Poly[[bis(salicylato-κO)copper(II)]-di-μ-3-pyridylmethanol-κ²N:O;κ²O:N]: a redetermination at 100 K

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The crystal structure of the polymeric title compound, [Cu(C₇H₅O₃)₂(C₆H₇NO)₂]ₙ, has been reported previously at room temperature by Hoang, Valach, Macášková & Melník [*Acta Cryst.* (1992) C**48**, 1933–1936]. The centrosymmetric coordination environment of Cu^{II} at 100 K displays elongation of the Cu—N bonds and contraction of the Cu—O bonds to the 3-pyridylmethanol ligands, compared with the room-temperature structure. The Cu—O bond lengths to the carboxylate groups of the salicylate ligands are comparable at both temperatures.

Comment

The crystal structure of the title compound, (I), has been reported previously at room temperature (Hoang *et al.*, 1992). We present here a redetermination at 100 K.

(I)
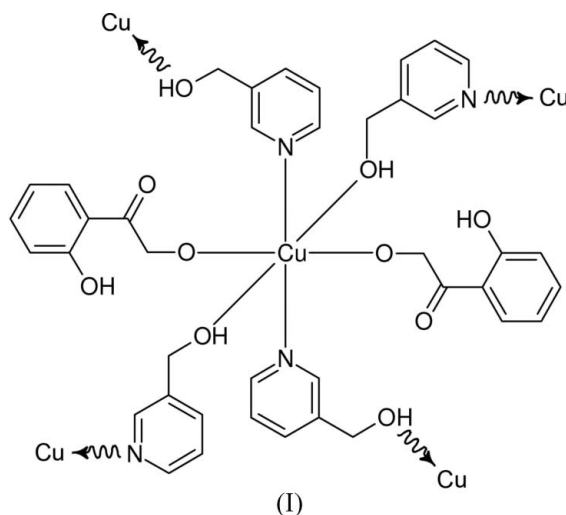
The structure of (I) contains two-dimensional polymeric sheets in which each Cu^{II} atom lies in a centrosymmetric tetragonally distorted octahedral coordination environment (Fig. 1). The equatorial plane comprises a pair of monodentate salicylate ligands bound through their carboxylate O atoms and a pair of neutral 3-pyridylmethanol (3-pyme) molecules coordinated through the N atom of the pyridine ring. The axial positions are occupied by two hydroxy O atoms from 3-pyme molecules.

This redetermination of the structure of (I) at 100 K provides significant improvement in the precision of the geometric parameters (Table 1). Compared with the room-temperature structure (Hoang *et al.*, 1992), the Cu—N1 bond length in (I) is elongated [2.039 (4) Å at 293 K], the Cu—O4^i bond length [symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, z$] is shortened
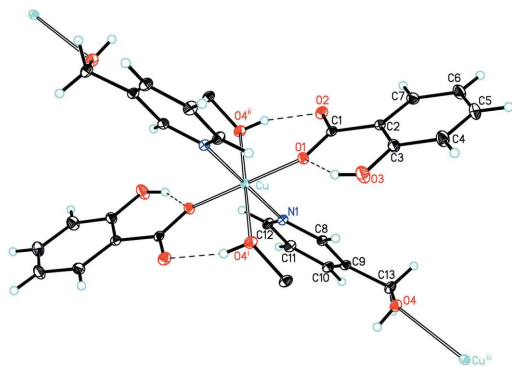
Figure 1
The coordination environment of Cu1 in (I), showing displacement ellipsoids at the 30% probability level. Dashed lines represent O—H···O hydrogen bonds. [Symmetry codes: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, z; (ii) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$; (iii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $1 - z$.]

[2.622 (4) Å at 293 K], and the Cu—O1 bond distance is closely comparable [1.944 (4) Å at 293 K].

The hydroxyl H atom of 3-pyme forms an O—H···O hydrogen bond to the uncoordinated O atom of the carboxylate group of the salicylate anion (Table 2), creating a six-membered metallacyclic ring. Additional intramolecular O—H···O hydrogen bonds are formed between the hydroxyl group and the coordinated O atom of each salicylate anion (Table 2), also generating six-membered rings.

The crystal structure of (I) can be compared with other two-dimensional coordination polymers of the general formula $[CuX_2(3\text{-pyme})_2]_n$, where X is 4-chlorosalicylate (Maroszová *et al.*, 2006) or 2-chlorobenzoate (Moncol *et al.*, 2006).

