Crystal structure of bis(μ_3-iodo)-(μ_2-iodo)-bis(μ_2-bis(diphenylphosphine)-ethane)tricopper(I) — dimethylformamide (1:1), $Cu_3I_3(C_{26}H_{24}P_2)_2 \cdot C_3H_7NO$

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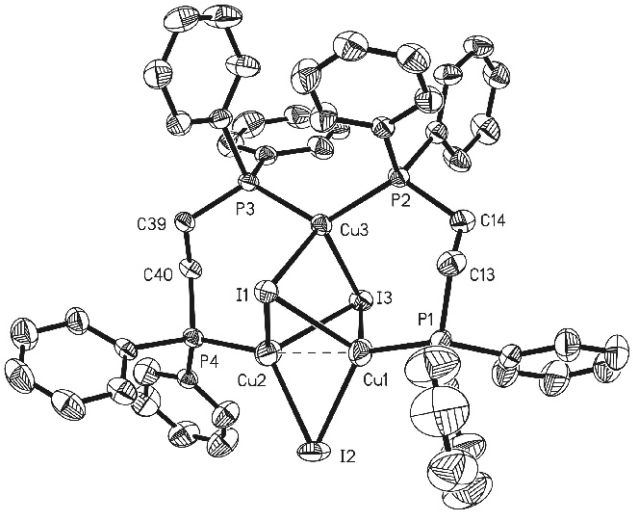

Abstract

$C_{55}H_{55}Cu_3I_3NOP_4$, monoclinic, $P2_1/n$ (no. 14), a = 14.567(3) Å, b = 12.543(3) Å, c = 31.248(7) Å, β = 90.278(4)°, V = 5709.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.051, $wR_{ref}(F^2)$ = 0.166, T = 293 K.

Source of material

CuI (38 mg, 0.2 mmol) and dppe (1,2-bis(diphenylphosphanyl)ethane, 80 mg, 0.2 mmol) were dissolved in DMF (*N*,*N*-dimethyformamide, 10 ml), and the solution was stirred for 30 min. Vapor of isopropanol was diffused slowly into the resulting solution. After about two weeks, colorless prism-like crystals were formed.

Experimental details

All non-hydrogen atoms were refined anisotropically. The H atoms were positioned geometrically and refined as riding atoms with d(C—H) = 0.93-0.97 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C).

Discussion

A long lasting interest in polynuclear copper(I) complexes has been manifest for years for their diverse structures, rich photoluminescece and potential applications in materials science. The crystal structures of the copper(I) complexes are formed by coordinating phosphine or bulky nitrogen-based ligands to Cu*X*. These complexes are polynuclear copper(I) species with μ_2-, μ_3- or μ_4-bridging *X* atoms. Their structures are affected by the ligand and method of preparation [1-5].

The crystal structure of the title complex is composed of neutral trinuclear copper(I) compound, $Cu_3I_3(dppe)_2$, and one DMF solvent. Both Cu1 and Cu2 are coordinated in distorted tetrahedral manner by one P atom from dppe, two μ_3-I^- ions (I1 and I3) and one μ_2-I^- ion (I2). Cu3 is surrounded by two P atoms from different dppe and two μ_3-I^- ions (I1 and I3) in distorted tetrahedral environment. The distances d(Cu—P) and d(Cu—I) are 2.1956(19) to 2698(17) Å and 2.5971(12) to 2.8256(12) Å, respectively. Three copper(I)-centered tetrahedra are connected by I^- ions to form the trinuclear structure with d(Cu1···Cu2) = 2.501(1) Å, indicating the existence of weak Cu–Cu interaction [6]. The presence of DMF may have a significant influence on the structure of the trinuclear copper compound and the molecular packing.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.10 × 0.20 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	28.79 cm^{-1}
Diffractometer, scan mode:	Rigaku Mercury CCD, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	35271, 1002
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8523
$N(param)_{refined}$:	604
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(2A)	4*e*	0.9684	0.7985	0.6280	0.098
H(3A)	4*e*	1.1061	0.7977	0.6663	0.130
H(4A)	4*e*	1.2230	0.6915	0.6445	0.125
H(5A)	4*e*	1.2202	0.6158	0.5786	0.124
H(6A)	4*e*	1.0864	0.6176	0.5382	0.102
H(8A)	4*e*	1.0049	0.8838	0.5142	0.152
H(9A)	4*e*	1.0383	0.9409	0.4449	0.188
H(10A)	4*e*	0.9783	0.8657	0.3900	0.178
H(11A)	4*e*	0.9133	0.7132	0.3941	0.228
H(12A)	4*e*	0.8644	0.6505	0.4640	0.195
H(13A)	4*e*	0.8255	0.5605	0.5270	0.071
H(13B)	4*e*	0.9316	0.5409	0.5243	0.071
H(14A)	4*e*	0.9096	0.5514	0.6062	0.072
H(14B)	4*e*	0.9155	0.4437	0.5811	0.072
H(16A)	4*e*	0.8509	0.5050	0.6820	0.087
H(17A)	4*e*	0.8968	0.3989	0.7396	0.103
H(18A)	4*e*	0.8821	0.2179	0.7359	0.086
H(19A)	4*e*	0.8110	0.1414	0.6786	0.083
H(20A)	4*e*	0.7576	0.2448	0.6230	0.070

