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Acetatobis(2,2′-bipyridyl)zinc(II) hexafluorophosphate monohydrate

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Key indicators

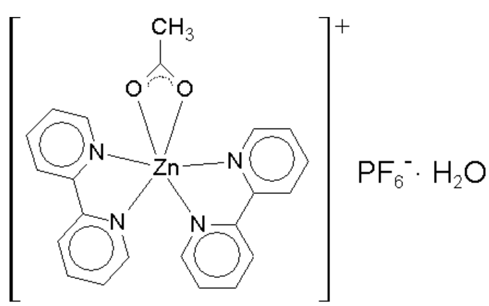
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.052
wR factor = 0.153
Data-to-parameter ratio = 12.9

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

The title compound, $[Zn(C_2H_3O_2)(bipy)_2]PF_6\cdot H_2O$, where bipy is 2,2′-bipyridyl ($C_{10}H_8N_2$), crystallizes in the triclinic space group $P\overline{1}$ with one independent molecule in a general position. The Zn atom is coordinated by one acetate and two bipyridine ligands in an approximate *mm*2 point-group symmetry. The two Zn—O bond distances are similar to each other, as are the Zn—N bond distances.

Comment

Structural studies have been previously published on transition metal complexes of the type ML_2(OXO)Y, where M is a transition metal, L is the bidentate ligand phen (1,10-phenanthroline) or bipy (2,2′-bipyridyl), OXO is a ligand such as acetate (ac), carbonate (COO) or nitrite (ONO), which can be mono- or bicoordinated to the metal atom, and Y is a negatively charged counter-ion, such as PF_6^- or Cl^-. Many complexes have the transition metal in a coordination geometry significantly different from the widely observed octahedral, tetragonal, square-planar, square-planar-pyramidal or bipyramid-trigonal, which are recognized as reference geometries for first row transition metal complexes (Shriver *et al.*, 1994).



(I)

Compounds containing copper or zinc are among the most studied. The zinc complexes, *e.g.* $[Zn(ONO)(bipy)_2]NO_3$ (Walsh *et al.*, 1981), $[Zn(ac)(bipy)_2]ClO_4\cdot H_2O$ (Chen *et al.*, 1994) and $[Zn(ac)(phen)_2]BF_4\cdot 2H_2O$ (Fitzgerald *et al.*, 1985), show the metal hexacoordinated, in approximate *mm*2 local symmetry. The distances Zn—N in the same complex are similar to each other, as are the Zn—O distances. Many copper complexes, on the other hand, show a strong distortion of the metal atom from *mm*2 symmetry. Among these, some, *viz*. $[Cu(ac)(bipy)_2]BF_4$ (Hathaway *et al.*, 1980) and $[Cu(ac)(phen)_2]BF_4$ (Fitzgerald & Hathaway, 1984), have long

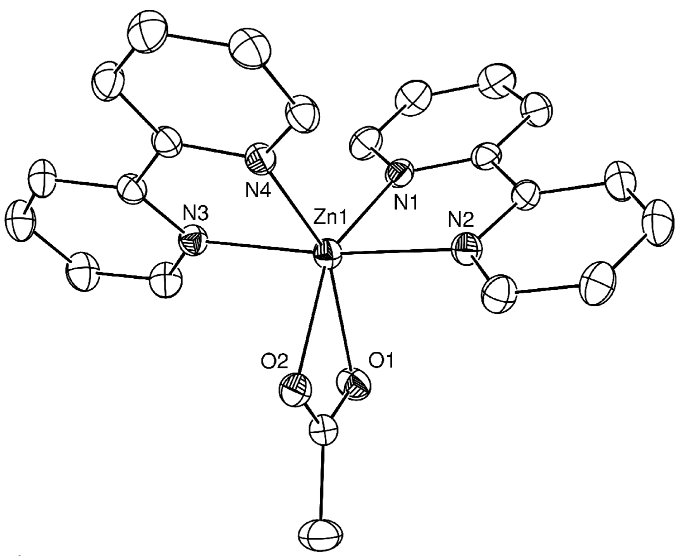


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the zinc coordination on (I), shown with 20% probability displacement ellipsoids. H atoms have been omitted for clarity, as have the anion and the water molecule.

Cu—O distances (2.6 Å or more), clearly suggesting that the two OXO O atoms interact with different strengths with the Cu atom. Other copper complexes, such as [Cu(ONO)-$(bipy)_2$]NO_3 (Simmons *et al.*, 1983), show the Cu atom in an approximate *mm*2 local symmetry.

