Crystal structure of (μ-bis(diphenylphosphino methane-κ^2P,P'))-bis(1,10-phenanthroline-κ^2N,N')-bis(thiocyanate-κN)copper(I) — water (1:0.25), $[Cu_2(C_{25}H_{22}P_2)(C_{12}H_8N_2)_2(CNS)_2]_2 \cdot 0.5H_2O$

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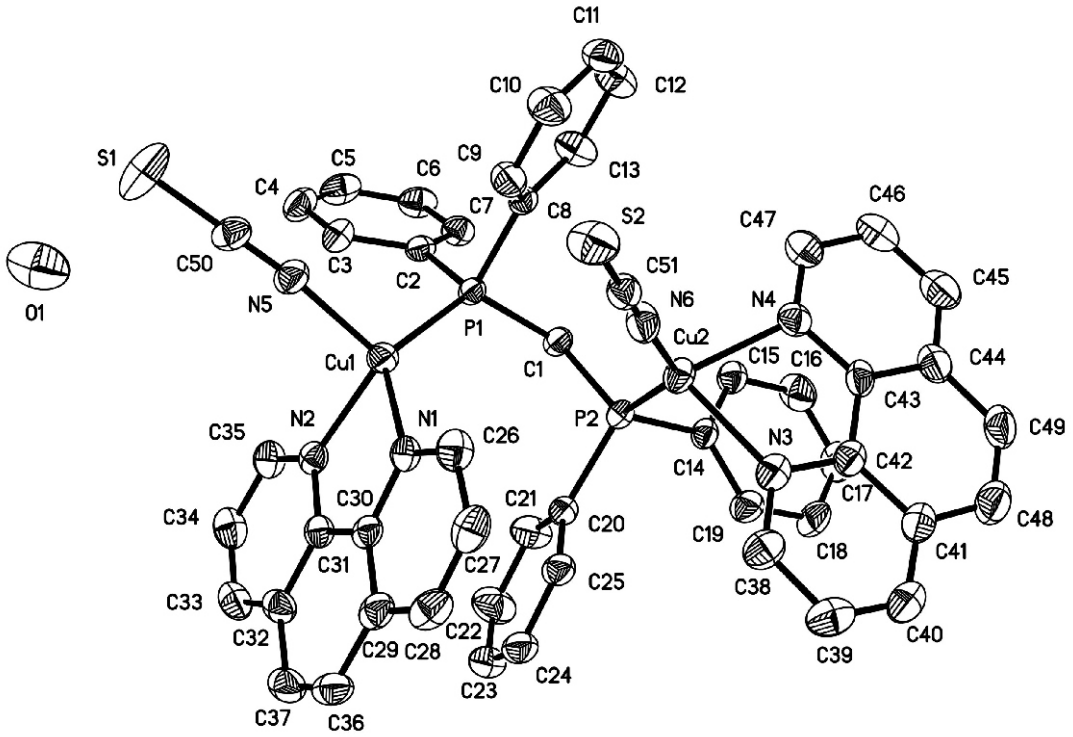

Abstract

$C_{102}H_{77}Cu_4N_{12}O_{0.5}P_4S_4$, monoclinic, *C*12/*c*1 (no. 15), a = 44.599(3) Å, b = 9.769(1) Å, c = 22.370(2) Å, β = 110.832(2)°, V = 9109.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.142, T = 298 K.

Source of material

The synthesis of the title compound was carried out by stirring the mixture of CuSCN (0.0594 g, 0.3 mmol), bis(diphenylphosphino)methane (dppm, 0.1154 g, 0.3 mmol) and 1,10-phenanthroline (1,10-phen, 0.05645 g, 0.3 mmol) in 5 ml of CH_3CN and 5 ml of CH_2Cl_2 for 6 hours at room temperature. The filtrate was allowed to stand at the room temperature. Slow evaporation of the solvent yielded yellow crystals.

Experimental details

The ratio $N_{gt}/N(param)$ is low because good quality single crystals of this compound are difficult to grow and hence the collection of data at room temperature is a challenge.

