Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1414). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(6-chloro-2-pyridonato-N,O)(4,4′-dimethyl-2,2′-bipyridine-N,N′)zinc(II) Hydrate at 150 K

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Abstract

The title compound, bis(6-chloro-2-pyridinolato-N,O)-(4,4′-dimethyl-2,2′-bipyridine-N,N′)zinc(II) hydrate, [Zn(C₅H₃ClNO)₂(C₁₂H₁₂N₂)].H₂O, is an example of a pyridonate complex of zinc. The complex has a distorted geometry imposed by the narrow bite angles of the ligands.

Comment

The pyridonate ligand has been widely used in the co-ordination chemistry of second and third row transition metals, but to a lesser degree with the first row metals. Our interest in this ligand with the 3d metals Mn, Fe, Co, Ni and Cu has resulted in a number of unusual structural types (see, for example, Brechin, Harris, Parsons & Winpenny, 1996; Parsons, Solan & Winpenny, 1995). In this paper, we report the preparation and crystal structure of [Zn(chp)₂(Me₂-bipy)].H₂O, (1).H₂O (chp is 6-chloro-2-pyridonate and bipy is 2,2′-bipyridine), which was obtained as part of the extension of our results involving zinc.

(1)
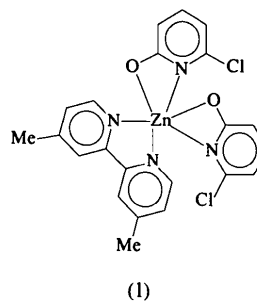
Compound (1) is an example of a pyridone complex of zinc (Fig. 1). While the Zn—N bond lengths to the N atoms (N1 and N1′) of the bipyridine ligand adopt normal values and are not significantly different, chemically similar bonds to the pyridonate ligands do differ, by 0.058 (4) Å in the case of Zn—O1R and Zn—O2R, and by 0.136 (4) Å in the case of Zn—N1R and Zn—N2R. The coordination geometry of complex (1) is irregular because of the characteristically narrow bite angles of the ligands, but can be very roughly described as 'distorted octahedral'. The longer Zn—O bond [Zn—O1R 2.097 (3) Å] lies trans with respect to Zn—N1 [2.098 (3) Å], while the shorter bond [Zn—O2R 2.039 (3) Å] is trans to Zn—N1R [2.237 (3) Å]. This is
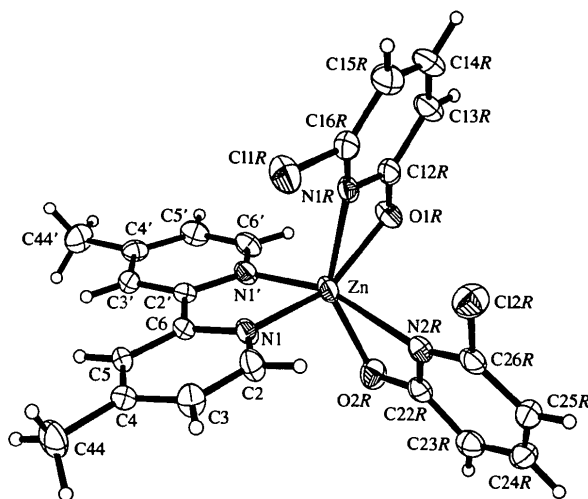

Fig. 1. A view of the title complex with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

consistent with the well known *trans* influence, which explains the difference in the Zn—O bond lengths. The bite angle adopted by bidentate pyridone ligands lies between 57 and 63° in structurally characterized complexes, and so the variation in the Zn—N distances in complex (1) is likely to be a geometric consequence of variation of the Zn—O bond lengths and the requirement for a planar Zn—O—C—N ring system enforced by the in-plane character of the nitrogen lone-pair.

Packing in the crystal structure of (1).H_2O is characterized by the linking of centrosymmetrically related molecules of (1) by pairs of water molecules *via* hydrogen bonding, with distances O1$S \cdots$O1$R(x, y-1, z)$ 2.779 (5) Å and O1$S \cdots$O2$R(1-x, 1-y, 1-z)$ 2.862 (5) Å. Although planar delocalized ligands, such as those in complex (1), have a tendency to interact *via* graphite-like stacking in solid-state structures, there appear to be no significant interactions of this kind between the hydrogen-bonded dimers, with the shortest intermolecular distance between ring centroids being 4.44 Å.

Experimental

Hydrated zinc(II) acetate (1.317 g, 6.0 mmol) was mixed intimately with a slightly greater than twofold excess of 6-chloro-2-hydroxypyridine (1.71 g, 13.2 mmol). The mixture was fused at 413 K under N_2 and after 1 h the acetic acid formed during the reaction was removed *in vacuo* and the unreacted chp removed by sublimation. The colourless product was dissolved in dichloromethane, filtered and then mixed with 4,4'-dimethyl-2,2'-bipyridine (1.140 g, 6.0 mmol). After stirring for 3 h, the colourless solution was filtered, concentrated and layered with diethyl ether to yield, after several days, colourless crystals suitable for X-ray analysis.

Crystal data

[Zn(C_5H_3ClNO)$_2$-($C_{12}H_{12}N_2$)].H_2O
$M_r = 524.69$
Triclinic
$P\bar{1}$
$a = 8.995 (6)$ Å
$b = 9.748 (7)$ Å
$c = 14.655 (11)$ Å
$\alpha = 97.39 (5)°$
$\beta = 99.85 (5)°$
$\gamma = 113.16 (3)°$
$V = 1136.5 (14)$ Å^3
$Z = 2$
$D_x = 1.533$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 15–16°$
$\mu = 1.348$ mm^{-1}
$T = 150.0 (2)$ K
Block
$0.58 \times 0.27 \times 0.23$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems variable temperature device (Cosier & Glazer, 1986)
ω–θ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.645$, $T_{max} = 0.714$
5899 measured reflections

4022 independent reflections
3023 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0593$
$\theta_{max} = 25.02°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 17$
3 standard reflections frequency: 60 min intensity decay: 5%

Refinement

Refinement on F^2
$R(F) = 0.0443$
$wR(F^2) = 0.1086$
$S = 1.031$
4017 reflections
295 parameters
H atoms riding, U(H) = $1.2U_{eq}$(C)

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1993P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.485$ e Å^{-3}
$\Delta\rho_{min} = -0.793$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O2R	2.039 (3)	Zn—N1	2.098 (3)
Zn—N1'	2.091 (3)	Zn—N1R	2.237 (3)
Zn—O1R	2.097 (3)	Zn—N2R	2.373 (3)
O2R—Zn—N1'	104.47 (12)	O1R—Zn—N1R	61.72 (12)
O2R—Zn—O1R	98.85 (12)	N1—Zn—N1R	97.72 (13)
N1'—Zn—O1R	96.84 (12)	O2R—Zn—N2R	60.62 (11)
O2R—Zn—N1	104.38 (13)	N1'—Zn—N2R	161.43 (11)
N1'—Zn—N1	78.48 (13)	O1R—Zn—N2R	96.50 (11)
O1R—Zn—N1	156.75 (11)	N1—Zn—N2R	94.00 (12)
O2R—Zn—N1R	143.74 (11)	N1R—Zn—N2R	89.80 (11)
N1'—Zn—N1R	107.92 (12)		

Data collection: *DIF4* (Stoe & Cie, 1990). Cell refinement: *DIF4*. Data reduction: *XRED* (Stoe & Cie, 1994). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1995).

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