Bis(di-2-pyridylphosphinato-κ³N,O,N′)copper(II) dichloromethane disolvate

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The solid-state structure of the first reported homoleptic copper di-2-pyridylphosphinate complex shows an extremely large 'z-out' tetragonal distortion, with an axial Cu···O distance of 2.430 (2) Å. The title complex, [Cu(C₁₀H₈N₂O₂P)₂]·2CH₂Cl₂ or Cu[py₂P(O)O]₂·2CH₂Cl₂, comprises two di-2-pyridylphosphinate ligands coordinated to the central copper(II) ion, which sits on an inversion center. The pyridyl rings of one ligand are *trans* to the pyridyl rings of their symmetry-related counterpart. The two *trans* py–Cu–py moieties are coplanar, as required by the inversion symmetry. A disordered dichloromethane solvent molecule is cocrystallized in the asymmetric unit cell.

Comment

Published examples of metal complexes of phosphinates, [R₂P(O)O⁻], are limited (Betz & Bino, 1988; Annan *et al.*, 1991; Chakraborty *et al.*, 2000; Kongprakaiwoot *et al.*, 2002). Their binding atoms are almost exclusively confined to O atoms. Derivation of the *R* groups [*e.g.* pyridyl (py)] enables the development of multidentate phosphinates and opens up a new field in coordination chemistry. However, there are even fewer examples of such compounds in the literature than there are of underivatized phosphinates. The *N,O*-bidentate mode only occurs in {bis(4,5-di-isopropylimidazol-2-yl)phosphinic acid}dichlorozinc monohydrate (Ball *et al.*, 1984) and the tridentate mode occurs only in the [Ru{py₃PO}{py₂P(O)O}]⁺ cation (Keene & Stephenson, 1991). The latter is the only structurally identified example of a metal complex bearing pyridylphosphinate. During the course of a study of metal complexes with pyridylphosphines, we accidentally isolated the title compound, (I), and found it to be the first reported homoleptic pyridylphosphinate–metal complex. The isolation

of this compound may encourage further studies of possible applications for the new tridentate ligand py₂P(O)OH, as well as other multidentate phosphinate derivatives.

