Crystal structure of a new polymorph of iodo-(benzthiazoline-2-thione-κ*S*)-bis(triphenylphosphine-κ*P*)copper(I), $[CuI(C_7H_5NS_2)(PPh_3)_2]$, $C_{43}H_{35}CuINP_2S_2$

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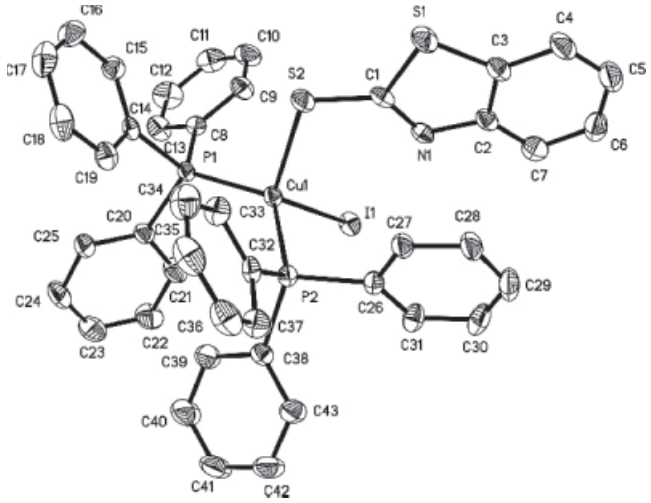

Abstract

$C_{43}H_{35}CuINP_2S_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.6136(8) Å, b = 12.406(1) Å, c = 16.729(1) Å, α = 96.807(1)°, β = 98.279(1)°, γ = 113.245(2)°, V = 1965.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.0314, $wR_{ref}(F^2)$ = 0.0828, T = 298 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.37×0.40×0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.60 cm^{-1}
Diffractometer, scan mode:	Bruker Smart CCD area detector, φ and ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9873, 6808
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5514
$N(param)_{refined}$:	451
Programs:	SHELX [13]

Source of material

A mixture of CuI (0.2 mmol) and benzthiazoline-2-thione (0.2 mmol) in MeOH and CH_2Cl_2 (10mL, *v*/*v* = 1:1) was stirred for 2h. PPh_3 (0.2 mmol) was added to the mixture, which was stirred for another 4h. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature for a week to yield colourless crystalline products.

Discussion

Various transition metal complexes with bridging phosphines or functionalized phosphines have drawn much attention in recent years [1-3]. The ligand benzthiazoline-2-thione (*BTZT*), with one N–H and two sulfur atoms able to coordinate metal centers, is excellent in building supramolecular structures [4-7]. We herein report a new triclinic polymorph of $[CuI(BTZT)(PPh_3)_2]$. Polymorphism can potentially be found for any crystalline material. For examples, the compound pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile has monoclinic and orthorhombic crystals [8, 9], and the compound 3,4,5-trihydroxybenzoic acid monohydrate has three polymorphs [10-12]. The difference of hydration, solvation or the effect of synthesis methods may lead to different crystal types. The title compound, has a polymorph which has been previously reported to be monoclinic (space group $P2_1/n$, Z = 4) [6], whereas the title structure undoubtely reveals triclinic symmetry. In the title structure, *BTZT* acts as a neutral, monodentate ligand with the S atom as coordination atom. Other sites of coordination tetrahedron are occupied by two P atoms from two PPh_3 ligands and an iodido ligand (Fig.1). The Cu–S, Cu–P and Cu–I bond lengths agree with those reported for the monoclinic polymorph. The largest deviation from the tetrahedral geometry at the Cu metal center is reflected by the P–Cu–P angle with a value of 127.15(3)°. Moreover, an intramolecular N–H···I hydrogen bond is observed (N···I distance = 3.523(3) Å, N–H···I angle = 163.86°). There is also π-π interactions between inversion related benzthiazoline rings [centroid-centroid distances = 3.789 Å, symmetry operation: -x, -y, 1-z].

