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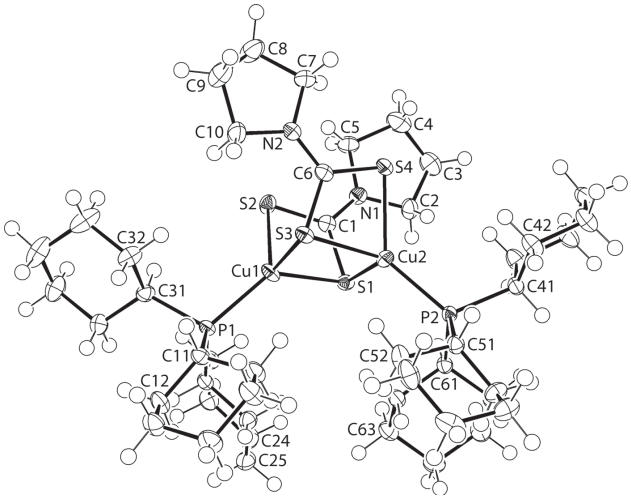
Crystal structure of bis(μ_2-pyrrolidine-1-carbodithioato-κ^3 *S*,*S*′:*S*;κ^3*S*:*S*:*S*′)-bis(tricyclohexylphosphane-*P*)-di-copper(I), $C_{46}H_{82}Cu_2N_2P_2S_4$



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Abstract

$C_{46}H_{82}Cu_2N_2P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 11.6189(2)$ Å, $b = 12.2846(2)$ Å, $c = 18.1744(2)$ Å, $\alpha = 97.3210(10)°$, $\beta = 106.3080(10)°$, $\gamma = 99.312(2)°$, $V = 2415.65(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.025$, $wR_{ref}(F^2) = 0.066$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure 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.

Source of materials

The title complex was prepared from the in situ reaction of CuCl, Cy_3P and $NH_4[S_2CN(CH_2)_4]$ in a 1:2:1 ratio. Cy_3P (Sigma–Aldrich; 0.6 mmol, 0.171 g) dissolved in hexane (10 mL) was added to a hexane solution (10 mL) of CuCl (Sigma–Aldrich; 0.3 mmol, 0.030 g). The temperature of reaction was maintained at below 4 °C in an ice-bath. Then, $NH_4[S_2CN(CH_2)_4]$ (Sigma–Aldrich, 0.3 mmol, 0.055 g) in hexane (10 mL) was added to the reaction mixture followed by stirring for 4 h. The resulting mixture was filtered and quickly evaporated to yield a brownish solid. This was recrystallised from its chloroform solution via slow evaporation at room temperature to yield colourless crystals. **Yield**: 0.089 g (61.5%). **M.p.**: 416 K.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.23 × 0.13 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	35.7 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	153.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	40039, 10075, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 9554
$N(param)_{refined}$:	505
Programs:	Rigaku programs [1], SHELX [2, 3], ORTEP [4]

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.99–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2\,U_{eq}(C)$. Owing to poor agreement, three reflections, i.e. (−3 5 20), (−2 6 19) and (−8 14 2), were omitted from the final cycles of refinement.

Comment

Motivations to investigate molecules of the general formula $[R_3PCu(S_2CNRR')]_2$, R, R′ = alkyl or aryl, are founded in materials science, e.g. as precursors for copper sulphide nanomaterials [5], and metal-based drugs, e.g. as anti-microbials [6]. It was the latter impetus that led to the synthesis of the title compound, namely $\{Cy_3PCu[S_2CN(CH_2)_4]\}_2$.

The binuclear molecular structure is shown in the Figure (70% displacement ellipsoids); there is no crystallographically-imposed symmetry in the molecule. Each of the pyrrolidinyldithiocarbamato ligands is μ_2-bridging, chelating one copper(I) centre while simultaneously binding to a second via one of the sulphur atoms only, i.e. S1 and S3. Non-systematic variations are noted in the Cu—S bond lengths. Thus, for the Cu1 centre, the Cu1—S1, S2 and S3 bond lengths of 2.4391(3), 2.4072(3) and 2.3653(3) Å, respectively,

