Crystal structure of (*N*-benzoyl-*N'*-(2-pyridylmethylene)hydrazine)-bis(trimethylphosphine)copper(I) tetrafluoroborate, $[Cu(C_{12}H_{10}N_4O)\{P(C_6H_5)_3\}_2]BF_4$

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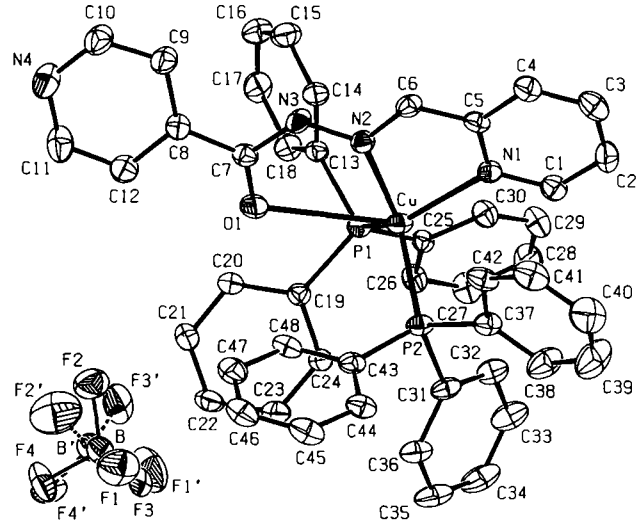

Abstract

$C_{48}H_{40}BCuF_4N_4OP_2$, triclinic, $P\bar{1}$ (no. 2),
$a = 11.909(2)$ Å, $b = 13.046(2)$ Å, $c = 15.144(3)$ Å,
$\alpha = 99.617(4)°$, $\beta = 96.925(4)°$, $\gamma = 96.039(3)°$,
$V = 2283.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.048$, $wR_{ref}(F^2) = 0.123$,
$T = 293$ K.

Source of material

0.1 mmol *N'*-[(1-*E*)-pyridine-2-ylmethylene]isonicotinohydrazide and 0.1 mmol $[Cu(PPh_3)_2(MeCN)]BF_4$ were dissolved in 10.0 mL methanol. The mixture was stirred for 1 h and filtered off. The filtrate was allowed to stand at room temperature. Red block-shaped crystals of the title compound afforded by slow evaporation after 24 hours (yield 75%).

Discussion

The title structure is not isotypic, but similar to the structure of $[Cu(C_{12}H_{10}N_4O)(PPh_3)_2](ClO_4) \cdot 0.75C_2H_5OH$ [1]. The asymmetric unit consists of one $[Cu(C_{12}H_{10}N_4O)(PPh_3)_2]^+$ cation and one BF_4^- anion ($C_{12}H_{10}N_4O$: *N'*-[(1-*E*)-pyridine-2-ylmethylene]isonicotinohydrazide). The tetrahedrally coordinated Cu(I) ion is surrounded by two N atoms from the Schiff base ligand and two P atoms from two PPh_3 groups. The Schiff base ligand acts as bidentate with N1 and N2 atoms chelating to Cu atom. The Cu—N bond lengths (d(Cu—N1) = 2.158(4) Å, d(Cu—N2) = 2.156(4) Å) are slightly longer than those observed of Cu(I) complex reported in [2] (2.084(4) Å, 2.032(3) Å). The Cu—P distances (2.264(2) Å, 2.280(2) Å) are comparable to those of another Cu(I) complex (2.275(3) Å, 2.281(3) Å) [3]. The chelating N1–Cu–N2 angle of 76.72(2)° is smaller than the ideal values for a tetrahedral environment. This may be due to the stable five-member cycle through Cu, N1, C6, and N2 atoms. The other bond lengths and angles are within the normal range reported for related complexes [4]. A reason for the small N_{gt}/N_{param} ratio could not be found.

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Table 1. Data collection and handling.

