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2006, Australia, and ^bCrystal Structure Analysis
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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.042
wR factor = 0.102
Data-to-parameter ratio = 14.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aqua[bis(2-pyridylmethyl)amine][chelidonato(1.5-)]-
copper(II) chelidonate(0.5-) monohydrate

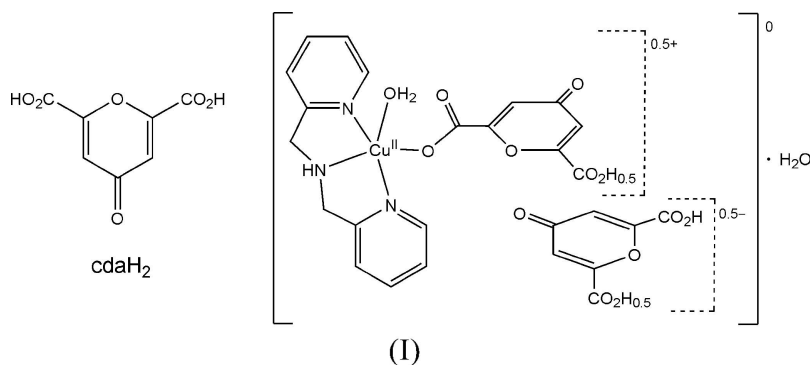
In the title compound, $[\text{Cu}(\text{C}_7\text{H}_{2.5}\text{O}_6)(\text{C}_{12}\text{H}_{13}\text{N}_3)(\text{H}_2\text{O})] \cdot (\text{C}_7\text{H}_{3.5}\text{O}_6) \cdot \text{H}_2\text{O}$, chelidonic acid coordinates to a $[\text{Cu}^{\text{II}}(\text{dpa})(\text{H}_2\text{O})]^{2+}$ core [dpa = bis(2-pyridylmethyl)amine] unit *via* a deprotonated carboxylic acid group. There is a three-dimensional hydrogen-bonding and $\pi-\pi$ interaction network present in the structure.

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Comment

We are investigating the coordination chemistry of Cu^{II} and polyfunctional ligands that contain endocyclic O atoms as models for species formed between Cu^{II} and carbohydrates, such as sialic acid (*N*-acetylneuraminic acid; Fainerman-Melnikova *et al.*, 2005). We are preparing Cu^{II} complexes with one mole-equivalent of a nitrogenous base [*e.g.* dpa = di-(2-picolyl)amine] and exchanging the remaining ligands for one mole-equivalent of a model carbohydrate. In this study, we have used chelidonic acid (cdaH_2 ; 4-oxo-4*H*-pyran-2,6-dicarboxylic acid) as the endocyclic oxygen-containing ligand.



The Cu^{II} ion in (I) exhibits a distorted square-pyramidal geometry (Fig. 1 and Table 1) with the coordinated water ligand defining the apical position and the basal plane occupied by the three N atoms from the dpa ligand and the O (carboxylic) atom from chelidonic acid. All of the N–Cu1 bond lengths in (I) are shorter than the corresponding bond lengths in $[\text{Cu}(\text{dpa})\text{Cl}_2]$ (Choi *et al.*, 2003) and comparable to the equivalent bond lengths in $[\text{Cu}(\text{dpa})(\text{MeOH})](\text{ClO}_4)_2$ (Niklas *et al.*, 2001).

The secondary amine of dpa in (I) is disordered and modelled over two positions with a total occupancy of 1, in which N2A or N2B lies above (0.48 Å) or below (0.42 Å), respectively, the trigonal plane defined by Cu1 and the two sp^3 -hybridized C atoms in dpa (C6··Cu1··C7). For the case of N2A, the trigonal distortion parameter $\tau = 0.07$ (Addison *et al.*, 1984; Marlin *et al.*, 2001). For the case of N2B, $\tau = 0.36$. An

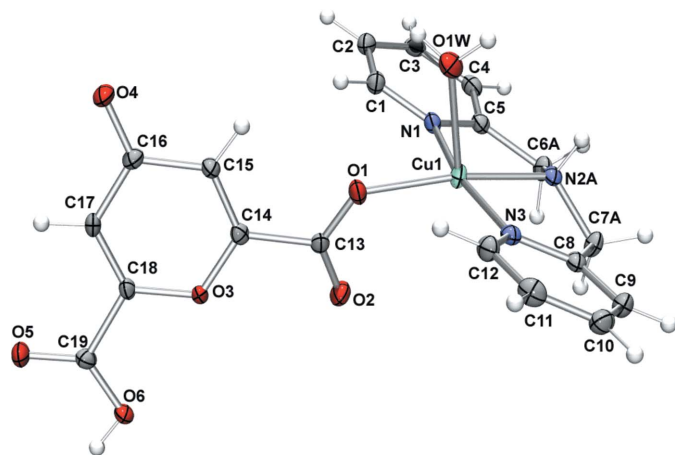


Figure 1
The structure of the copper complex in (I), shown with 50% probability displacement ellipsoids. Disorder components with less than 50% occupancy have been omitted for clarity.