Discussion

Copper(I) complexes containing diphosphine and N-heterocyclic ligands have been in focus of investigation in the last few years because of their interesting structures, luminescence and novel reactivity performances.The design and synthesis of Cu(I) complexes can be influenced by many factors, especially by the ligands, anions, solvent and reaction time.The diphosphine ligands known in the literature with the general formula R_2P-$(X)_n$-PR_2 [X = CH_2, n = 1-4] have been studied extensively [1-3]. The dppm has been confirmed to be a very efficient bridging bidentate ligand, and its chelating tendency is very suitable to lock two metal atoms together in close proximity [4]. The *N*-heterocyclic 1,10-phen is an efficient chelating ligand. In previous work, we succeeded in synthesizing a series of copper(I) complexes with dppm and nitrogen containing heterocycle ligands, such as $\{[Cu_2(dppm)_2(BF_4)_2(pyz)](CH_2Cl_2)_2\}_n$ (pyz = pyrazine), $\{[Cu_2(dppm)_2(4,4'\text{-bpy})(CF_3SO_3)](CF_3SO_3)(CH_3OH)\}_n$, $\{[Cu_3(dppm)_3Br_2][Cu_2(dppm)(pyz)Br_2]Br \cdot (CH_3OH)_2\}_n$, $\{[Cu_2(dppm)_2(NO_3)(pyz)](pyz)\}_n$ [5,6].

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The asymmetric unit of the title crystal structure consists of the moiety $[Cu_2(dppm)(phen)_2(SCN)_2]$ and a half solvent water molecule. In the complex, the Cu(I) center is bonded to two phophorous atoms from dppm ligand, two nitrogen atoms from 1,10-phen ligand and one nitrogen atom from the SCN anion. The two Cu atoms are bridged by P atoms from dppm ligand. The structure is similar to that of $\{[Cu_2(dppe)_2(phen)_2](ClO_4)_2(CH_2Cl_2)\}_n$ (**1**) [5], but different from $\{[Cu_2(dppm)_2(BF_4)_2(pyz)](CH_2Cl_2)_2\}_n$ (**2**) [5]. *d*(Cu—P) = 2.194(2)-2.212(2) Å are shorter than the corresponding distances in (**1**) (2.212(6)-2.266(1) Å) and (**2**) (2.224(2)-2.227(2) Å). Furthermore, *d*(Cu—N) = 1.945(5)-2.134(5) Å in the title complex are different from the corresponding distances in (**1**) (2.070(1)-2.120(1) Å) and in (**2**) (2.091(4) Å).The difference of the distances in the three similar complexes above is due to the difference of the nitrogen heterocycle ligands, anions and solvents in them. ∠N–Cu–P = 99.7(1)° to 138.3(4)° in the title complex are different from those in (**1**) (108.1(4)°-114.1(4)°) and those in (**2**) (103.8(3)°-106.2(3)°). It is noticeable that although the title complex and (**1**) have the similar basic unit N_2Cu-PP-CuN_2, complex (**1**) is a polymer while the title complex is a binuclear compound. This can be explained as follows. In (**1**), the uncoordinated perchlorate provides the coordination site to the flexible ligand dppe and thus helps dppe to bridge N_2Cu-PP-CuN_2 and to form a chain, while in the title complex both the coordinated thiocyanate and the rigid ligand dppm prevent the unit N_2Cu-PP-CuN_2 from forming a chain.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.26 × 0.37 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.40 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19989, 7956
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4124
$N(param)_{refined}$:	573
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1E)	8*f*	0.0165	0.7490	0.2583	0.154
H(1A)	8*f*	0.1442	1.0493	0.0664	0.048
H(1B)	8*f*	0.1072	1.0555	0.0287	0.048
H(3)	8*f*	0.0792	0.9117	0.1869	0.062
H(4)	8*f*	0.0630	1.0802	0.2426	0.073
H(5)	8*f*	0.0787	1.3018	0.2409	0.075
H(6)	8*f*	0.1106	1.3605	0.1839	0.071
H(7)	8*f*	0.1280	1.1956	0.1307	0.059
H(9)	8*f*	0.1504	0.6570	0.1722	0.064
H(10)	8*f*	0.2017	0.5968	0.2374	0.079
H(11)	8*f*	0.2411	0.7590	0.2715	0.077
H(12)	8*f*	0.2301	0.9807	0.2368	0.082
H(13)	8*f*	0.1789	1.0431	0.1724	0.070
H(15)	8*f*	0.1663	1.1489	0.0090	0.060
H(16)	8*f*	0.1864	1.2934	–0.0502	0.082
H(17)	8*f*	0.1779	1.2445	–0.1555	0.087
H(18)	8*f*	0.1476	1.0583	–0.2030	0.080
H(19)	8*f*	0.1260	0.9184	–0.1460	0.065
H(21)	8*f*	0.0723	1.0502	–0.0671	0.079
H(22)	8*f*	0.0215	1.0179	–0.1414	0.095
H(23)	8*f*	0.0076	0.8094	–0.1904	0.080
H(24)	8*f*	0.0446	0.6385	–0.1703	0.071
H(25)	8*f*	0.0953	0.6689	–0.0942	0.057
H(26)	8*f*	0.1201	0.4704	0.0553	0.069
H(27)	8*f*	0.1072	0.3119	–0.0273	0.077
H(28)	8*f*	0.0566	0.3059	–0.1014	0.075
H(33)	8*f*	–0.0481	0.7602	–0.0743	0.072
H(34)	8*f*	–0.0305	0.9071	0.0105	0.074
H(35)	8*f*	0.0220	0.9004	0.0782	0.065
H(36)	8*f*	–0.0005	0.4010	–0.1415	0.074
H(37)	8*f*	–0.0359	0.5546	–0.1327	0.075
H(38)	8*f*	0.1398	0.5140	–0.1118	0.074
H(39)	8*f*	0.1450	0.4855	–0.2102	0.084
H(40)	8*f*	0.1795	0.6196	–0.2372	0.076
H(45)	8*f*	0.2662	1.0611	–0.0239	0.088
H(46)	8*f*	0.2595	1.0720	0.0731	0.088
H(47)	8*f*	0.2225	0.9241	0.0930	0.079
H(48)	8*f*	0.2214	0.8070	–0.2062	0.091
H(49)	8*f*	0.2510	0.9601	–0.1327	0.085