(I)
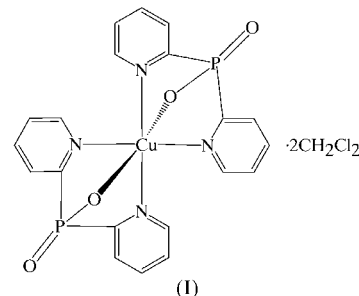
X-ray structural analysis was carried out in order to elucidate the coordination mode of the di-2-pyridylphosphonate ligand (*L*). The molecular structure of (I) is illustrated in Fig. 1. The asymmetric unit contains half of the Cu*L₂* complex and a dichloromethane solvent molecule. The Cu^II center sits at the inversion center and is coordinated with both pyridyl rings from both ligands. Each phosphinate ligand further provides an O atom to occupy the axial positions above and below the CuN₄ plane (Fig. 1). The Cu—O1 distance is extremely long [2.429 (2) Å] but falls between the sum of the covalent radii (2.11 Å) and the sum of the van der Waals radii (2.95 Å). One other notable feature is that the O1—Cu—O1ⁱ [symmetry code: (i) 1 − x, 1 − y, 1 − z] vector is tilted away from the normal of the CuN₄ plane. These facts may cast some doubt on the existence of the Cu—O interaction in (I). However, the presence of the interaction is evidenced by the bending of the P1—O1 segment towards the Cu center, which is manifested by a reduction of the P—C—N angles as well as an enlargement of the P—C—C angles from their ideal (120°) value (Table 1). The off-normal O1—Cu1—O1ⁱ vector and the extremely long Cu—O distances may be the result of a balance
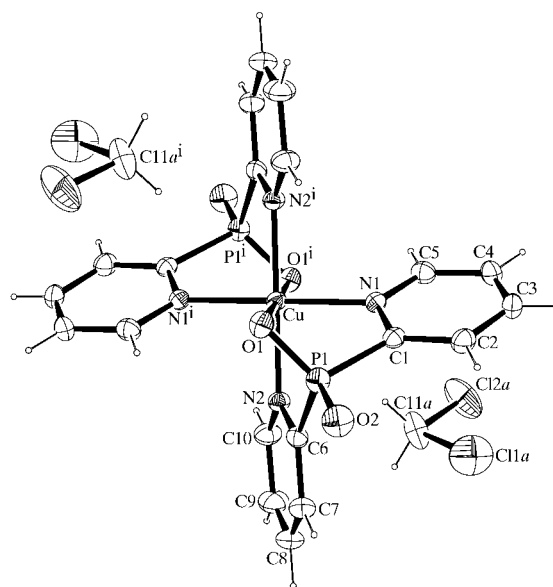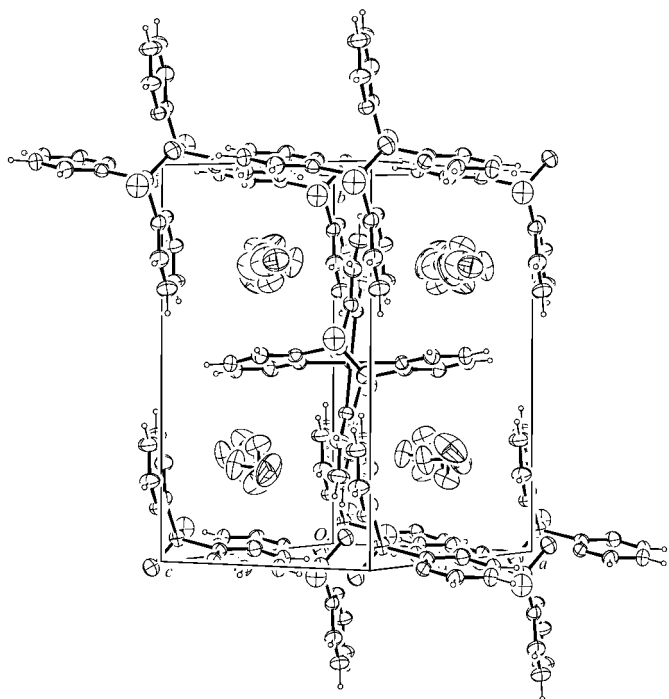

Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. For clarity, only one of the two orientations of the disordered dichloromethane molecule is shown. [Symmetry code: (i) 1 − x, 1 − y, 1 − z.]

metal-organic compounds

Figure 2
The molecular packing of (I), showing the space around the dichloromethane solvent molecules.

between the tendency of the axial O atoms to bond (electronic attraction) and the resistance to distortion of the phosphinate ligand (steric rigidity). The elongatation of the Cu—O bond may also arise for the same reason as the often-observed Jahn–Teller distortion in Cu^{II} complexes. Although the ligand field in (I) hardly produces the electronically degenerate state required by the Jahn–Teller theorem, the argument of lowering energy due to the tetragonal distortion still holds true in the case of (I).

The only other example of a metal–dipyridylphosphinate in the literature, as mentioned above, is $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]BF_4$ (Keene & Stephenson, 1991). The N,N,O-tridentate mode of the dipyridylphosphinate in this Ru complex is similar to that observed in (I) but differs in its strong M—O interaction [Ru—O = 2.11 (2) Å]. The strength of this interaction may be due to the electronic configuration (d^6) of Ru^{II}. Because the need for electronic input from the ligand is greater for Ru^{II} (d^6) than for Cu^{II} (d^9), Ru^{II} ions are usually six-coordinated, while Cu^{II} ions usually prefer four-(square planar) or five-coordination (square pyramid) modes. This argument may explain why the Ru^{II} ion forms normal Ru—O bonds in $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]BF_4$ and may provide additional evidence of the existence of elongated Cu—O bonds in (I). The distortion of the py–Ru–py moieties (mean $Ru-N\cdots X = 173.5°$; X is the centroid of the py ring) is more obvious than in (I) [mean $Cu-N\cdots X = 176.1 (2)°$], and this result is consistent with the stronger M—O interaction in the Ru complex.