This work presents the crystal structure of [Zn(ac)-$(bipy)_2$]PF_6·H_2O, (I). This structure and the structure of [Zn(ac)$(phen)_2$]BF_4 (Rodrigues, 2004) are of the above-described ML_2(OXO)Y type. Therefore, the study can be helpful in understanding the non-conventional coordination type.

The Zn atom in [Zn(ac)$(bipy)_2$]PF_6·H_2O is hexacoordinated by two bipyridine and one acetate ligand (Fig. 1). The dihedral angle between the least-squares planes through the two bipyridine ligands, *viz*. bipy12 (containing N1 and N2) and bipy34 (containing N3 and N4), is 71.26 (7)° and the Zn atom is close to the intersection line of these two planes. Atom N2 lies near [0.025 (5) Å] the plane formed by bipy34 and Zn. The Zn atom and the carboxylate group are coplanar, the greatest deviation being for atom C21 [0.003 (3) Å]. The mean Zn—N values in bipy12 and bipy34 are 2.125 (3) and 2.129 (3) Å, respectively (Table 1). These show that the coordination of zinc in (I) is close to the coordination of zinc in the previously cited [Zn(ac)$(phen)_2$]Y compounds, such as [Zn(ac)-$(phen)_2$]BF_4, as well as in other [Zn(OXO)$(bipy)_2$]Y structures (Tables 2 and 3).

It is helpful to compare the structures of [Zn(OXO)L_2]Y with those of [Cu(OXO)L_2]Y. Each bipyridine ligand compound shows Zn–bipy12 interactions of similar strength to the Zn–bipy34 interactions. This is also seen for the interactions Zn–phen12 and Zn–phen34 of each phenanthroline ligand. Copper complexes (Simmons *et al.*, 1987), on the other hand, show Cu—N1 systematically shorter than Cu—N4, and Cu—N2 systematically shorter than Cu—N3. This suggests that the interaction Cu–bipy12 is stronger than the interaction Cu–bipy34 in bipyridine complexes. It also occurs between interactions Cu–phen12 and Cu–phen34 of phenanthroline complexes. The comparison of M—O bond distances of compounds [M(ac)L_2]Y is also informative: zinc compounds show Zn—O distances close to each other, with mean values around 2.2 Å (Table 1). Cu—O bond distances, on the other hand, vary over a wide range, 2.0–2.9 Å. The differences between zinc and copper complexes described in this paragraph are in agreement with the more symmetrical electron distribution of Zn^{2+} (d^{10}) in comparison with Cu^{2+} (d^9).

Experimental

An aqueous solution containing Zn(ac)·$4H_2O$ (0.11 g), bipyridine (0.078 g), NH_4PF_6 (0.085 g), water (3.00 ml) and acetic acid (pH = 4) was heated to 323 K for 4 h, then left at 298 K and filtered. Slow evaporation resulted in single crystals of (I).

Crystal data

[Zn($C_2H_3O_2$)($C_{10}H_8N_2$)$_2$]PF_6·H_2O	Z = 2
M_r = 599.79	D_x = 1.616 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 8.4489 (4) Å	Cell parameters from 11273 reflections
b = 10.0482 (5) Å	θ = 0.4–27.1°
c = 14.9191 (8) Å	μ = 1.14 mm^{-1}
α = 77.264 (3)°	T = 293 (2) K
β = 87.306 (3)°	Prism, colorless
γ = 86.554 (3)°	0.15 × 0.13 × 0.09 mm
V = 1232.44 (11) Å^3	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.053
ω and φ scans	θ_{max} = 25°
13542 measured reflections	$h = -8 \rightarrow 10$
4308 independent reflections	$k = -11 \rightarrow 11$
3411 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0986P)^2 + 0.1996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.153	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.50 e Å^{-3}
4308 reflections	
334 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.226 (3)	Zn1—N2	2.124 (3)
Zn1—O2	2.170 (3)	Zn1—N3	2.136 (3)
Zn1—N1	2.125 (3)	Zn1—N4	2.122 (3)
N1—Zn1—O1	95.68 (11)	N2—Zn1—N4	96.52 (11)
N1—Zn1—O2	152.55 (12)	N3—Zn1—O1	93.98 (11)
N1—Zn1—N2	77.38 (12)	N3—Zn1—O2	92.81 (12)
N1—Zn1—N3	100.36 (12)	N3—Zn1—N4	77.18 (11)
N1—Zn1—N4	107.45 (12)	N4—Zn1—O1	156.31 (11)
N2—Zn1—O1	93.42 (11)	N4—Zn1—O2	98.87 (11)
N2—Zn1—O2	92.27 (12)	O1—Zn1—O2	59.19 (10)
N2—Zn1—N3	172.44 (12)		

Table 2
Comparative bond lengths (Å) for $[Zn(OXO)L_2]Y$ complexes.