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.2435	0.1138	0.6552	0.044
H(4)	2*i*	0.0579	–0.2412	0.4136	0.070
H(5)	2*i*	–0.1622	–0.3061	0.4454	0.075
H(6)	2*i*	–0.2005	–0.2071	0.5569	0.068
H(7)	2*i*	–0.0222	–0.0348	0.6391	0.060
H(9)	2*i*	0.4614	0.4440	0.6092	0.058
H(10)	2*i*	0.3714	0.5505	0.5325	0.073
H(11)	2*i*	0.4523	0.7535	0.5717	0.073
H(12)	2*i*	0.6308	0.8537	0.6847	0.082
H(13)	2*i*	0.7244	0.7501	0.7611	0.064
H(15)	2*i*	0.8020	0.5890	0.6128	0.053
H(16)	2*i*	0.9900	0.5872	0.5599	0.071
H(17)	2*i*	1.1338	0.5116	0.6243	0.078
H(18)	2*i*	1.0889	0.4344	0.7406	0.071
H(19)	2*i*	0.8982	0.4319	0.7928	0.058
H(21)	2*i*	0.5553	0.5608	0.8771	0.067
H(22)	2*i*	0.6280	0.6709	1.0087	0.083
H(23)	2*i*	0.8630	0.7733	1.0659	0.089
H(24)	2*i*	1.0253	0.7659	0.9914	0.094

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Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(25)	2*i*	0.9550	0.6549	0.8586	0.067
H(27)	2*i*	0.4688	–0.0382	0.7218	0.048
H(28)	2*i*	0.2679	–0.2137	0.6828	0.063
H(29)	2*i*	0.0840	–0.2427	0.7476	0.072
H(30)	2*i*	0.0964	–0.0928	0.8482	0.068
H(31)	2*i*	0.2934	0.0871	0.8842	0.055
H(33)	2*i*	0.7558	0.2069	0.7264	0.056
H(34)	2*i*	0.9299	0.1417	0.7126	0.076

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(35)	2*i*	0.9734	0.0246	0.7986	0.077
H(36)	2*i*	0.8447	–0.0312	0.8978	0.074
H(37)	2*i*	0.6765	0.0393	0.9158	0.057
H(39)	2*i*	0.7171	0.4075	0.9359	0.075
H(40)	2*i*	0.7738	0.4853	1.0756	0.096
H(41)	2*i*	0.6911	0.3644	1.1668	0.086
H(42)	2*i*	0.5495	0.1667	1.1198	0.079
H(43)	2*i*	0.4900	0.0858	0.9814	0.062