Although the py–Cu–py moieties are coplanar, as required by the existence of an inversion center, none of the pyridine rings around the Cu^{II} center is coplanar with the CuN_4 plane.

Therefore, there are no significant $p\pi$–$d\pi$ interactions strengthening the Cu—N bonds. The Cu—N bond lengths (Table 1) are, however, still comparable to the literature values (2.00–2.07 Å; *International Tables for Crystallography*, 1992, Vol. C, pp. 738–739).

Because H atoms are not always located in X-ray analysis, the possibility exists for one of the ligands to be neutral in charge. However, the distinct blue color (a common color for Cu^{II} complexes) of the crystal and the equality of the P—O distances in the moiety support the anionic assignment of $py_2P(O)O^-$. The normal atomic displacement parameters of the two O atoms (Fig. 1) also indicate that disorder of the $py_2P(O)OH$ group is unlikely.

The dichloromethane solvent molecule is disordered. The non-H atoms of the two major orientations (A, with an occupancy of 40%, and B, with an occupancy of 60%) were located and refined anisotropically. The crystal packing of (I) is illustrated in Fig. 2.

Experimental

The title complex was obtained by mixing an acetonitrile solution of $[Cu(CH_3CN)_4]BF_4$ with Ppy_3 in a 2:3 molar ratio for 24 h. After filtration, CH_2Cl_2 was added to the precipitate. Deep-blue crystals were obtained after simple evaporation of the CH_2Cl_2 solution. Analysis calculated for $C_{20}H_{16}CuN_4O_4P_2$: C 42.98, H 3.09, N 9.55%; found: C 43.02, H 3.81, N 9.36%. During the synthesis of Ppy_3, incomplete substitution of PCl_3 by 2-pyridyl anions would lead to the formation of hydroxybis(2-pyridyl)phosphine, which would give rise to the production of bis(2-pyridyl)phosphinic acid in the subsequent air oxidation. This is believed to be the route for the generation of the pyridylphosphinate observed in the title complex.

Crystal data

$[Cu(C_{10}H_8N_2O_2P)_2]\cdot 2CH_2Cl_2$	$D_x = 1.665$ Mg m^{-3}
$M_r = 671.70$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 20
$a = 8.404 (3)$ Å	reflections
$b = 14.392 (2)$ Å	$\theta = 4.3–7.1°$
$c = 11.167 (2)$ Å	$\mu = 1.37$ mm^{-1}
$\beta = 97.42 (2)°$	$T = 293 (2)$ K
$V = 1339.5 (6)$ Å^3	Prism, blue
$Z = 2$	$0.64 \times 0.60 \times 0.30$ mm

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.024$
ω–2θ scans	$\theta_{max} = 25.0°$
Absorption correction: ψ scan	$h = 0 \rightarrow 9$
(North *et al.*, 1968)	$k = 0 \rightarrow 17$
$T_{min} = 0.425$, $T_{max} = 0.663$	$l = -13 \rightarrow 13$
2647 measured reflections	3 standard reflections
2358 independent reflections	every 150 reflections
1664 reflections with $I > 2\sigma(I)$	intensity decay: 0.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 0.3429P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
2358 reflections	$\Delta\rho_{min} = -0.37$ e Å^{-3}
197 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0184 (15)

Table 1
Selected geometric parameters (Å, °).

Cu—N2	2.012 (3)	P1—O2	1.480 (2)
Cu—N1	2.034 (2)	P1—O1	1.502 (3)
Cu—O1	2.429 (2)		
N2—Cu—N1	88.30 (10)	C2—C1—P1	126.6 (2)
N2—Cu—O1	81.56 (9)	N2—C6—P1	112.3 (2)
N1—Cu—O1	81.14 (9)	C7—C6—P1	126.8 (3)
N1—C1—P1	112.3 (2)		

H atoms of the pyridyl rings were placed in calculated positions, with C—H distances of 0.93 Å. Fixed positions, isotropic displacement parameters (0.05 Å^2) and occupancy factors (40/60%) of the H atoms of the disordered CH_2Cl_2 molecule were included in the final cycle of least-squares refinement. All other H atoms were included as riding, with U_{iso}(H) values equal to $1.2U_{eq}$ of the carrier atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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