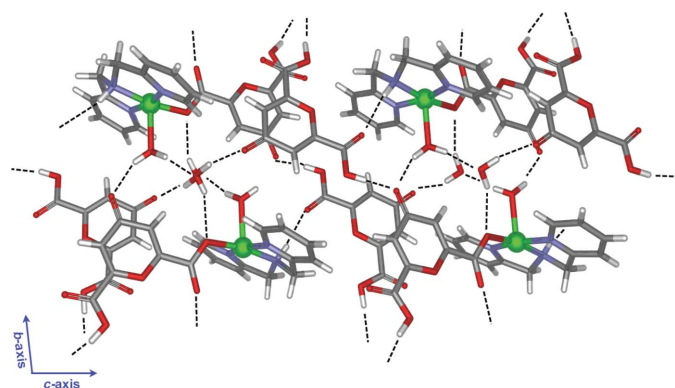


Figure 2
A schematic representation of part of the hydrogen-bonding network in (I). Dashed lines indicate hydrogen bonds.

occupancy correction factor yields $\tau = 0.17$. The aromatic ring of the Cu^{II} -coordinated $\text{cdaH}_{0.5}$ ligand in (I) is positioned approximately normal to the plane of the dpa ligand [angle between the planes defined by $\text{C6}\cdots\text{Cu1}\cdots\text{C7}$ and $\text{C14}\cdots\text{C16}\cdots\text{C18} = 82.76(11)^\circ$].

The coordinated chelidonic acid is not fully deprotonated and there is a second partially deprotonated chelidonic acid along with a solvent water molecule present in the structure. The occupancy of H1A and H1B were modelled as $\frac{1}{2}$, giving the charge-neutral (I).

An extensive network of intermolecular hydrogen bonding exists in (I) (Fig. 2 and Table 2). A similar hydrogen-bonding network is observed in the structure of the trihydrate of 3-hydroxychelidonic acid (Lovell *et al.*, 1999). The hydrogen bonding results in an infinite three-dimensional network, which is further stabilized by π - π interactions between the two aromatic rings. The distance in (I) between the two aromatic rings, $\text{cdaH}_{0.5}$ (Cu^{II} -coordinated) and $\text{cdaH}_{1.5}$ (non-coordinated) is 3.3 \AA ($\text{C16}\cdots\text{C21}$), indicative of strong offset face-to-face π - π interactions.

Experimental

$[\text{Cu}(\text{dpa})\text{Cl}_2]$ was prepared as described in the literature (Choi *et al.*, 2003). An aqueous solution (3 ml) of chelidonic acid (0.0510 g, 0.277 mmol) was added to an ethanol-water (50:50) solution (3 ml) containing $[\text{Cu}(\text{dpa})\text{Cl}_2]$ (0.0925 g, 0.277 mmol) and the resulting blue solution was stirred for 2 h at room temperature. Diethyl ether was diffused into the solution; dark-blue needle-shaped crystals appeared after 4 d.

Crystal data

| | |
|---|---|
| $[\text{Cu}(\text{C}_7\text{H}_{2.5}\text{O}_6)(\text{C}_{12}\text{H}_{13}\text{N}_3)(\text{H}_2\text{O})] \cdot (\text{C}_7\text{H}_{3.5}\text{O}_6) \cdot \text{H}_2\text{O}$ | $\gamma = 105.337(4)^\circ$ |
| $M_r = 665.03$ | $V = 1283.7(6) \text{ \AA}^3$ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 8.0667(19) \text{ \AA}$ | $D_x = 1.721 \text{ Mg m}^{-3}$ |
| $b = 12.705(3) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $c = 13.688(4) \text{ \AA}$ | $\mu = 0.94 \text{ mm}^{-1}$ |
| $\alpha = 91.861(6)^\circ$ | $T = 150(2) \text{ K}$ |
| $\beta = 107.121(4)^\circ$ | Needle, blue |
| | $0.32 \times 0.08 \times 0.06 \text{ mm}$ |