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cu1	0.37887(2)	0.67751(2)	0.19565(2)	0.01476(5)
Cu2	0.25867(2)	0.50466(2)	0.27472(2)	0.01404(5)
S1	0.16191(3)	0.60450(2)	0.17490(2)	0.01315(6)
S2	0.30616(3)	0.56556(3)	0.06661(2)	0.01568(7)
S3	0.47423(3)	0.56008(2)	0.27617(2)	0.01313(6)
S4	0.29599(3)	0.34516(2)	0.20530(2)	0.01375(6)
P1	0.48033(3)	0.85298(2)	0.22485(2)	0.01118(6)
P2	0.17179(3)	0.51897(3)	0.36781(2)	0.01129(6)
N1	0.09549(10)	0.43162(9)	0.05676(6)	0.0144(2)
N2	0.50598(10)	0.39946(9)	0.17479(6)	0.0148(2)
C1	0.17887(11)	0.52350(11)	0.09394(7)	0.0132(2)
C2	−0.00783(12)	0.38684(12)	0.08375(8)	0.0182(3)
H2A	−0.0668	0.4373	0.0791	0.022*
H2B	0.0215	0.3773	0.1387	0.022*
C3	−0.06624(15)	0.27407(13)	0.02981(10)	0.0312(3)
H3A	−0.0965	0.2182	0.0584	0.037*
H3B	−0.1356	0.2813	−0.0143	0.037*
C4	0.03500(16)	0.23996(13)	0.00122(10)	0.0315(3)
H4A	0.0010	0.1895	−0.0502	0.038*
H4B	0.0855	0.2013	0.0386	0.038*
C5	0.11010(13)	0.34977(11)	−0.00479(7)	0.0183(3)
H5A	0.1973	0.3455	0.0047	0.022*
H5B	0.0781	0.3696	−0.0568	0.022*
C6	0.43209(11)	0.43076(10)	0.21358(7)	0.0129(2)
C7	0.47548(13)	0.29293(11)	0.11917(8)	0.0192(3)
H7A	0.3903	0.2793	0.0840	0.023*
H7B	0.4855	0.2290	0.1468	0.023*
C8	0.56748(14)	0.31027(14)	0.07400(9)	0.0261(3)
H8A	0.5348	0.3440	0.0278	0.031*
H8B	0.5887	0.2385	0.0568	0.031*
C9	0.67864(13)	0.39053(14)	0.13335(9)	0.0254(3)
H9A	0.7277	0.3499	0.1700	0.031*
H9B	0.7317	0.4309	0.1071	0.031*
C10	0.62090(12)	0.47072(12)	0.17522(8)	0.0201(3)
H10A	0.6744	0.5020	0.2292	0.024*
H10B	0.6046	0.5332	0.1471	0.024*
C11	0.59368(11)	0.89390(10)	0.32407(7)	0.0136(2)
H11	0.6625	0.8552	0.3224	0.016*
C12	0.65160(12)	1.01932(11)	0.35035(7)	0.0174(3)
H12A	0.5866	1.0619	0.3518	0.021*
H12B	0.6907	1.0450	0.3120	0.021*
C13	0.74775(13)	1.04398(12)	0.43117(8)	0.0207(3)
H13A	0.8175	1.0085	0.4285	0.025*
H13B	0.7792	1.1260	0.4475	0.025*
C14	0.69306(14)	0.99941(12)	0.49135(8)	0.0220(3)
H14A	0.7577	1.0127	0.5423	0.026*
H14B	0.6286	1.0401	0.4978	0.026*
C15	0.63808(14)	0.87402(12)	0.46555(8)	0.0229(3)
H15A	0.6007	0.8472	0.5044	0.027*
H15B	0.7041	0.8330	0.4634	0.027*
C16	0.54075(13)	0.84839(11)	0.38558(7)	0.0174(3)
H16A	0.4707	0.8830	0.3889	0.021*
H16B	0.5102	0.7662	0.3695	0.021*
C21	0.38760(11)	0.96245(10)	0.21276(7)	0.0131(2)
H21	0.4429	1.0360	0.2173	0.016*
C22	0.29320(12)	0.93166(11)	0.13062(7)	0.0165(2)
H22A	0.3368	0.9270	0.0911	0.020*
H22B	0.2409	0.8570	0.1248	0.020*
C23	0.21251(12)	1.01827(12)	0.11629(8)	0.0186(3)
H23A	0.2637	1.0912	0.1167	0.022*
H23B	0.1504	0.9939	0.0642	0.022*
C24	0.14789(13)	1.03312(12)	0.17832(9)	0.0214(3)
H24A	0.0884	0.9631	0.1734	0.026*
H24B	0.1020	1.0941	0.1699	0.026*
C25	0.24021(13)	1.06150(12)	0.25999(8)	0.0193(3)
H25A	0.1958	1.0654	0.2991	0.023*
H25B	0.2933	1.1361	0.2669	0.023*
C26	0.31997(12)	0.97402(11)	0.27392(7)	0.0164(2)