Y	Zn—N1	Zn—N2	Zn—N3	Zn—N4	Zn—O1	Zn—O2
NO_3[a]	2.077 (9)	2.129 (9)	2.151 (9)	2.092 (9)	2.223 (8)	2.217 (9)
ClO_4[b]	2.090 (4)	2.129 (4)	2.135 (4)	2.085 (4)	2.216 (5)	2.197 (5)
$Cl_4\cdot H_2O$[c]	2,131 (4)	2.121 (5)	2.127 (4)	2.129 (4)	2.246 (4)	2.155 (4)
$[Mn(dca)_3(H_2O)]$[d]	2.115 (2)	2.137 (2)	2.121 (2)	2.107 (2)	2.347 (2)	2.120 (1)
$PF_6\cdot H_2O$[e]	2.125 (3)	2.124 (3)	2.136 (3)	2.122 (3)	2.226 (3)	2.170 (3)
BF_4[f]	2.091 (3)	2.151 (3)	2.148 (3)	2.119 (3)	2.293 (3)	2.149 (3)
$BF_4\cdot 2H_2O$[g]	2.116 (2)	2.147 (2)	2.147 (2)	2.116 (2)	2.184 (2)	2.184 (2)
ClO_4[h]	2.135 (6)	2.143 (6)	2.160 (5)	2.100 (5)	2.296 (5)	2.156 (5)

Notes: (*a*) $[Zn(ONO)(bipy)_2]NO_3$ (Walsh *et al.*, 1981); (*b*) $[Zn(ONO)(bipy)_2]ClO_4$ (Murphy *et al.*, 2003); (*c*) $[Zn(ac)(bipy)_2]Cl_4\cdot H_2O$ (Chen *et al.*, 1994); (*d*) $[Zn(ac)(bipy)_2][Mn(dca)_3(H_2O)]$ (Wang *et al.*, 2003); (*e*) [Zn(ac)(bipy)2]$PF_6\cdot H_2O$ (this work); (*f*) $[Zn(ac)(phen)_2]BF_4$ (Rodrigues, 2004); (*g*) $[Zn(ac)(phen)_2]BF_4\cdot 2H_2O$ (Fitzgerald *et al.*, 1985); (*h*) $[Zn(ac)(phen)_2]ClO_4$ (Chen *et al.*, 1994).

Table 3
Comparative bond angles (°) for $[Zn(OXO)L_2]Y$ complexes.

	N1—Zn—N2	N3—Zn—N4	O1—Zn—O2
$[Zn(ONO)(bipy)_2]NO_3$[a]	77.94	78.53	56.5
$[Zn(ONO)(bipy)_2]ClO_4$[b]	77.76 (16)	77.88 (17)	55.80 (18)
$[Zn(ac)(bipy)_2]Cl_4\cdot H_2O$[c]	77.2 (2)	77.8 (2)	59.0 (1)
$[Zn(ac)(bipy)_2][Mn(dca)_3(H_2O)]$[d]	77.03 (6)	78.07 (6)	58.29 (5)
$[Zn(ac)(bipy)_2]PF_6\cdot H_2O)$[e]	77.38 (12)	77.18 (11)	59.19 (10)
$[Zn(ac)(phen)_2]BF_4$[f]	78.94 (12)	77.92 (12)	58.12 (11)
$[Zn(ac)(phen)_2]BF_4\cdot 2H_2O$[g]	78.47	78.47	57.2
$[Zn(ac)(phen)_2]ClO_4$[h]	78.1 (2)	78.6 (2)	57.8 (2)

Notes: (*a*) Walsh *et al.* (1981); (*b*) Murphy *et al.* (2003); (*c*) Chen *et al.* (1994); (*d*) Wang *et al.* (2003); (*e*) this work; (*f*) Rodrigues (2004); (*g*) Fitzgerald *et al.* (1985); (*h*) Chen *et al.* (1994).

H atoms bonded to carbon were positioned geometrically and refined as riding, with C—H = 0.93 Å for CH and 0.96 Å for CH_3. Water H atoms were positioned geometrically (O—H = 0.85–0.86 Å). H-atom U_{iso} parameters were set equal to 1.2 (CH) or 1.5 (CH_3) times U_{eq} of the parent atom. Displacement parameters for water H atoms were fixed at 0.076 Å^2.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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