) [1.948 (6) Å; Spodine *et al.*, 1996].

The carbon chain (C11—C16) of the D-gluconate ligand extends in a nearly planar zigzag form. Atoms O3, O1, C11 and C12 atoms of the D-gluconate ligand lie in almost the same plane, as indicated by the torsion angle of 8.2 (6)° for O1—C11—C12—O3. In most metal–D-gluconate complexes [*e.g.* Na^I, K^I, Rb^I (Lis, 1984b; Littleton, 1953; Jeffrey & Fasiska, 1972), Pb^{II} (Lis, 1984a) and Mn^{II} (Lis, 1979)], both O atoms of the deprotonated α-hydroxyl group and the carboxylate group are coordinated to the metal ions, as found in (I).

The crystal structure is stabilized by all of the available O—H···O and N—H···O hydrogen bonds (Table 2 and Fig. 2). There are π–π stacking interactions between the pyridine rings of BPA ligands [the distance between the centers of gravity of the pyridine rings, $Cg1$ (N1/C1–C5) and $Cg2$ (N3/C6–C10), is 3.76 (7) Å (McArdle, 1995)], which also stabilize the crystal packing.

Experimental

Equimolar quantities of di-2-pyridylamine (3.8 mg) and copper(II) gluconate (10 mg) were dissolved in a 70% (*v/v*) methanol–water mixture (6 ml). The solution was concentrated to *ca* 1 ml at 343 K and allowed to evaporate slowly at room temperature. After several weeks, light-blue needles of (I) were obtained from the mother liquor.

Crystal data

[Cu(C$_6$H$_{10}$O$_7$)(C$_{10}$H$_9$N$_3$)-(H$_2$O)]·3H$_2$O	$V = 1021.3$ (14) Å^3
$M_r = 500.96$	$Z = 2$
Monoclinic, $P2_1$	$D_x = 1.629$ Mg m^{-3}
$a = 13.02$ (1) Å	Mo $K\alpha$ radiation
$b = 5.447$ (5) Å	$\mu = 1.14$ mm^{-1}
$c = 14.52$ (1) Å	$T = 123.0$ K
$\beta = 97.34$ (4)°	Needle, light blue
	$0.40 \times 0.05 \times 0.01$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	10058 measured reflections
ω scans	4365 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	2251 reflections with $F^2 > 2\sigma(F^2)$
$T_{min} = 0.576$, $T_{max} = 0.989$	$R_{int} = 0.074$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.85$	$\Delta\rho_{max} = 0.58$ e Å^{-3}
4365 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
294 parameters	Absolute structure: Flack (1983), 1792 Friedel pairs
H-atom parameters constrained	Flack parameter: −0.05 (2)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.965 (3)	Cu1—N3	1.985 (4)
Cu1—O3	1.932 (3)	O1—C11	1.271 (6)
Cu1—O8	2.342 (3)	O2—C11	1.259 (6)
Cu1—N1	2.015 (4)	O3—C12	1.417 (5)
O1—Cu1—O3	84.5 (1)	N1—Cu1—N3	91.4 (2)
O1—C11—C12—O3	8.2 (6)		

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

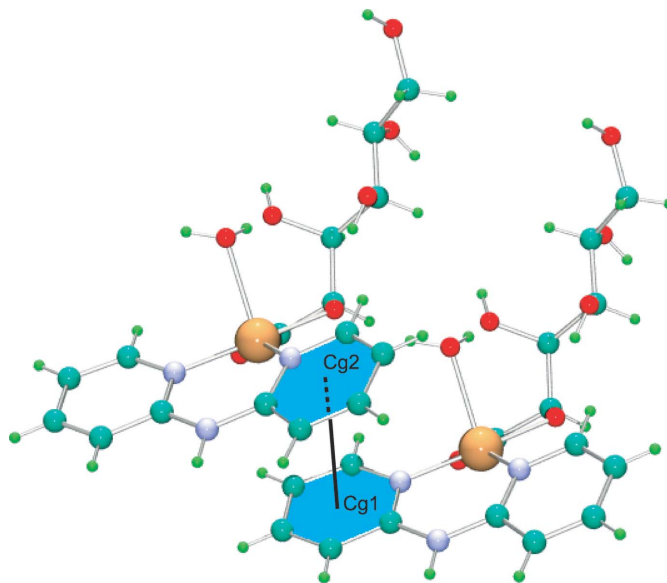| $D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O4—H16···O2[i]	0.82	1.88	2.693 (6)	173
O5—H17···O3	0.82	1.87	2.606 (5)	148
O6—H18···O2[ii]	0.82	2.11	2.908 (5)	164
O7—H19···O11[iii]	0.82	1.94	2.716 (6)	158
O8—H20···O3[iv]	0.89	1.85	2.723 (5)	166
O8—H21···O4	0.92	1.83	2.740 (6)	168
O9—H22···O11	0.90	1.81	2.713 (6)	180
O9—H23···O8	0.96	1.93	2.890 (6)	180
O10—H24···O5	1.00	1.73	2.722 (6)	173
O10—H25···O9[v]	0.91	1.82	2.737 (6)	180
O11—H26···O10[iii]	0.95	1.86	2.807 (6)	179
O11—H27···O10	0.93	1.80	2.729 (7)	178
N2—H5···O7[vi]	0.86	1.93	2.747 (6)	157

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

H atoms were included in the riding-model approximation with C—H = 0.93-0.98 Å, O—H = 0.82-1.00 Å, and N—H = 0.86 Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$ and $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976), *ORTEP-3 for Windows* (Farrugia, 1997) and *ORTEX* (McArdle, 1995); software used to prepare material for publication: *CrystalStructure*.

Figure 3
A view of the π–π stacking interaction in (I). *Cg*1 is the centroid of the pyridine ring N1/C1–C5, and *Cg*2 is that of N3/C6–C10.

References

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Carballo, R., Covelo, B., Balvoa, S., Castineiras, A. & Niclos, J. (2001). *Z. Anorg. Allg. Chem.* **627**, 948–954.
Escandar, G. M., Salas Peregrin, J. M., Gonzalez Sierra, M. & Martino, D. (1996). *Polyhedron*, **15**, 2251–2261.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.
Jeffrey, G. A. & Fasiska, E. J. (1972). *Carbohydr. Res.* **21**, 187–199.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lis, T. (1979). *Acta Cryst.* B**35**, 1699–1701.
Lis, T. (1984*a*). *Acta Cryst.* C**40**, 374–376.
Lis, T. (1984*b*). *Acta Cryst.* C**40**, 376–378.
Littleton, C. D. (1953). *Acta Cryst.* **6**, 775–781.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Rigaku (1998). *RAPID-AUTO.* Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
Rigaku/MSC (2005). *CrystalStructure.* Version 3.7. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97.* University of Göttingen, Germany.
Spodine, E., Atria, A. M., Baggio, R. & Garland, M. T. (1996). *Acta Cryst.* C**52**, 1407–1410.
Tajmir-Riahi, H. A. (1990). *J. Inorg. Biochem.* **39**, 33–41.