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(1)	8*f*		0.08512(2)	0.72129(7)	0.09349(3)	0.0462(4)	0.0451(4)	0.0401(4)	–0.0082(3)	0.0141(3)	–0.0012(3)
Cu(2)	8*f*		0.16573(2)	0.72228(7)	0.00626(3)	0.0511(4)	0.0450(4)	0.0439(4)	0.0068(4)	0.0226(4)	0.0085(3)
N(1)	8*f*		0.0785(1)	0.5625(5)	0.0288(2)	0.045(3)	0.040(3)	0.047(3)	–0.002(2)	0.022(3)	0.004(2)
N(2)	8*f*		0.0363(1)	0.7479(4)	0.0389(2)	0.051(3)	0.034(3)	0.045(3)	–0.006(2)	0.023(2)	0.001(2)
N(3)	8*f*		0.1712(1)	0.6597(5)	–0.0794(2)	0.055(3)	0.048(3)	0.049(3)	0.009(3)	0.022(3)	0.005(3)
N(4)	8*f*		0.2074(1)	0.8346(5)	0.0102(2)	0.041(3)	0.053(3)	0.050(3)	0.007(2)	0.012(3)	0.007(3)
N(5)	8*f*		0.0851(1)	0.6392(5)	0.1758(2)	0.065(3)	0.055(3)	0.042(3)	–0.011(3)	0.020(3)	0.005(3)
N(6)	8*f*		0.1763(1)	0.5600(6)	0.0602(2)	0.044(3)	0.062(4)	0.062(3)	0.008(3)	0.023(3)	0.016(3)
O(1)	4*e*	0.50	0	0.800(2)	¼	0.13(1)	0.09(1)	0.13(2)	0	0.00(1)	0
P(1)	8*f*		0.11805(3)	0.8961(1)	0.11147(6)	0.0392(8)	0.0351(8)	0.0307(8)	–0.0033(7)	0.0141(7)	–0.0022(6)
P(2)	8*f*		0.13019(3)	0.8904(1)	–0.01702(6)	0.0407(8)	0.0338(8)	0.0326(8)	0.0010(7)	0.0160(7)	0.0020(6)
S(1)	8*f*		0.07140(7)	0.6125(3)	0.2861(1)	0.180(2)	0.120(2)	0.080(2)	0.012(2)	0.084(2)	0.015(1)
S(2)	8*f*		0.19272(4)	0.3223(2)	0.13240(8)	0.079(1)	0.057(1)	0.067(1)	–0.005(1)	0.009(1)	0.0245(9)
C(1)	8*f*		0.1251(1)	0.9937(5)	0.0474(2)	0.048(3)	0.040(3)	0.035(3)	–0.005(3)	0.018(3)	–0.003(3)
C(2)	8*f*		0.1058(1)	1.0354(6)	0.1533(2)	0.039(3)	0.044(4)	0.031(3)	0.004(3)	0.009(3)	–0.004(3)
C(3)	8*f*		0.0859(1)	1.0016(6)	0.1865(3)	0.061(4)	0.054(4)	0.046(4)	0.005(3)	0.025(3)	0.005(3)
C(4)	8*f*		0.0761(2)	1.1034(7)	0.2197(3)	0.066(4)	0.075(5)	0.047(4)	0.014(4)	0.029(3)	0.000(4)
C(5)	8*f*		0.0853(2)	1.2351(7)	0.2187(3)	0.077(5)	0.061(5)	0.048(4)	0.022(4)	0.018(4)	–0.015(3)
C(6)	8*f*		0.1045(2)	1.2698(7)	0.1851(3)	0.065(4)	0.052(4)	0.054(4)	0.008(3)	0.011(4)	–0.013(3)
C(7)	8*f*		0.1148(1)	1.1708(6)	0.1530(3)	0.050(4)	0.047(4)	0.048(4)	0.001(3)	0.015(3)	–0.010(3)
C(8)	8*f*		0.1589(1)	0.8557(6)	0.1639(2)	0.043(3)	0.040(4)	0.032(3)	–0.006(3)	0.015(3)	–0.005(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(9)	8*f*	0.1663(1)	0.7237(6)	0.1848(3)	0.046(4)	0.055(4)	0.055(4)	–0.003(3)	0.012(3)	0.012(3)