H26A	0.2678	0.9006	0.2715	0.020*
H26B	0.3805	0.9964	0.3266	0.020*
C31	0.57032(12)	0.87303(11)	0.15526(7)	0.0148(2)
H31	0.5160	0.8283	0.1038	0.018*
C32	0.68220(13)	0.81816(13)	0.17662(8)	0.0205(3)
H32A	0.7416	0.8610	0.2263	0.025*
H32B	0.6558	0.7408	0.1843	0.025*
C33	0.74462(15)	0.81468(16)	0.11279(9)	0.0302(3)
H33A	0.8188	0.7828	0.1295	0.036*
H33B	0.6881	0.7653	0.0646	0.036*
C34	0.78059(15)	0.93146(17)	0.09595(9)	0.0323(4)
H34A	0.8447	0.9782	0.1423	0.039*
H34B	0.8152	0.9260	0.0520	0.039*
C35	0.67074(14)	0.98739(14)	0.07558(9)	0.0256(3)
H35A	0.6107	0.9453	0.0259	0.031*
H35B	0.6981	1.0647	0.0682	0.031*
C36	0.60842(13)	0.99142(12)	0.13981(8)	0.0198(3)
H36A	0.6657	1.0396	0.1883	0.024*
H36B	0.5351	1.0246	0.1237	0.024*
C41	0.06916(11)	0.38728(10)	0.37059(7)	0.0137(2)
H41	0.0234	0.4051	0.4082	0.016*
C42	0.14093(12)	0.29734(11)	0.39701(8)	0.0186(3)
H42A	0.1915	0.2830	0.3626	0.022*
H42B	0.1967	0.3251	0.4508	0.022*
C43	0.05451(13)	0.18733(12)	0.39463(8)	0.0214(3)
H43A	0.1035	0.1303	0.4097	0.026*
H43B	0.0100	0.2001	0.4330	0.026*
C44	−0.03765(12)	0.14318(11)	0.31400(8)	0.0188(3)
H44A	−0.0949	0.0750	0.3155	0.023*
H44B	0.0060	0.1225	0.2765	0.023*
C45	−0.10956(13)	0.23157(12)	0.28721(9)	0.0220(3)
H45A	−0.1606	0.2457	0.3214	0.026*
H45B	−0.1650	0.2033	0.2334	0.026*
C46	−0.02392(13)	0.34139(11)	0.28948(8)	0.0197(3)
H46A	−0.0734	0.3980	0.2741	0.024*
H46B	0.0207	0.3286	0.2511	0.024*
C51	0.27541(11)	0.55784(11)	0.46964(7)	0.0132(2)
H51	0.3043	0.4877	0.4811	0.016*
C52	0.39300(12)	0.64410(12)	0.48048(8)	0.0194(3)
H52A	0.3728	0.7182	0.4738	0.023*
H52B	0.4316	0.6209	0.4406	0.023*
C53	0.48258(13)	0.65283(12)	0.56233(8)	0.0224(3)
H53A	0.5081	0.5803	0.5671	0.027*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H53B	0.5567	0.7109	0.5699	0.027*
C54	0.42394(14)	0.68289(12)	0.62543(8)	0.0233(3)
H54A	0.4048	0.7583	0.6236	0.028*
H54B	0.4825	0.6852	0.6773	0.028*
C55	0.30678(13)	0.59743(13)	0.61404(8)	0.0205(3)
H55A	0.2685	0.6203	0.6542	0.025*
H55B	0.3268	0.5232	0.6204	0.025*
C56	0.21629(12)	0.58859(12)	0.53288(7)	0.0172(3)
H56A	0.1909	0.6612	0.5281	0.021*
H56B	0.1422	0.5306	0.5257	0.021*
C61	0.06681(11)	0.61861(10)	0.34756(7)	0.0132(2)
H61	0.0218	0.5966	0.2905	0.016*
C62	0.14004(12)	0.73865(10)	0.35756(7)	0.0146(2)
H62A	0.1844	0.7677	0.4135	0.018*
H62B	0.2014	0.7376	0.3293	0.018*
C63	0.05458(13)	0.81620(11)	0.32611(8)	0.0179(3)
H63A	0.1030	0.8934	0.3348	0.021*
H63B	0.0154	0.7906	0.2693	0.021*
C64	−0.04413(13)	0.81669(12)	0.36639(8)	0.0192(3)
H64A	−0.0999	0.8651	0.3438	0.023*
H64B	−0.0053	0.8482	0.4226	0.023*
C65	−0.11766(13)	0.69799(12)	0.35664(8)	0.0207(3)
H65A	−0.1630	0.6695	0.3008	0.025*
H65B	−0.1783	0.6998	0.3854	0.025*
C66	−0.03388(12)	0.61844(11)	0.38711(8)	0.0172(2)
H66A	−0.0834	0.5414	0.3770	0.021*
H66B	0.0043	0.6420	0.4442	0.021*

