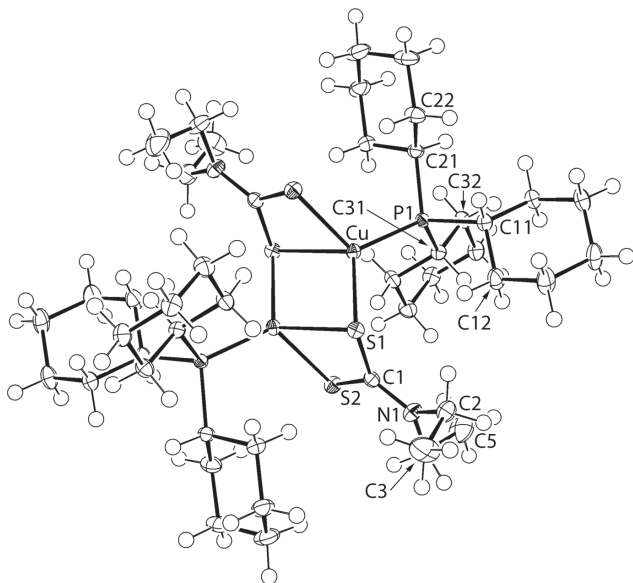


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Crystal structure of bis(μ_2 -diethyldithiocarbamato- $\kappa^3S,S':S'$)-bis(tricyclohexylphosphane- κP)dicopper(I), $C_{46}H_{86}Cu_2N_2P_2S_4$



<https://doi.org/10.1515/ncrs-2017-0402>

Received December 12, 2017; accepted February 23, 2018; available online March 10, 2018

Abstract

$C_{46}H_{86}Cu_2N_2P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.9626(3)$ Å, $b = 11.0489(3)$ Å, $c = 12.3604(3)$ Å, $\alpha = 106.205(3)^\circ$, $\beta = 99.165(2)^\circ$, $\gamma = 100.306(3)^\circ$, $V = 1253.53(6)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0232$, $wR_{ref}(F^2) = 0.0555$, $T = 100(2)$ K.

CCDC no.: 1825489

The structure of the title complex is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.53 × 0.30 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	11.1 cm ⁻¹
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	59.4°, 88.4%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	25023, 6283, 0.026
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5853
$N(param)_{refined}$:	255
Programs:	Rigaku programs [1], SHELX [2, 3], ORTEP [4]

Source of materials

The title complex was prepared from the *in situ* reaction of CuCl, Cy₃P and Na[S₂CNEt₂] in a 1:1:1 ratio. Cy₃P (Sigma–Aldrich; 1.0 mmol, 0.283 g) dissolved in hexane (10 mL) was added to a hexane solution (10 mL) of CuCl (Sigma–Aldrich; 1.0 mmol, 0.100 g). The temperature of reaction was maintained at below 4 °C. Then, Na[S₂CNEt₂] (BDH, 1.0 mmol, 0.250 g) in hexane (10 mL) was added to the reaction mixture, followed by stirring for 4 h. The resulting mixture was filtered and left for evaporation at room temperature to yield bright-yellow crystals. **Yield:** 0.239 (68.7%). **M.p.:** 418–420 K. **IR** (cm⁻¹): 2909 (s), 2843 (s) ν (C–H); 1474 (s) ν (C–N); 1072 (m), 995 (m) ν (C–S).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5 U_{eq}(C)$.

