π-π interactions in the supramolecular structure of (4,7-dimethyl-1,10 phenanthroline)(triphenylphosphine) tetrahydridoborato-copper(I)

Ján Moncol[a], Klaudia Jomová[b], Michael Lawson[a], Marianna Karsayová[b]

[a] Faculty of Chemical and Food Technology, Slovak Technical University, Radlinského 9, SK-812 37, Bratislava, Slovakia,
[b] Department of Chemistry, Faculty of Natural Sciences, Constantine The Philosopher University, SK-949 74 Nitra, Slovakia

jan.moncol@stuba.sk

Abstract

The title compound, $[Cu(C_{12}H_{12}N_2)(C_{18}H_{15}P)(BH_4)]$, crystallizes with two molecules in the asymmetric unit. Each Cu^+ ion is pentacoordinated by 4.7-dimethyl-1,10-phenanthroline, triphenylphosphine and tetrahydroborate anions in η^2-coordination mode. A π-π stacking interaction is observed between the aromatic rings of adjacent 4,7-dimethyl-1,10 phenanthroline ligands.

Keywords: copper(I), X-ray, phenanthroline, weak interactions

Introduction

Transition metal tetrahydrato complexes are known to play an important role in syntheses and catalysis, but also they represent a very interesting topic in structure and bonding of coordination chemistry (Marks & Kolb, 1977). In many tetrahydroborato complexes, the BH_4^- ligand is usually coordinated to metal atoms in η^1-, η^2- or η^3- coordination mode (Xu & Lin, 1996; Besora & Agusti, 2008).

Experimental

Synthesis

$[Cu(PPh_3)_2(BH_4)]$ was prepared by the procedure reported by (Moncol et al., 2005). $[Cu(C_{12}H_{12}N_2)(C_{18}H_{15}P)(BH_4)]$ was prepared by a modification of the procedure reported by (Green et al., 1984), by adding 4,7-dimethyl-1,10-phenanthroline (0.21 g, 1 mmol) dissolved

in methylene chloride (5 mL) with a methylene chloride solution (10 mL) of

$[Cu(PPh_3)_2(BH_4)]$ (0.60 g, 1 mmol) in dry-box.

Table 1. Experimental details.

Chemical formula	$C_{32}H_{31}BCuN_2P$
M_r	548.91
Crystal system, space group	Triclinic, *P*–1
Temperature (K)	200
a, *b*, *c* (Å)	9.9652 (5), 16.9171 (9), 18.3356 (9)
α, β, γ (°)	64.419 (2), 82.757 (2), 84.550 (2)
V (Å^3)	2763.0 (2)
Z	4
Radiation type	Mo K_α
μ (mm^{-1})	0.87
Crystal size (mm)	$0.25 \times 0.05 \times 0.04$
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan SADABS (Bruker, 2008)
T_{min}, T_{max}	0.812, 0.966
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38041, 11247, 8868
R_{int}	0.027
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.125, 1.06
No. of reflections	11247
No. of parameters	665
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.74, -0.71
CCDC no.	624024

X-ray Crystallography

Crystal data and conditions of data collection and refinement are reported in Table 1. Data

collection and cell refinement were carried out using diffractometer Bruker SMART APEXII

CCD (Bruker, 2008) at 200 K with graphite monochromated Mo Kα radiation. The semi-empirical absorption corrections were applied the using multi-scan method. The structures were solved by direct methods using SIR-97 (Altomare et al., 1999) and refined by the full-matrix least-squares procedure with SHELXL-97 (Sheldrick, 2008). Geometrical analyses were performed with SHELXL-97. The structures were drawn with XP in SHELXTL (Sheldrick, 2008) and MERCURY (Macrae et al., 2006).

Table 2. Selected geometric parameters (Å).

| Cu1—N2	2.129(2)	Cu2—N4	2.096(2)
Cu1—N1	2.151(2)	Cu2—N3	2.125(2)
Cu1—P1	2.2191(7)	Cu2—P2	2.1964(7)
Cu1—H5B	1.68	Cu2—H1B	1.82
Cu1—H6B	2.03	Cu2—H4B	1.86