C(10)	8*f*	0.1971(2)	0.6873(7)	0.2244(3)	0.057(5)	0.065(5)	0.067(5)	0.011(4)	0.010(4)	0.015(4)
C(11)	8*f*	0.2206(2)	0.7832(8)	0.2443(3)	0.050(4)	0.082(6)	0.051(4)	0.010(4)	0.006(3)	0.000(4)
C(12)	8*f*	0.2140(2)	0.9151(8)	0.2242(3)	0.049(4)	0.068(5)	0.078(5)	–0.007(4)	0.009(4)	–0.015(4)
C(13)	8*f*	0.1832(1)	0.9522(6)	0.1849(3)	0.052(4)	0.041(4)	0.070(4)	0.001(3)	0.007(4)	–0.007(3)
C(14)	8*f*	0.1437(1)	1.0188(6)	–0.0621(3)	0.042(3)	0.043(4)	0.039(3)	0.001(3)	0.019(3)	0.006(3)
C(15)	8*f*	0.1621(1)	1.1305(6)	–0.0341(3)	0.053(4)	0.052(4)	0.049(4)	–0.007(3)	0.023(3)	0.002(3)
C(16)	8*f*	0.1745(2)	1.2167(7)	–0.0694(3)	0.066(4)	0.058(4)	0.077(5)	–0.019(4)	0.022(4)	0.011(4)
C(17)	8*f*	0.1693(2)	1.1884(8)	–0.1321(4)	0.075(5)	0.080(6)	0.069(5)	–0.006(4)	0.032(4)	0.029(4)
C(18)	8*f*	0.1513(2)	1.0775(8)	–0.1603(3)	0.076(5)	0.087(6)	0.043(4)	0.001(4)	0.029(4)	0.015(4)
C(19)	8*f*	0.1384(1)	0.9932(6)	–0.1260(3)	0.061(4)	0.059(4)	0.041(4)	–0.005(3)	0.018(3)	0.007(3)
C(20)	8*f*	0.0893(1)	0.8631(6)	–0.0714(2)	0.043(3)	0.043(4)	0.037(3)	–0.004(3)	0.016(3)	–0.002(3)
C(21)	8*f*	0.0669(2)	0.9655(7)	–0.0871(3)	0.056(4)	0.065(5)	0.064(5)	0.005(4)	0.007(4)	–0.013(4)
C(22)	8*f*	0.0363(2)	0.9468(8)	–0.1318(3)	0.054(5)	0.088(6)	0.081(5)	0.014(4)	0.006(4)	–0.007(5)
C(23)	8*f*	0.0283(2)	0.8235(8)	–0.1613(3)	0.056(4)	0.087(6)	0.049(4)	–0.013(4)	0.010(3)	–0.002(4)
C(24)	8*f*	0.0500(2)	0.7213(7)	–0.1487(3)	0.070(5)	0.063(5)	0.044(4)	–0.023(4)	0.021(4)	–0.009(3)
C(25)	8*f*	0.0806(1)	0.7403(6)	–0.1032(3)	0.055(4)	0.049(4)	0.040(3)	–0.007(3)	0.018(3)	0.002(3)
C(26)	8*f*	0.0995(2)	0.4705(6)	0.0246(3)	0.058(4)	0.055(4)	0.064(4)	0.004(3)	0.027(4)	0.005(3)
C(27)	8*f*	0.0918(2)	0.3734(7)	–0.0248(3)	0.082(5)	0.054(5)	0.070(5)	0.007(4)	0.044(4)	0.002(4)
C(28)	8*f*	0.0619(2)	0.3699(6)	–0.0686(3)	0.095(6)	0.043(4)	0.054(4)	–0.009(4)	0.034(4)	–0.006(3)
C(29)	8*f*	0.0387(2)	0.4611(6)	–0.0649(3)	0.070(5)	0.048(4)	0.045(4)	–0.009(3)	0.026(4)	0.004(3)
C(30)	8*f*	0.0481(1)	0.5578(6)	–0.0156(3)	0.053(4)	0.037(3)	0.038(3)	–0.007(3)	0.020(3)	0.006(3)