Crystal:	red block, size 0.28 × 0.30 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.04 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	41.82°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7944, 4818
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3246
$N(param)_{refined}$:	590
Programs:	SHELXS-97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	2*i*	0.4981	0.4516	0.3376	0.074
H(1)	2*i*	0.6497	0.7292	0.0480	0.077
H(2)	2*i*	0.4936	0.7210	−0.0593	0.093
H(3)	2*i*	0.3257	0.6187	−0.0474	0.098
H(4)	2*i*	0.3217	0.5307	0.0729	0.083
H(6)	2*i*	0.4161	0.4858	0.2104	0.070
H(9)	2*i*	0.5162	0.3198	0.4080	0.092
H(10)	2*i*	0.5194	0.2224	0.5210	0.112
H(11)	2*i*	0.7424	0.4293	0.6781	0.114
H(12)	2*i*	0.7520	0.5302	0.5696	0.090
H(14)	2*i*	0.7093	0.4226	0.2267	0.074
H(15)	2*i*	0.7048	0.2443	0.2169	0.097
H(16)	2*i*	0.8715	0.1695	0.2255	0.105
H(17)	2*i*	1.0434	0.2741	0.2470	0.100
H(18)	2*i*	1.0514	0.4539	0.2550	0.082
H(20)	2*i*	0.9552	0.5458	0.4223	0.075
H(21)	2*i*	1.0690	0.6330	0.5525	0.094
H(22)	2*i*	1.1625	0.7974	0.5589	0.094
H(23)	2*i*	1.1371	0.8777	0.4370	0.092
H(24)	2*i*	1.0212	0.7947	0.3067	0.072
H(26)	2*i*	1.1153	0.6511	0.2150	0.077
H(27)	2*i*	1.1954	0.6892	0.0925	0.090
H(28)	2*i*	1.0864	0.6784	−0.0448	0.101
H(29)	2*i*	0.8912	0.6331	−0.0577	0.097
H(30)	2*i*	0.8087	0.6047	0.0672	0.077
H(32)	2*i*	0.8234	0.8384	0.1449	0.091
H(33)	2*i*	0.9921	0.9239	0.1175	0.117
H(34)	2*i*	1.1004	1.0484	0.2302	0.125

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(35)	2*i*	1.0464	1.0827	0.3700	0.113
H(36)	2*i*	0.8774	0.9996	0.3992	0.088
H(38)	2*i*	0.6718	0.9994	0.1896	0.124
H(39)	2*i*	0.5137	1.0650	0.1285	0.165
H(40)	2*i*	0.3350	0.9885	0.1342	0.145
H(41)	2*i*	0.3102	0.8533	0.2129	0.107

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(42)	2*i*	0.4649	0.7870	0.2754	0.085
H(44)	2*i*	0.6244	1.0039	0.4121	0.085
H(45)	2*i*	0.6150	1.0435	0.5656	0.101
H(46)	2*i*	0.6749	0.9326	0.6602	0.103
H(47)	2*i*	0.7586	0.7882	0.6030	0.101
H(48)	2*i*	0.7734	0.7509	0.4506	0.084