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	0.52966(4)	0.30747(3)	0.74743(2)	0.0299(2)	0.0261(2)	0.0333(2)	0.0098(2)	0.0023(2)	0.0041(2)
P(1)	2*i*	0.67641(8)	0.50025(7)	0.75132(5)	0.0295(4)	0.0241(4)	0.0292(4)	0.0090(3)	0.0009(3)	0.0021(3)
P(2)	2*i*	0.56098(8)	0.18415(7)	0.83191(5)	0.0285(4)	0.0264(4)	0.0364(4)	0.0118(3)	0.0040(3)	0.0074(3)
I(1)	2*i*	0.28552(2)	0.30554(2)	0.76714(1)	0.0349(1)	0.0454(2)	0.0459(2)	0.0215(1)	0.0066(1)	0.0001(1)
N(1)	2*i*	0.2433(3)	0.0678(2)	0.6124(2)	0.042(2)	0.037(2)	0.029(1)	0.018(1)	0.003(1)	–0.004(1)
S(1)	2*i*	0.3217(1)	–0.02053(9)	0.49566(6)	0.0582(6)	0.0467(6)	0.0451(5)	0.0183(5)	0.0096(5)	–0.0142(4)
S(2)	2*i*	0.51203(9)	0.20904(9)	0.61179(5)	0.0452(5)	0.0458(5)	0.0354(5)	0.0142(4)	0.0061(4)	–0.0055(4)
C(1)	2*i*	0.3569(4)	0.0913(3)	0.5802(2)	0.048(2)	0.036(2)	0.026(2)	0.022(2)	–0.002(2)	–0.002(1)
C(2)	2*i*	0.1241(4)	–0.0351(3)	0.5734(2)	0.048(2)	0.032(2)	0.032(2)	0.017(2)	–0.003(2)	0.005(1)
C(3)	2*i*	0.1491(4)	–0.0953(3)	0.5066(2)	0.052(2)	0.036(2)	0.037(2)	0.019(2)	–0.001(2)	0.001(2)
C(4)	2*i*	0.0419(5)	–0.1993(3)	0.4580(2)	0.074(3)	0.040(2)	0.044(2)	0.016(2)	–0.001(2)	–0.007(2)
C(5)	2*i*	–0.0886(5)	–0.2381(4)	0.4778(3)	0.064(3)	0.042(2)	0.060(3)	0.008(2)	–0.008(2)	0.006(2)
C(6)	2*i*	–0.1118(4)	–0.1781(4)	0.5445(3)	0.046(2)	0.048(2)	0.069(3)	0.012(2)	0.002(2)	0.021(2)
C(7)	2*i*	–0.0061(4)	–0.0752(4)	0.5940(2)	0.052(2)	0.054(2)	0.048(2)	0.029(2)	0.005(2)	0.011(2)
C(8)	2*i*	0.6036(3)	0.5857(3)	0.6930(2)	0.037(2)	0.035(2)	0.034(2)	0.018(2)	0.007(1)	0.008(1)
C(9)	2*i*	0.4968(4)	0.5267(4)	0.6248(2)	0.048(2)	0.049(2)	0.044(2)	0.023(2)	–0.002(2)	0.007(2)
C(10)	2*i*	0.4421(4)	0.5906(4)	0.5791(2)	0.058(3)	0.086(3)	0.045(2)	0.038(3)	–0.001(2)	0.018(2)
C(11)	2*i*	0.4910(5)	0.7117(4)	0.6020(3)	0.077(3)	0.076(3)	0.062(3)	0.056(3)	0.022(2)	0.033(2)
C(12)	2*i*	0.5965(5)	0.7711(4)	0.6694(3)	0.096(4)	0.053(3)	0.076(3)	0.050(3)	0.017(3)	0.021(2)
C(13)	2*i*	0.6527(4)	0.7089(3)	0.7150(2)	0.060(2)	0.038(2)	0.058(2)	0.022(2)	–0.001(2)	0.006(2)
C(14)	2*i*	0.8293(3)	0.5114(3)	0.7092(2)	0.029(2)	0.023(2)	0.039(2)	0.006(1)	–0.001(1)	–0.002(1)
C(15)	2*i*	0.8591(4)	0.5573(3)	0.6389(2)	0.044(2)	0.041(2)	0.043(2)	0.017(2)	0.008(2)	0.004(2)
C(16)	2*i*	0.9720(4)	0.5567(4)	0.6073(3)	0.058(3)	0.062(3)	0.058(3)	0.022(2)	0.027(2)	0.003(2)
C(17)	2*i*	1.0573(4)	0.5112(4)	0.6454(3)	0.046(2)	0.052(3)	0.091(3)	0.018(2)	0.026(2)	–0.014(2)
C(18)	2*i*	1.0306(4)	0.4651(4)	0.7147(3)	0.038(2)	0.048(2)	0.090(3)	0.026(2)	0.001(2)	0.000(2)