C(31)	8*f*	0.0260(1)	0.6576(6)	–0.0101(3)	0.045(4)	0.039(4)	0.043(3)	–0.005(3)	0.018(3)	0.004(3)
C(32)	8*f*	–0.0059(2)	0.6580(6)	–0.0537(3)	0.051(4)	0.046(4)	0.053(4)	–0.013(3)	0.013(3)	0.006(3)
C(33)	8*f*	–0.0271(2)	0.7557(7)	–0.0458(3)	0.045(4)	0.061(5)	0.069(5)	–0.004(3)	0.014(4)	0.017(4)
C(34)	8*f*	–0.0166(2)	0.8433(7)	0.0038(3)	0.052(4)	0.056(4)	0.080(5)	0.008(3)	0.026(4)	0.016(4)
C(35)	8*f*	0.0152(1)	0.8377(6)	0.0448(3)	0.057(4)	0.049(4)	0.062(4)	0.000(3)	0.028(4)	0.003(3)
C(36)	8*f*	0.0062(2)	0.4648(7)	–0.1085(3)	0.081(5)	0.057(5)	0.041(4)	–0.023(4)	0.014(4)	–0.003(3)
C(37)	8*f*	–0.0150(2)	0.5564(7)	–0.1035(3)	0.062(5)	0.064(5)	0.053(4)	–0.021(4)	0.010(4)	0.009(4)
C(38)	8*f*	0.1543(2)	0.5688(7)	–0.1221(3)	0.073(5)	0.056(4)	0.056(4)	0.008(4)	0.024(4)	0.000(4)
C(39)	8*f*	0.1572(2)	0.5511(7)	–0.1818(3)	0.084(5)	0.063(5)	0.055(4)	0.014(4)	0.015(4)	–0.004(4)
C(40)	8*f*	0.1777(2)	0.6297(7)	–0.1973(3)	0.074(5)	0.069(5)	0.052(4)	0.017(4)	0.030(4)	0.007(4)
C(41)	8*f*	0.1963(2)	0.7264(7)	–0.1550(3)	0.054(4)	0.067(5)	0.051(4)	0.020(4)	0.023(3)	0.018(4)
C(42)	8*f*	0.1925(1)	0.7366(6)	–0.0942(3)	0.047(4)	0.055(4)	0.046(4)	0.017(3)	0.019(3)	0.010(3)
C(43)	8*f*	0.2115(1)	0.8309(6)	–0.0477(3)	0.039(3)	0.058(4)	0.052(4)	0.011(3)	0.022(3)	0.014(3)
C(44)	8*f*	0.2336(1)	0.9150(7)	–0.0618(3)	0.045(4)	0.071(5)	0.064(5)	0.001(3)	0.019(4)	0.019(4)
C(45)	8*f*	0.2514(2)	1.0042(8)	–0.0157(4)	0.053(4)	0.081(6)	0.078(6)	–0.009(4)	0.011(4)	0.012(5)
C(46)	8*f*	0.2476(2)	1.0107(7)	0.0419(4)	0.049(4)	0.074(5)	0.082(6)	–0.004(4)	0.006(4)	–0.004(4)
C(47)	8*f*	0.2250(2)	0.9211(7)	0.0534(3)	0.050(4)	0.075(5)	0.066(5)	0.008(4)	0.014(4)	0.004(4)
C(48)	8*f*	0.2187(2)	0.8126(8)	–0.1669(3)	0.074(5)	0.099(6)	0.063(5)	0.012(5)	0.036(4)	0.015(4)
C(49)	8*f*	0.2366(2)	0.9040(8)	–0.1228(3)	0.055(4)	0.094(6)	0.073(5)	0.001(4)	0.034(4)	0.025(4)
C(50)	8*f*	0.0795(2)	0.6296(6)	0.2209(3)	0.070(4)	0.047(4)	0.042(4)	–0.003(3)	0.015(3)	0.004(3)
C(51)	8*f*	0.1832(1)	0.4607(6)	0.0894(3)	0.041(3)	0.051(4)	0.047(4)	0.002(3)	0.015(3)	0.007(3)

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