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	2*i*		0.70372(5)	0.65708(5)	0.24382(4)	0.0457(4)	0.0431(4)	0.0703(5)	0.0007(3)	0.0027(3)	0.0046(3)
P(1)	2*i*		0.8764(1)	0.5988(1)	0.24815(9)	0.0469(9)	0.0430(9)	0.055(1)	0.0041(7)	0.0030(7)	0.0040(7)
P(2)	2*i*		0.7046(1)	0.8316(1)	0.2959(1)	0.0440(9)	0.0431(9)	0.075(1)	0.0011(7)	0.0055(7)	0.0034(7)
N(1)	2*i*		0.5815(4)	0.6395(3)	0.1232(3)	0.059(3)	0.046(3)	0.054(3)	0.008(2)	0.008(2)	0.005(2)
N(2)	2*i*		0.5661(4)	0.5489(3)	0.2681(3)	0.052(3)	0.050(3)	0.060(3)	0.002(2)	0.006(3)	0.011(2)
N(3)	2*i*		0.5588(4)	0.4937(3)	0.3375(3)	0.047(3)	0.061(3)	0.079(4)	−0.008(2)	0.006(3)	0.029(3)
N(4)	2*i*		0.6290(5)	0.3166(5)	0.6113(4)	0.060(4)	0.115(5)	0.114(5)	0.011(3)	0.011(4)	0.061(4)
O(1)	2*i*		0.7302(3)	0.5687(3)	0.4106(2)	0.062(3)	0.077(3)	0.078(3)	−0.024(2)	−0.003(2)	0.017(2)
C(1)	2*i*		0.5824(5)	0.6890(4)	0.0533(4)	0.063(4)	0.064(4)	0.063(4)	0.009(3)	0.008(4)	0.008(3)
C(2)	2*i*		0.4893(6)	0.6844(5)	−0.0119(4)	0.087(5)	0.088(5)	0.062(5)	0.026(4)	0.004(4)	0.022(3)
C(3)	2*i*		0.3900(6)	0.6241(5)	−0.0046(4)	0.061(5)	0.098(5)	0.075(5)	0.018(4)	−0.004(4)	−0.007(4)
C(4)	2*i*		0.3878(5)	0.5722(4)	0.0671(4)	0.065(5)	0.069(4)	0.070(5)	0.005(3)	0.004(4)	0.007(4)
C(5)	2*i*		0.4834(5)	0.5815(4)	0.1302(4)	0.044(4)	0.049(4)	0.064(4)	0.001(3)	−0.003(3)	−0.002(3)
C(6)	2*i*		0.4800(5)	0.5311(4)	0.2060(4)	0.045(4)	0.051(4)	0.078(5)	0.000(3)	0.007(3)	0.018(3)
C(7)	2*i*		0.6476(5)	0.5052(4)	0.4066(4)	0.051(4)	0.057(4)	0.058(4)	−0.001(3)	0.009(3)	0.005(3)
C(8)	2*i*		0.6351(4)	0.4377(4)	0.4751(4)	0.037(3)	0.071(4)	0.064(4)	0.005(3)	0.008(3)	0.018(3)
C(9)	2*i*		0.5643(5)	0.3440(5)	0.4623(4)	0.057(4)	0.080(5)	0.093(5)	−0.010(4)	−0.001(3)	0.034(4)
C(10)	2*i*		0.5658(6)	0.2864(5)	0.5315(6)	0.071(5)	0.095(5)	0.116(6)	−0.013(4)	−0.001(5)	0.050(5)
C(11)	2*i*		0.6963(6)	0.4064(7)	0.6227(5)	0.069(5)	0.138(7)	0.087(6)	0.012(5)	0.009(4)	0.050(5)
C(12)	2*i*		0.7024(5)	0.4680(5)	0.5577(5)	0.052(4)	0.082(5)	0.088(5)	−0.001(3)	0.002(4)	0.023(4)
C(13)	2*i*		0.8807(5)	0.4583(4)	0.2434(3)	0.060(4)	0.041(3)	0.049(3)	0.008(3)	0.002(3)	0.001(2)
C(14)	2*i*		0.7773(5)	0.3935(4)	0.2309(3)	0.075(5)	0.046(4)	0.062(4)	0.014(3)	0.009(3)	0.001(3)