correspond to the bridging atom of the chelating ligand, the non-bridging atom and the incoming sulphur-bridge from the second dithiocarbamate ligand. The corresponding atoms for the Cu2 atom are S3, S4 and S1, respectively, and the bond lengths are 2.4787(3), 2.3603(3) and 2.4346(3) Å, respectively. These values indicate that the S1 atom forms a more symmetric bridge than the S3 atom, as seen in the value of $\Delta(Cu—S1_{bridge}) = 0.004$ Å, cf. $\Delta(Cu—S3_{bridge}) = 0.113$ Å. By contrast, the different modes of association of the sulphur atoms result in systematic differences in the associated S—C bond lengths with the S1 and S3 atoms, each forming two Cu—S interactions, being longer at 1.7456(13) and 1.7413(13) Å cf. the S—C bonds formed by the S2 and S4 atoms of 1.7123(13) and 1.7078(13) Å.

The central Cu_2S_2 core is based on a skewed rectangle with the range of Cu—S bond lengths being 2.3653(3) to 2.4787(3) Å, and the r.m.s. of the best plane through the Cu_2S_2 atoms is 0.0931 Å with deviations above and below the plane of 0.0957(1) Å for the Cu1 atom and 0.0935(1) Å for S3. The CuS_2C chelate rings lie to the same side of the central Cu_2S_2 core and form dihedral angles of 75.66(12)° [Cu1-chelate] and 74.21(13)° [Cu2-chelate] with the core; the dihedral angle between the chelate rings is 30.14(3)°. The PS_3 coordination geometry for each copper(I) atom is completed by the phosphorus atom of a Cy_3P ligand; both of these lie to the same side of the Cu_2S_2 core. The coordination geometries exhibit significant distortions from the ideal geometry none the least owing to the acute chelate angles of 75.400(11)° [Cu1-chelate] and 75.494(11)° [Cu2-chelate]. The widest angle in each coordination geometry is the one involving the bridging-S atom and the phosphane ligand, i.e. S1—Cu1—P1 of 129.119(14)° and S3—Cu2—P1 of 132.003(13)°.

There are three direct literature precedents for the structure of the title compound, namely $[R_3PCu(S_2CNEt_2)]_2$ for R = Me and Et [5], and Cy [7]. These adopt the same structural motif in that each is centrosymmetric and each features a similar μ_2-bridging mode for the dithiocarbamate ligand. Crucially, the symmetry implies the CuS_2C chelate rings lie to opposite sides of the Cu_2S_2 core with the result the $Cu_2S_4C_2$ atoms describe a chair (or step-ladder topology) as opposed to the boat form seen in the structure of $\{Cy_3PCu[S_2CN(CH_2)_4]\}_2$. A search of the Cambridge Structural Database [8] shows there are seven examples silver analogues of general formula $[R_3PAg(S_2CNRR')]_2$, R, R′ = alkyl or aryl. Each of these adopts the chair form so it seems the structure reported herein stands alone in this class of compound.

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References

1. Rigaku/Oxford Diffraction. CrysAlisPro. Rigaku Corporation, The Woodlands, TX, USA (2015).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Cryst. **45** (2012) 849–854.
5. Afzaal, M.; Rosenberg, C. L.; Malik, M. A.; White, A. J. P.; O'Brien, P.: Phosphine stabilized copper(I) complexes of dithiocarbamates and xanthates and their decomposition pathways. New J. Chem. **35** (2011) 2773–2780.
6. Jamaludin, N. S.; Halim, S. N. A.; Khoo, C.-H.; Chen, B.-J.; See, T.-H.; Sim, J.-H.; Cheah, Y.-K.; Seng, H.-L.; Tiekink, E. R. T.: Bis(phosphane)copper(I) and silver(I) dithiocarbamates: crystallography and anti-microbial assay. Z. Kristallogr. –CM **231** (2016) 341–349.
7. Tan, Y. J.; Yeo, C. I.; Halcovitch N. R.; Tiekink, E. R. T.: Crystal structure of bis(μ_2-diethyldithiocarbamato-$\kappa^3S,S':S'$)-bis(tricyclohexylphosphane-κP)dicopper(I), $C_{46}H_{86}Cu_2N_2P_2S_4$. Z. Kristallogr. –NCS **233** (2018) 507–509.
8. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C.: The Cambridge Structural Database. Acta Crystallogr. **B72** (2016) 171–179.