C(19)	2*i*	0.9166(4)	0.4644(3)	0.7462(2)	0.041(2)	0.043(2)	0.056(2)	0.018(2)	0.002(2)	0.007(2)
C(20)	2*i*	0.7476(3)	0.5966(3)	0.8536(2)	0.041(2)	0.032(2)	0.033(2)	0.012(2)	0.003(2)	0.002(1)
C(21)	2*i*	0.6506(4)	0.6021(4)	0.8998(2)	0.052(2)	0.060(3)	0.049(2)	0.023(2)	0.005(2)	–0.008(2)
C(22)	2*i*	0.6940(5)	0.6678(4)	0.9785(2)	0.077(3)	0.075(3)	0.047(2)	0.031(3)	0.015(2)	–0.013(2)
C(23)	2*i*	0.8337(5)	0.7288(4)	1.0126(3)	0.088(3)	0.068(3)	0.041(2)	0.017(3)	0.004(2)	–0.017(2)
C(24)	2*i*	0.9302(5)	0.7241(4)	0.9681(3)	0.059(3)	0.086(4)	0.047(3)	0.001(3)	–0.007(2)	–0.019(2)
C(25)	2*i*	0.8884(4)	0.6578(4)	0.8882(2)	0.045(2)	0.056(3)	0.042(2)	0.001(2)	0.005(2)	–0.007(2)
C(26)	2*i*	0.4044(3)	0.0428(3)	0.8087(2)	0.029(2)	0.031(2)	0.042(2)	0.013(1)	0.001(1)	0.013(2)
C(27)	2*i*	0.3939(4)	–0.0484(3)	0.7475(2)	0.039(2)	0.034(2)	0.042(2)	0.011(2)	0.002(2)	0.007(2)
C(28)	2*i*	0.2738(4)	–0.1540(3)	0.7244(2)	0.053(2)	0.033(2)	0.051(2)	0.004(2)	–0.005(2)	0.001(2)
C(29)	2*i*	0.1639(4)	–0.1708(4)	0.7623(3)	0.041(2)	0.039(2)	0.079(3)	0.000(2)	–0.005(2)	0.015(2)
C(30)	2*i*	0.1715(4)	–0.0813(4)	0.8224(3)	0.032(2)	0.052(3)	0.089(3)	0.014(2)	0.019(2)	0.033(2)
C(31)	2*i*	0.2904(4)	0.0261(3)	0.8447(2)	0.037(2)	0.036(2)	0.067(2)	0.017(2)	0.013(2)	0.016(2)
C(32)	2*i*	0.6979(3)	0.1305(3)	0.8227(2)	0.026(2)	0.025(2)	0.049(2)	0.008(1)	–0.001(2)	0.003(2)
C(33)	2*i*	0.7742(4)	0.1601(3)	0.7619(2)	0.042(2)	0.046(2)	0.057(2)	0.023(2)	0.011(2)	0.010(2)
C(34)	2*i*	0.8782(4)	0.1205(4)	0.7531(3)	0.048(2)	0.073(3)	0.080(3)	0.034(2)	0.021(2)	0.011(2)
C(35)	2*i*	0.9036(4)	0.0507(4)	0.8043(3)	0.048(2)	0.072(3)	0.077(3)	0.040(2)	–0.003(2)	–0.005(2)
C(36)	2*i*	0.8278(4)	0.0182(4)	0.8641(3)	0.057(3)	0.059(3)	0.072(3)	0.037(2)	–0.011(2)	0.007(2)
C(37)	2*i*	0.7261(4)	0.0594(3)	0.8742(2)	0.044(2)	0.049(2)	0.057(2)	0.027(2)	0.006(2)	0.015(2)
C(38)	2*i*	0.5959(3)	0.2377(3)	0.9426(2)	0.040(2)	0.034(2)	0.037(2)	0.018(2)	0.002(2)	0.006(1)
C(39)	2*i*	0.6820(5)	0.3577(3)	0.9724(2)	0.077(3)	0.037(2)	0.046(2)	0.002(2)	–0.002(2)	0.010(2)
C(40)	2*i*	0.7166(5)	0.4045(4)	1.0564(3)	0.105(4)	0.048(3)	0.049(3)	0.002(3)	–0.007(3)	–0.002(2)
C(41)	2*i*	0.6673(5)	0.3329(4)	1.1107(2)	0.098(4)	0.063(3)	0.035(2)	0.023(3)	–0.009(2)	0.004(2)
C(42)	2*i*	0.5834(5)	0.2155(4)	1.0826(2)	0.095(3)	0.056(3)	0.043(2)	0.028(3)	0.006(2)	0.019(2)
C(43)	2*i*	0.5474(4)	0.1668(3)	0.9995(2)	0.069(3)	0.036(2)	0.044(2)	0.017(2)	0.003(2)	0.013(2)

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