C(15)	2*i*		0.7746(6)	0.2865(5)	0.2248(4)	0.086(5)	0.055(5)	0.095(5)	0.002(4)	0.006(4)	0.008(3)
C(16)	2*i*		0.8738(7)	0.2417(5)	0.2301(4)	0.117(7)	0.052(4)	0.091(5)	0.009(5)	0.011(5)	0.009(3)
C(17)	2*i*		0.9760(6)	0.3042(5)	0.2424(4)	0.101(6)	0.069(5)	0.083(5)	0.041(4)	0.007(4)	0.012(4)
C(18)	2*i*		0.9812(5)	0.4126(5)	0.2481(3)	0.076(5)	0.058(4)	0.074(4)	0.026(3)	0.012(3)	0.007(3)
C(19)	2*i*		0.9758(4)	0.6599(4)	0.3491(4)	0.052(3)	0.045(4)	0.052(4)	0.010(3)	0.005(3)	0.004(3)
C(20)	2*i*		0.9913(5)	0.6131(4)	0.4242(4)	0.073(4)	0.049(4)	0.059(4)	0.000(3)	0.002(3)	0.001(3)
C(21)	2*i*		1.0601(5)	0.6653(5)	0.5022(4)	0.101(5)	0.071(5)	0.056(4)	0.011(4)	−0.010(4)	0.010(4)
C(22)	2*i*		1.1152(5)	0.7634(5)	0.5065(4)	0.091(5)	0.055(4)	0.074(5)	0.001(4)	−0.012(4)	−0.010(4)
C(23)	2*i*		1.1003(5)	0.8105(5)	0.4342(5)	0.079(5)	0.060(4)	0.082(5)	−0.008(3)	−0.007(4)	0.007(4)
C(24)	2*i*		1.0309(4)	0.7605(4)	0.3557(4)	0.064(4)	0.047(4)	0.064(4)	0.000(3)	−0.003(3)	0.010(3)
C(25)	2*i*		0.9514(4)	0.6242(4)	0.1553(3)	0.045(4)	0.047(3)	0.050(4)	0.013(3)	−0.005(3)	0.006(3)
C(26)	2*i*		1.0688(5)	0.6490(4)	0.1607(4)	0.053(4)	0.082(4)	0.057(4)	0.013(3)	0.007(3)	0.010(3)
C(27)	2*i*		1.1170(5)	0.6704(5)	0.0866(5)	0.053(4)	0.096(5)	0.079(5)	0.020(3)	0.018(4)	0.016(4)
C(28)	2*i*		1.0526(6)	0.6648(5)	0.0050(5)	0.080(5)	0.112(6)	0.065(5)	0.009(4)	0.027(4)	0.019(4)
C(29)	2*i*		0.9367(6)	0.6386(5)	−0.0023(4)	0.082(6)	0.102(5)	0.054(5)	0.011(4)	−0.001(4)	0.008(4)
C(30)	2*i*		0.8876(5)	0.6202(4)	0.0728(4)	0.054(4)	0.079(4)	0.060(4)	0.008(3)	0.007(4)	0.010(3)
C(31)	2*i*		0.8319(4)	0.9093(4)	0.2743(4)	0.052(4)	0.038(3)	0.097(5)	0.010(3)	0.015(4)	0.009(3)
C(32)	2*i*		0.8676(5)	0.8879(4)	0.1907(5)	0.069(5)	0.061(4)	0.099(6)	0.002(3)	0.025(4)	0.013(4)
C(33)	2*i*		0.9684(6)	0.9391(6)	0.1740(5)	0.085(5)	0.073(5)	0.145(7)	0.008(4)	0.046(5)	0.027(5)
C(34)	2*i*		1.0333(6)	1.0128(6)	0.2416(7)	0.066(5)	0.066(5)	0.192(9)	0.001(4)	0.038(6)	0.044(6)
C(35)	2*i*		1.0007(6)	1.0340(5)	0.3246(6)	0.063(5)	0.049(4)	0.163(8)	−0.009(4)	0.012(5)	0.011(4)
C(36)	2*i*		0.9000(5)	0.9838(4)	0.3423(4)	0.055(4)	0.048(4)	0.110(5)	0.001(3)	0.006(4)	0.006(4)
C(37)	2*i*		0.5871(5)	0.8876(4)	0.2416(4)	0.051(4)	0.050(4)	0.078(4)	0.011(3)	0.004(3)	0.004(3)