Results and discussion

Compound (I), $[Cu(C_{12}H_{12}N_2)(C_{18}H_{15}P)(BH_4)]$, crystallizes in a centrosymmetric space group, the asymmetric unit containing two independent molecules (Fig. 1 (molecule A) and 2 (molecule B), Table 2). The Cu^+ ion is five coordinate for both molecules. For both molecules, unidentate triphenylphosphine [Cu1–P1 = 2.2191(7)Å (A); Cu2–P2 = 2.1964(7) Å (B)], bidentate 4.7-dimethyl-1,10-phenanthroline [Cu1–N1 = 2.151(2) Å and Cu1–N2 = 2.129(2) Å for molecule A; Cu2–N3 = 2.125(2) Å and Cu2–N4 = 2.096(2) Å for molecule B] and unsymmetrical bidentate BH_4^- [Cu1–H5B = 1.68 Å and Cu1–H6B = 2.03 Å for molecule A; Cu2–H1B = 1.82 Å and Cu2–H2B = 1.86 Å for molecule B] completes the copper(I) coordination, but there are subtle differences between the two complex molecules. The τ parameters (Addison et al., 1984) are 0.34 for molecule A and 0.20 for molecule B, respectively.
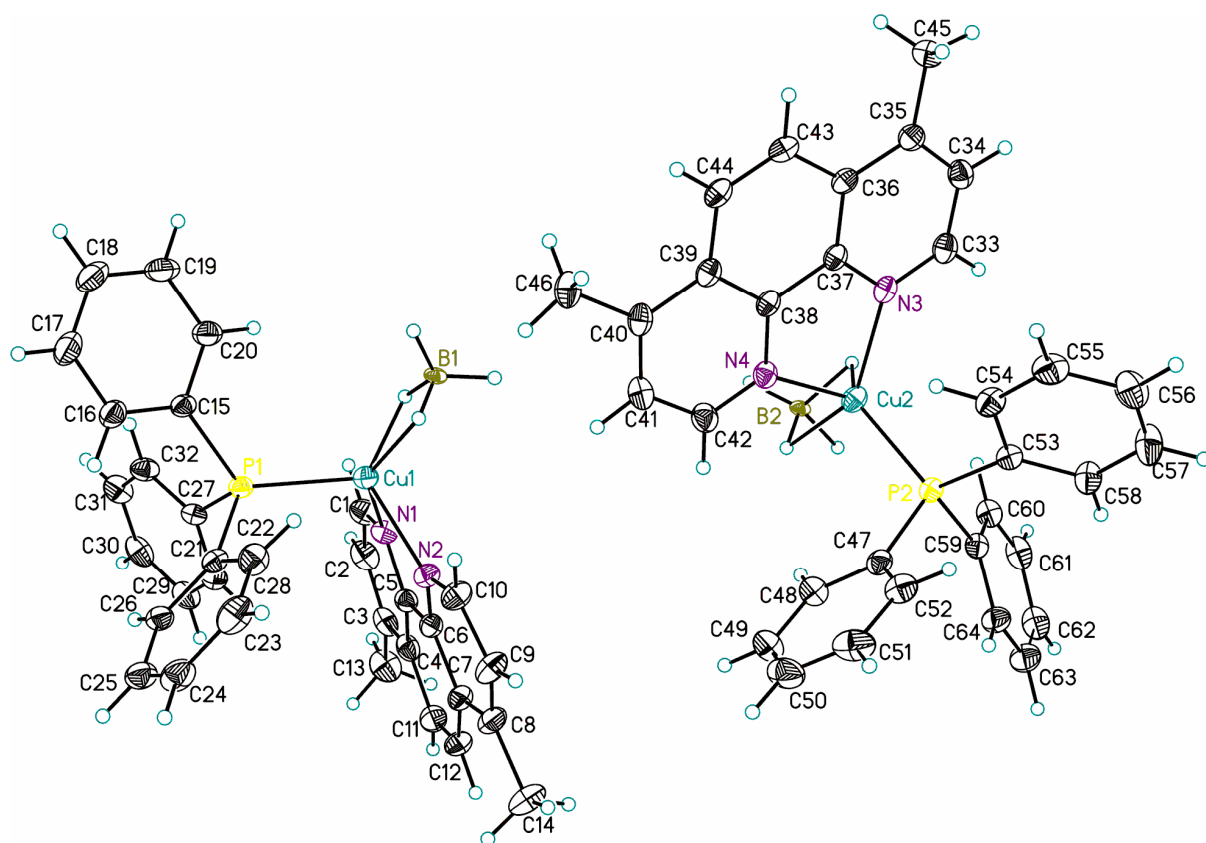
Fig. 1. Perspective view of the complex containing Cu1, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.
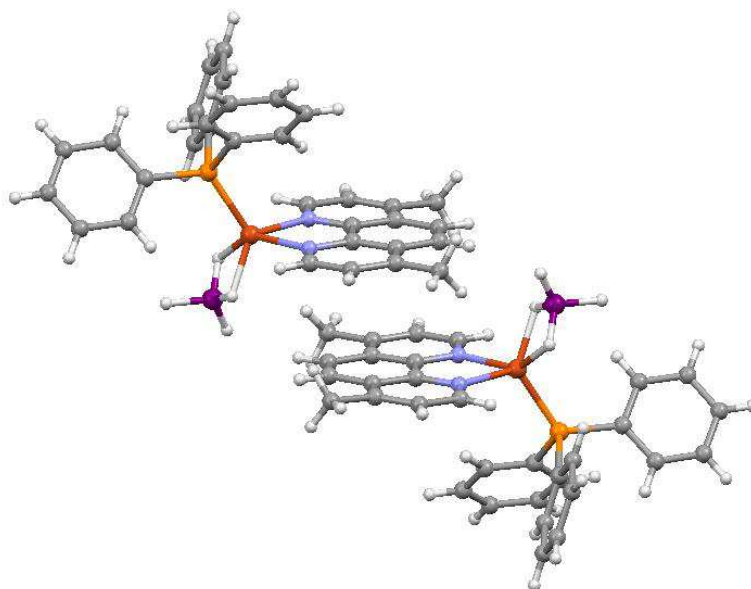
Fig. 2. The π-π stacking interactions in crystal structure of **I**.

The distances between Cu and B atoms in molecule A and B are 2.286(2) Å and 2.307(2) Å, respectively. The molecular structure of both molecules of **I** are very similar with molecular structure of α and β forms of [Cu(PPh$_3$)(1,10-phenanthroline)(BH$_4$)] (Green et al., 1984; Green et al., 1981) as well as [Cu(P(OEt)$_3$)(1,10-phenanthroline)(BH$_4$)] (Makhaev et al., 1993). On the other hand, the copper atom is only four-coordinated in [Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)(BH$_4$)] (Green et al., 1984; Moncol et al., 2006) and [Cu(2,9-dimethyl-1,10-phenanthroline)(BH$_4$)] (Green et al., 1980). The additional interactions between molecules of **I** are π-π stacking interactions (Fig. 2) (Janiak, 2000) between the symmetry-related adjacent phenanthroline rings of molecule B (atoms N3/N4/C33–C44) (-x + 2, -y + 1, -z) [distances between the planes of phenanthroline rings is 3.47 Å].

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