Data collection

| | |
|---|--|
| Bruker SMART 1000 CCD diffractometer | 12779 measured reflections |
| ω scans | 5981 independent reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1999) | 4603 reflections with $I > 2\sigma(I)$ |
| $T_{\text{min}} = 0.794$, $T_{\text{max}} = 0.949$ | $R_{\text{int}} = 0.036$ |
| | $\theta_{\text{max}} = 28.3^\circ$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.5834P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.102$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| $S = 1.03$ | $\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$ |
| 5981 reflections | $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$ |
| 412 parameters | |
| H atoms treated by a mixture of independent and constrained refinement | |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-----------------------------------|------------|------------------------------------|------------|
| $\text{N1}-\text{Cu1}$ | 1.972(2) | $\text{N3}-\text{Cu1}$ | 1.967(2) |
| $\text{N2B}-\text{Cu1}$ | 2.010(7) | $\text{O1}-\text{Cu1}$ | 1.9956(18) |
| $\text{N2A}-\text{Cu1}$ | 2.007(3) | $\text{O1W}-\text{Cu1}$ | 2.2713(19) |
| $\text{N3}-\text{Cu1}-\text{N1}$ | 165.10(8) | $\text{N1}-\text{Cu1}-\text{N2B}$ | 83.36(19) |
| $\text{N3}-\text{Cu1}-\text{O1}$ | 99.04(8) | $\text{O1}-\text{Cu1}-\text{N2B}$ | 143.4(2) |
| $\text{N1}-\text{Cu1}-\text{O1}$ | 95.33(8) | $\text{N3}-\text{Cu1}-\text{O1W}$ | 94.53(8) |
| $\text{N3}-\text{Cu1}-\text{N2A}$ | 82.88(11) | $\text{N1}-\text{Cu1}-\text{O1W}$ | 90.95(8) |
| $\text{N1}-\text{Cu1}-\text{N2A}$ | 82.27(11) | $\text{O1}-\text{Cu1}-\text{O1W}$ | 83.52(7) |
| $\text{O1}-\text{Cu1}-\text{N2A}$ | 169.27(11) | $\text{N2A}-\text{Cu1}-\text{O1W}$ | 106.92(11) |
| $\text{N3}-\text{Cu1}-\text{N2B}$ | 82.77(19) | $\text{N2B}-\text{Cu1}-\text{O1W}$ | 133.0(2) |

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-----------|-------------|-------------|---------------|
| $\text{N2A}-\text{H1N}\cdots\text{O11}^{\text{i}}$ | 0.886(10) | 2.22(3) | 2.935(4) | 137(4) |
| $\text{N2A}-\text{H1N}\cdots\text{O5}^{\text{ii}}$ | 0.886(10) | 2.63(3) | 3.307(4) | 134(3) |
| $\text{O8}-\text{H1A}\cdots\text{O8}^{\text{iii}}$ | 0.84 | 1.63 | 2.457(3) | 173 |
| $\text{O8}-\text{H1A}\cdots\text{O7}^{\text{iii}}$ | 0.84 | 2.68 | 3.191(3) | 121 |
| $\text{O12}-\text{H2A}\cdots\text{O4}^{\text{iv}}$ | 0.84 | 1.71 | 2.550(3) | 174 |
| $\text{O1W}-\text{H1W}\cdots\text{O2W}^{\text{v}}$ | 0.84 | 2.05 | 2.878(3) | 173 |

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|------------|-------------|-------------|---------------|
| $O1W-H2W\cdots O4^v$ | 0.83 | 2.08 | 2.861 (3) | 157 |
| $O2W-H3W\cdots O10^v$ | 0.85 | 2.00 | 2.821 (3) | 165 |
| $O2W-H4W\cdots O1$ | 0.84 | 2.37 | 3.147 (3) | 153 |
| $O2W-H4W\cdots O1W$ | 0.84 | 2.47 | 3.124 (3) | 134 |
| $N2B-H2N\cdots O2^{vi}$ | 0.890 (10) | 2.05 (3) | 2.920 (8) | 164 (8) |
| $O6-H1B\cdots O6^{vii}$ | 0.84 | 1.65 | 2.485 (3) | 173 |

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

C-bound H atoms were included in idealized positions and refined using a riding model. Aromatic and methylene C—H bond lengths were fixed at 0.95 and 0.99 Å, respectively. $U_{iso}(H)$ values were fixed at $1.2U_{eq}$ of the parent C atoms. N-bound and O-bound H atoms were located in a difference Fourier map and were refined with bond length restraints of 0.89 (1) Å and a riding model (O—H = 0.83–0.85 Å), respectively. $U_{iso}(H)$ values were fixed at $1.5U_{eq}$ of the parent atoms. The amine N atom of the dpa ligand is disordered and modelled over two positions with occupancies of 0.67 (N2A) and 0.33 (N2B), respectively. The adjacent methylene atoms were modelled with identical geometric and anisotropic displacement parameters. Two of the carboxylic acid H atoms (H1A and H1B) were modelled with 50% occupancy each.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997), *WinGX32* (Farrugia, 1999), *POV-RAY 3.5* (Cason, 2002) and *WebLab ViewerPro 3.7* (Molecular Simulations, 2000); software used to prepare material for publication: *enCIFer 1.0* (Allen *et al.*, 2004).

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