Experimental

Copper(II) acetylsalicylate monohydrate was prepared by the method of Viossat *et al.* (2003). Complex (I) was prepared by addition of 3-pyridylmethanol (0.02 mol) to copper(II) acetylsalicylate monohydrate (0.01 mol) in hot methanol (40 ml). The mixture was stirred and filtered, then left to cool and stand at room temperature. The precipated product was recrystallized from methanol solution to give air-stable blue crystals.

Crystal data

$[Cu(C_7H_5O_3)_2(C_6H_7NO)_2]$	$Z = 4$
$M_r = 556.03$	$D_x = 1.471$ Mg m^{-3}
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 12.823$ (2) Å	$\mu = 0.92$ mm^{-1}
$b = 9.914$ (3) Å	$T = 100$ (2) K
$c = 19.750$ (4) Å	Block, blue
$V = 2510.8$ (10) Å^3	$0.50 \times 0.40 \times 0.20$ mm

Data collection

Kuma KM-4 CCD area-detector diffractometer	15502 measured reflections
ω scans	2889 independent reflections
	2653 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2002)	$R_{int} = 0.044$
	$\theta_{max} = 28.0°$
$T_{min} = 0.655$, $T_{max} = 0.837$	
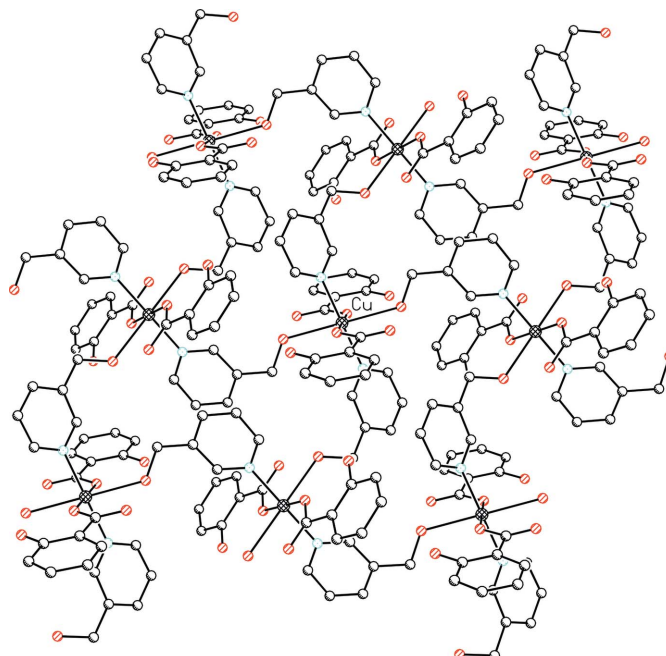
Figure 2
The two-dimensional layer of coordination polymer (I).

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 3.2095P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
2889 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
171 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9579 (13)	Cu—O4^i	2.5654 (13)
Cu—N1	2.1233 (16)		
O1—Cu—N1	88.78 (6)	O1—Cu—O4^{ii}	95.57 (5)
O1—Cu—O4^i	84.43 (5)	N1—Cu—O4^{ii}	81.19 (5)
N1—Cu—O4^i	98.81 (5)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O1	0.84	1.80	2.532 (2)	145
O4—H4O···O2^{iii}	0.84	1.90	2.707 (2)	160

Symmetry code: (iii) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$.

The hydroxyl H atoms were placed in calculated positions, with O—H = 0.84 Å, and allowed to ride, with $U_{iso}(H) = 1.5U_{eq}(O)$. Carbon-bound H atoms were placed in calculated positions, with C—H = 0.95 Å for pyridyl H and 0.99 Å for methylene H, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97*

(Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Hoang, N. N., Valach, F., Macášková, L. & Melník, M. (1992). *Acta Cryst.* C**48**, 1933–1936.

Maroszová, J., Martiška, L., Valigura, D., Koman, M. & Glowiak, T. (2006). *Acta Cryst.* E**62**, m1164–m1166.

Moncol, J., Seǧla, P., Mikloš, D., Mazúr, M., Melník, M., Głowiak, T., Valko, M. & Koman, M. (2006). *Polyhedron*, **25**, 1561–1566.

Oxford Diffraction (2002). KM-4 CCD/Xcalibur software, including *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Poland, Wrocław, Poland.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Viossat, B., Daran, J.-C., Savouret, G., Morgant, G., Greenaway, F. T., Dung, N.-H., Phan-Tran, V. A. & Sorenson, J. R. J. (2003). *J. Inorg. Biochem.* **96**, 375–385.