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(22A)	4*e*	0.5971	0.4486	0.5600	0.080
H(23A)	4*e*	0.5369	0.3385	0.5068	0.101
H(24A)	4*e*	0.6256	0.2115	0.4765	0.088
H(25A)	4*e*	0.7769	0.1969	0.4946	0.089
H(26A)	4*e*	0.8378	0.3035	0.5481	0.073
H(28A)	4*e*	0.5041	0.3594	0.6633	0.101
H(29A)	4*e*	0.4202	0.2267	0.6298	0.122
H(30A)	4*e*	0.3440	0.2602	0.5671	0.105
H(31A)	4*e*	0.3338	0.4331	0.5416	0.087
H(32A)	4*e*	0.4095	0.5670	0.5770	0.070
H(34A)	4*e*	0.4029	0.5865	0.7245	0.086
H(35A)	4*e*	0.4182	0.5277	0.7955	0.116
H(36A)	4*e*	0.5511	0.4515	0.8176	0.105
H(37A)	4*e*	0.6730	0.4368	0.7740	0.103
H(38A)	4*e*	0.6626	0.4984	0.7039	0.079
H(39A)	4*e*	0.4416	0.7197	0.6180	0.057
H(39B)	4*e*	0.3867	0.6705	0.6560	0.057
H(40A)	4*e*	0.5142	0.7743	0.6970	0.058

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(40B)	4*e*	0.4146	0.8181	0.6899	0.058
H(42A)	4*e*	0.3838	1.0089	0.7006	0.098
H(43A)	4*e*	0.3895	1.1467	0.7512	0.117
H(44A)	4*e*	0.5273	1.2256	0.7670	0.106
H(45A)	4*e*	0.6543	1.1828	0.7288	0.118
H(46A)	4*e*	0.6487	1.0485	0.6782	0.091
H(48A)	4*e*	0.3143	0.8907	0.6393	0.080
H(49A)	4*e*	0.2053	0.9549	0.5917	0.116
H(50A)	4*e*	0.2517	1.0412	0.5306	0.117
H(51A)	4*e*	0.4034	1.0669	0.5165	0.105
H(52A)	4*e*	0.5128	1.0096	0.5651	0.087
H(53A)	4*e*	0.3450	0.7265	0.7742	0.493
H(53B)	4*e*	0.3302	0.7438	0.8234	0.493
H(53C)	4*e*	0.4109	0.8020	0.8000	0.493
H(54A)	4*e*	0.3263	0.9371	0.8408	0.395
H(54B)	4*e*	0.2244	0.9546	0.8259	0.395
H(54C)	4*e*	0.3047	1.0111	0.8016	0.395
H(55A)	4*e*	0.2154	0.8989	0.7332	0.310