C(38)	2*i*		0.5992(6)	0.9695(5)	0.1954(5)	0.075(5)	0.076(5)	0.168(7)	0.018(4)	0.007(5)	0.047(5)
C(39)	2*i*		0.5041(8)	1.0078(6)	0.1575(6)	0.106(7)	0.114(7)	0.21(1)	0.042(6)	0.009(7)	0.079(6)
C(40)	2*i*		0.3980(8)	0.9638(7)	0.1620(6)	0.084(7)	0.122(8)	0.152(8)	0.037(6)	−0.016(6)	0.020(6)
C(41)	2*i*		0.3834(5)	0.8823(6)	0.2078(5)	0.049(4)	0.100(6)	0.109(6)	0.013(4)	0.002(4)	−0.004(4)
C(42)	2*i*		0.4759(5)	0.8436(4)	0.2460(4)	0.047(4)	0.067(4)	0.086(5)	0.006(3)	−0.003(3)	−0.011(3)
C(43)	2*i*		0.6972(4)	0.8715(4)	0.4145(4)	0.038(3)	0.051(4)	0.075(4)	−0.001(3)	−0.004(3)	0.005(3)
C(44)	2*i*		0.6512(5)	0.9600(5)	0.4500(4)	0.064(4)	0.062(4)	0.078(5)	0.009(3)	0.004(3)	−0.008(3)
C(45)	2*i*		0.6448(5)	0.9833(5)	0.5422(5)	0.059(4)	0.083(5)	0.098(6)	0.019(4)	0.001(4)	−0.022(5)
C(46)	2*i*		0.6824(5)	0.9183(6)	0.5991(5)	0.066(5)	0.104(6)	0.076(5)	−0.002(4)	0.005(4)	−0.008(5)
C(47)	2*i*		0.7311(5)	0.8315(5)	0.5647(5)	0.070(5)	0.083(5)	0.088(6)	−0.004(4)	−0.013(4)	0.010(4)
C(48)	2*i*		0.7392(5)	0.8089(5)	0.4731(5)	0.064(4)	0.068(4)	0.064(5)	−0.005(3)	0.001(3)	−0.014(4)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
B	2*i*	0.64(1)	0.6723(5)	0.7175(4)	0.7901(4)	0.084(9)	0.072(7)	0.080(8)	–0.002(7)	0.014(8)	0.019(6)
F(1)	2*i*	0.64	0.5616(6)	0.7320(8)	0.7862(7)	0.098(7)	0.180(9)	0.16(1)	0.028(6)	0.002(6)	0.061(7)
F(2)	2*i*	0.64	0.7045(7)	0.6787(8)	0.8651(6)	0.092(6)	0.142(9)	0.108(7)	–0.007(6)	–0.010(5)	0.049(7)
F(3)	2*i*	0.64	0.686(1)	0.6486(6)	0.7163(6)	0.26(2)	0.091(6)	0.16(1)	0.004(8)	0.10(1)	–0.010(6)
F(4)	2*i*	0.64	0.7368(9)	0.8093(5)	0.7927(7)	0.131(9)	0.064(5)	0.156(9)	–0.028(5)	0.039(6)	0.009(5)
B′	2*i*	0.36	0.6975(8)	0.7232(8)	0.7961(8)	0.084(9)	0.072(7)	0.080(8)	–0.002(7)	0.014(8)	0.019(6)
F(1′)	2*i*	0.36	0.602(1)	0.695(1)	0.736(1)	0.11(1)	0.11(1)	0.15(2)	–0.09(1)	–0.10(1)	0.07(1)
F(2′)	2*i*	0.36	0.670(2)	0.763(2)	0.878(1)	0.22(2)	0.26(2)	0.13(2)	0.06(2)	0.09(2)	0.04(2)
F(3′)	2*i*	0.36	0.7491(9)	0.6371(9)	0.803(2)	0.069(9)	0.10(1)	0.21(2)	–0.003(7)	–0.06(1)	0.03(1)
F(4′)	2*i*	0.36	0.768(1)	0.796(1)	0.769(1)	0.056(8)	0.18(2)	0.10(1)	–0.052(9)	–0.008(8)	0.08(1)

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