Comment

The initial interest in complexes related to the title compound, *i.e.* of general formula $[R_3PCu(S_2CNR'R')]_2$, $R, R' = \text{alkyl or aryl}$, arose as a result of the desire to generate more efficacious synthetic precursors for copper sulfide nanomaterials [5]. Thus, the addition of base, in this case triorganophosphanes with relatively small R substituents, disrupted the polymeric structure of $[Cu(S_2CNR'R')]_n$ to provide soluble materials that were more suitable for decomposition studies. However, it was in recognition of the biological potential of metal dithiocarbamates [6] that prompted more recent investigations into these types of ternary compounds.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
Cu	0.12237(2)	0.49233(2)	0.56887(2)	0.01060(5)
N1	0.19361(11)	0.79619(10)	0.41105(9)	0.0150(2)
P1	0.28568(3)	0.59326(3)	0.73101(3)	0.00891(6)
S1	0.12240(3)	0.54656(3)	0.39823(2)	0.01103(6)
S2	-0.03819(3)	0.73773(3)	0.48691(3)	0.01220(7)
C1	0.10318(12)	0.70499(12)	0.43227(10)	0.0114(2)
C2	0.30950(14)	0.76790(14)	0.35599(12)	0.0195(3)
H2A	0.3413	0.6958	0.3768	0.023*
H2B	0.3889	0.8451	0.3854	0.023*
C3	0.26620(17)	0.73107(18)	0.22524(13)	0.0303(4)
H3A	0.1918	0.6513	0.1954	0.045*
H3B	0.3470	0.7170	0.1916	0.045*
H3C	0.2319	0.8012	0.2045	0.045*
C4	0.18069(15)	0.93151(13)	0.44115(12)	0.0212(3)
H4A	0.0805	0.9331	0.4301	0.025*
H4B	0.2216	0.9732	0.3888	0.025*
C5	0.25463(17)	1.00744(14)	0.56534(14)	0.0300(3)
H5A	0.2133	0.9671	0.6174	0.045*
H5B	0.2441	1.0969	0.5828	0.045*
H5C	0.3542	1.0074	0.5760	0.045*
C11	0.46488(12)	0.62587(12)	0.70495(10)	0.0116(2)
H11	0.4815	0.5394	0.6656	0.014*
C12	0.47318(13)	0.70237(14)	0.61921(11)	0.0185(3)
H12A	0.4583	0.7898	0.6543	0.022*
H12B	0.3981	0.6575	0.5489	0.022*
C13	0.61556(14)	0.71546(15)	0.58591(12)	0.0224(3)
H13A	0.6262	0.6286	0.5436	0.027*
H13B	0.6200	0.7692	0.5339	0.027*
C14	0.73512(13)	0.77773(14)	0.69273(11)	0.0197(3)
H14A	0.8258	0.7805	0.6692	0.024*
H14B	0.7302	0.8679	0.7307	0.024*
C15	0.72666(13)	0.70130(13)	0.77774(11)	0.0162(3)
H15A	0.8023	0.7455	0.8478	0.019*
H15B	0.7406	0.6137	0.7421	0.019*
C16	0.58515(12)	0.68917(12)	0.81185(10)	0.0126(2)
H16A	0.5747	0.7763	0.8536	0.015*
H16B	0.5810	0.6362	0.8645	0.015*
C21	0.29670(12)	0.49601(12)	0.83101(10)	0.0114(2)
H21	0.3654	0.5500	0.9043	0.014*
C22	0.34733(14)	0.37356(12)	0.77842(11)	0.0158(3)
H22A	0.2846	0.3230	0.7024	0.019*
H22B	0.4427	0.3991	0.7660	0.019*
C23	0.34917(15)	0.28893(13)	0.85759(12)	0.0202(3)
H23A	0.3754	0.2081	0.8189	0.024*
H23B	0.4210	0.3356	0.9297	0.024*
C24	0.20768(16)	0.25474(13)	0.88752(12)	0.0228(3)
H24A	0.2151	0.2053	0.9429	0.027*
H24B	0.1380	0.1990	0.8167	0.027*
C25	0.15820(15)	0.37659(13)	0.94044(11)	0.0192(3)
H25A	0.0639	0.3516	0.9551	0.023*
H25B	0.2228	0.4283	1.0153	0.023*
C26	0.15317(13)	0.45857(12)	0.85934(11)	0.0145(2)
H26A	0.1236	0.5383	0.8960	0.017*
H26B	0.0830	0.4091	0.7869	0.017*
C31	0.26895(12)	0.75415(11)	0.82070(10)	0.0104(2)

Table 2 (continued)

Atom	x	y	z	U _{iso} */U _{eq}
H31	0.3246	0.8203	0.7938	0.012*
C32	0.32714(13)	0.79275(12)	0.95165(10)	0.0127(2)
H32A	0.2747	0.7306	0.9831	0.015*
H32B	0.4265	0.7885	0.9664	0.015*
C33	0.31514(13)	0.93010(12)	1.01325(11)	0.0147(2)
H33A	0.3747	0.9931	0.9871	0.018*
H33B	0.3495	0.9510	1.0976	0.018*
C34	0.16414(13)	0.94275(12)	0.98858(11)	0.0153(2)
H34A	0.1059	0.8858	1.0211	0.018*
H34B	0.1600	1.0333	1.0261	0.018*
C35	0.10698(13)	0.90498(12)	0.85875(11)	0.0155(2)
H35A	0.1605	0.9669	0.8277	0.019*
H35B	0.0080	0.9105	0.8440	0.019*
C36	0.11688(12)	0.76766(12)	0.79637(11)	0.0134(2)
H36A	0.0822	0.7473	0.7122	0.016*
H36B	0.0570	0.7049	0.8225	0.016*

Specifically, a recent report [7] highlighted the species-specific anti-microbial activity of certain (Ph₃P)₂Cu(S₂CNRR') derivatives and it was this observation that prompted the synthesis of the title compound, [Cy₃PCu(S₂CNEt₂)₂].

As seen from the Figure (70% displacement ellipsoids; the C4 atom is obscured), the title compound is binuclear and indeed, disposed about a centre of inversion; unlabelled atoms are related by the symmetry operation: $-x, 1-y, 1-z$. The diethyldithiocarbamate ligand is μ_2 -bridging, chelating one copper(I) centre, while simultaneously binding to a second *via* one of the sulfur atoms only. The bridging Cu—S1 bond length of 2.5169(3) Å is systematically longer than the chelating Cu—S1ⁱ, S2ⁱ bond lengths of 2.3480(3) and 2.3905(3) Å; the internal Cu...Cuⁱ separation is 2.8034(3) Å. These variations are reflected in the associated C—S bond lengths with the bond formed by the bridging-S1 atom being systematically longer than the bond involving the chelating-S2 atom, *i.e.* 1.7356(13) *cf.* 1.7087(13) Å. The pattern in Cu—S bond lengths implies the central Cu₂S₂ core is rectangular. The overall Cu₂S₄ arrangement resembles a partial step-ladder as the edge-shared CuS₂ triangles lie above and below the plane through the central core. The four-coordinate geometry of the copper(I) atom is completed by a phosphane-P atom and the resultant PS₃ donor set approximates a tetrahedron but, with significant distortions. Thus, the smallest angle subtended at copper(I) of 73.827(11)° corresponds to the chelate angle and the widest angle of 123.178(12)° corresponds to S1—Cu—P1, *i.e.* involving the bridging-S1 and sterically crowded phosphorous atoms.

There are two direct literature precedents for the structure of the title compound, namely [R₃PCu(S₂CNEt₂)₂] for

$R = Me$ and Et [5]. These adopt the same structural motif and they are both located around a inversion centre.

Acknowledgements: Sunway University is thanked for support of biological and crystal engineering studies of metal dithiocarbamates.

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