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)	4*e*	0.79157(6)	0.79490(8)	0.58316(3)	0.0503(5)	0.0630(6)	0.0901(7)	0.0048(4)	0.0109(5)	–0.0151(5)
Cu(2)	4*e*	0.64780(7)	0.86965(8)	0.61464(4)	0.0622(6)	0.0611(6)	0.0974(7)	0.0010(4)	0.0249(5)	–0.0144(5)
Cu(3)	4*e*	0.66768(5)	0.60849(6)	0.61974(2)	0.0460(4)	0.0384(4)	0.0481(4)	0.0030(3)	–0.0065(3)	–0.0050(3)
I(1)	4*e*	0.62824(3)	0.72374(3)	0.54837(1)	0.0527(3)	0.0457(2)	0.0405(2)	–0.0034(2)	–0.0119(2)	–0.0008(2)
I(2)	4*e*	0.76871(4)	1.00104(4)	0.58410(2)	0.0942(4)	0.0409(3)	0.0928(4)	–0.0185(2)	0.0176(3)	–0.0001(2)
I(3)	4*e*	0.76151(3)	0.74643(3)	0.66894(1)	0.0588(3)	0.0427(2)	0.0466(3)	–0.0052(2)	–0.0141(2)	–0.0073(2)
P(1)	4*e*	0.9038(1)	0.7125(1)	0.54997(6)	0.0384(8)	0.0501(9)	0.064(1)	–0.0034(7)	0.0037(8)	–0.0063(8)
P(2)	4*e*	0.7643(1)	0.4734(1)	0.60240(5)	0.0434(8)	0.0341(7)	0.0460(8)	0.0009(6)	–0.0098(7)	–0.0049(6)
P(3)	4*e*	0.5281(1)	0.5857(1)	0.65017(5)	0.0450(8)	0.0307(7)	0.0428(8)	–0.0004(6)	–0.0080(7)	0.0004(6)
P(4)	4*e*	0.5159(1)	0.9068(1)	0.64490(5)	0.0472(9)	0.0331(8)	0.0475(9)	0.0033(6)	–0.0005(7)	–0.0041(6)
O(1)	4*e*	0.267(1)	0.764(2)	0.7307(6)	0.21(1)	0.26(1)	0.25(1)	–0.025(8)	0.015(8)	–0.029(8)
N(1)	4*e*	0.294(1)	0.859(1)	0.7888(5)	0.171(8)	0.170(9)	0.147(8)	0.027(7)	0.036(7)	–0.012(7)
C(1)	4*e*	1.0143(4)	0.7124(5)	0.5779(2)	0.042(3)	0.051(4)	0.075(4)	–0.003(3)	0.008(3)	0.002(3)
C(2)	4*e*	1.0192(6)	0.7625(7)	0.6174(3)	0.062(5)	0.097(6)	0.086(5)	–0.007(4)	–0.008(4)	–0.023(4)
C(3)	4*e*	1.1007(8)	0.7590(9)	0.6411(4)	0.080(6)	0.131(7)	0.114(7)	–0.014(5)	–0.027(5)	–0.012(6)
C(4)	4*e*	1.1713(7)	0.700(1)	0.6272(4)	0.071(5)	0.113(7)	0.129(7)	–0.004(5)	–0.017(5)	0.020(6)
C(5)	4*e*	1.1686(6)	0.6513(9)	0.5887(4)	0.058(5)	0.111(7)	0.142(7)	0.017(5)	0.008(5)	0.017(6)
C(6)	4*e*	1.0893(6)	0.6543(8)	0.5640(3)	0.063(5)	0.088(5)	0.105(6)	0.012(4)	0.003(4)	–0.009(5)
C(7)	4*e*	0.9309(5)	0.7601(6)	0.4963(3)	0.052(4)	0.063(4)	0.066(4)	–0.002(3)	0.004(3)	0.001(3)
C(8)	4*e*	0.9820(9)	0.847(1)	0.4908(4)	0.135(8)	0.127(8)	0.119(7)	–0.048(6)	0.011(6)	0.032(6)
C(9)	4*e*	1.001(1)	0.882(1)	0.4488(6)	0.149(9)	0.161(9)	0.160(9)	–0.053(7)	0.033(7)	0.045(8)
C(10)	4*e*	0.970(1)	0.835(2)	0.4168(5)	0.168(9)	0.153(9)	0.124(8)	–0.016(8)	0.035(7)	0.029(7)
C(11)	4*e*	0.928(2)	0.751(2)	0.4188(7)	0.23(1)	0.19(1)	0.15(1)	–0.035(9)	–0.016(9)	0.003(8)
C(12)	4*e*	0.902(1)	0.711(1)	0.4616(5)	0.20(1)	0.165(9)	0.118(8)	–0.053(8)	–0.012(8)	0.024(7)
C(13)	4*e*	0.8832(5)	0.5700(6)	0.5420(2)	0.065(4)	0.059(4)	0.055(4)	–0.010(3)	0.006(3)	–0.010(3)
C(14)	4*e*	0.8801(5)	0.5087(5)	0.5842(3)	0.055(4)	0.048(4)	0.077(4)	–0.005(3)	–0.008(3)	0.000(3)
C(15)	4*e*	0.7975(4)	0.3858(5)	0.6464(2)	0.048(3)	0.047(3)	0.039(3)	0.002(2)	–0.009(3)	–0.001(2)
C(16)	4*e*	0.8411(6)	0.4317(6)	0.6813(2)	0.092(5)	0.052(4)	0.072(4)	0.015(4)	–0.040(4)	–0.006(3)
C(17)	4*e*	0.8703(7)	0.3676(8)	0.7155(3)	0.104(6)	0.084(5)	0.069(5)	0.017(5)	–0.043(4)	–0.012(4)
C(18)	4*e*	0.8602(6)	0.2603(6)	0.7136(3)	0.084(5)	0.070(5)	0.061(4)	0.010(4)	–0.018(4)	0.006(4)
C(19)	4*e*	0.8185(6)	0.2150(6)	0.6796(3)	0.089(5)	0.050(4)	0.067(4)	–0.007(3)	–0.009(4)	0.017(3)
C(20)	4*e*	0.7868(5)	0.2772(5)	0.6462(2)	0.075(4)	0.046(3)	0.053(4)	–0.012(3)	–0.013(3)	0.001(3)
C(21)	4*e*	0.7220(4)	0.3855(4)	0.5603(2)	0.049(3)	0.035(3)	0.040(3)	0.000(2)	–0.010(3)	–0.008(2)
C(22)	4*e*	0.6340(5)	0.3968(6)	0.5475(2)	0.063(4)	0.072(5)	0.065(4)	–0.002(3)	–0.014(3)	–0.026(3)
C(23)	4*e*	0.5978(6)	0.3308(8)	0.5154(3)	0.072(5)	0.100(6)	0.080(5)	–0.001(4)	–0.029(4)	–0.024(5)
C(24)	4*e*	0.6506(7)	0.2567(6)	0.4971(3)	0.097(6)	0.066(4)	0.057(4)	–0.006(4)	–0.020(4)	–0.015(3)
C(25)	4*e*	0.7400(7)	0.2467(6)	0.5083(3)	0.094(6)	0.061(4)	0.067(5)	0.006(4)	–0.003(4)	–0.019(4)
C(26)	4*e*	0.7765(5)	0.3108(6)	0.5402(2)	0.064(4)	0.056(4)	0.062(4)	0.003(3)	–0.004(3)	–0.016(3)
C(27)	4*e*	0.4615(4)	0.4789(5)	0.6249(2)	0.049(3)	0.041(3)	0.054(3)	–0.008(3)	–0.001(3)	–0.001(3)
C(28)	4*e*	0.4679(7)	0.3754(6)	0.6395(3)	0.123(6)	0.047(4)	0.082(5)	–0.011(4)	–0.021(5)	0.004(4)
C(29)	4*e*	0.4200(8)	0.2954(7)	0.6186(3)	0.148(8)	0.056(5)	0.101(6)	–0.027(5)	–0.019(6)	–0.009(4)
C(30)	4*e*	0.3727(7)	0.3156(8)	0.5818(3)	0.102(6)	0.072(5)	0.089(5)	–0.028(4)	–0.009(5)	–0.023(4)
C(31)	4*e*	0.3673(6)	0.4182(7)	0.5662(3)	0.074(5)	0.071(5)	0.072(5)	0.001(4)	–0.012(4)	–0.025(4)
C(32)	4*e*	0.4122(5)	0.4979(6)	0.5877(2)	0.061(4)	0.053(4)	0.062(4)	–0.001(3)	–0.012(3)	–0.011(3)
C(33)	4*e*	0.5293(4)	0.5465(5)	0.7066(2)	0.057(4)	0.039(3)	0.050(3)	–0.005(3)	–0.012(3)	0.001(3)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(34)	4*e*	0.4577(6)	0.5563(7)	0.7339(3)	0.074(5)	0.079(5)	0.062(4)	–0.006(4)	0.004(4)	0.009(4)
C(35)	4*e*	0.4668(8)	0.5207(9)	0.7765(3)	0.108(6)	0.107(6)	0.076(5)	–0.025(5)	0.023(5)	0.016(5)
C(36)	4*e*	0.5465(8)	0.4764(7)	0.7896(3)	0.116(6)	0.069(5)	0.077(5)	–0.008(5)	–0.018(5)	0.027(4)
C(37)	4*e*	0.6188(8)	0.4670(7)	0.7639(3)	0.112(6)	0.065(5)	0.081(5)	0.003(4)	–0.033(5)	0.022(4)
C(38)	4*e*	0.6121(6)	0.5031(5)	0.7219(2)	0.086(5)	0.056(4)	0.055(4)	0.006(3)	–0.015(4)	0.013(3)
C(39)	4*e*	0.4465(4)	0.6968(5)	0.6475(2)	0.048(3)	0.036(3)	0.058(4)	0.002(2)	–0.012(3)	–0.002(3)
C(40)	4*e*	0.4698(5)	0.7950(5)	0.6753(2)	0.059(4)	0.037(3)	0.050(3)	0.007(3)	0.000(3)	0.001(3)
C(41)	4*e*	0.5162(4)	1.0151(5)	0.6844(2)	0.053(3)	0.037(3)	0.044(3)	0.002(2)	–0.007(3)	–0.002(2)
C(42)	4*e*	0.4390(6)	1.0437(7)	0.7062(3)	0.078(5)	0.072(5)	0.094(5)	0.003(4)	0.004(4)	–0.037(4)
C(43)	4*e*	0.4425(7)	1.1258(8)	0.7370(3)	0.101(6)	0.091(6)	0.101(6)	0.013(5)	0.018(5)	–0.041(5)
C(44)	4*e*	0.5238(7)	1.1740(8)	0.7457(3)	0.104(6)	0.074(5)	0.088(5)	–0.017(5)	0.008(5)	–0.032(4)
C(45)	4*e*	0.5993(7)	1.1473(9)	0.7236(3)	0.096(6)	0.105(6)	0.094(6)	–0.033(5)	0.000(5)	–0.036(5)
C(46)	4*e*	0.5958(6)	1.0669(7)	0.6930(3)	0.070(5)	0.079(5)	0.078(5)	–0.015(4)	0.009(4)	–0.029(4)
C(47)	4*e*	0.4254(5)	0.9451(5)	0.6078(2)	0.064(4)	0.034(3)	0.041(3)	0.009(3)	–0.011(3)	–0.003(2)
C(48)	4*e*	0.3327(5)	0.9277(6)	0.6150(3)	0.064(4)	0.067(4)	0.069(4)	0.009(3)	–0.013(4)	0.002(4)
C(49)	4*e*	0.2675(7)	0.9648(9)	0.5864(3)	0.090(6)	0.092(6)	0.107(6)	0.010(5)	–0.030(5)	0.002(5)
C(50)	4*e*	0.2956(8)	1.0167(8)	0.5499(3)	0.124(7)	0.082(5)	0.087(6)	0.027(5)	–0.048(5)	–0.003(5)
C(51)	4*e*	0.3857(8)	1.0327(7)	0.5416(3)	0.129(7)	0.069(5)	0.064(5)	0.017(5)	–0.016(5)	0.004(4)
C(52)	4*e*	0.4509(7)	0.9977(6)	0.5706(3)	0.096(5)	0.058(4)	0.064(4)	0.008(4)	–0.009(4)	–0.001(3)
C(53)	4*e*	0.349(2)	0.777(3)	0.797(1)	0.33(2)	0.33(2)	0.32(2)	0.04(1)	0.00(1)	0.01(1)
C(54)	4*e*	0.287(2)	0.948(2)	0.8165(8)	0.27(1)	0.26(1)	0.26(1)	–0.00(1)	0.02(1)	–0.02(1)
C(55)	4*e*	0.251(2)	0.847(3)	0.746(1)	0.24(2)	0.26(2)	0.27(2)	0.01(1)	–0.01(1)	0.01(1)

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