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[Disulphidothionitrato(1−)](triphenylphosphine sulphide)copper(I), [Cu(NS₃)(C₁₈H₁₅PS)]: a Trigonally Coordinated Cu^I Complex

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Abstract. $M_r = 468.08$, $P2_1/c$, $a = 10.523$ (9), $b = 21.748$ (6), $c = 8.880$ (2) Å, $\beta = 98.74$ (3)°, $U = 2008.6$ Å³, $Z = 4$, $D_x = 1.548$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.57$ mm⁻¹, $F(000) = 952$, $T = 291$ K, $R = 0.046$ for 2677 observed reflections. The complex was prepared from S_7NH and $CuCl(PPh_3)_3$. Cu is trigonally coordinated by Ph_3PS and the two terminal S atoms of a bidentate $[SSNS]^-$ ligand [Cu–S distances are 2.214 (2), 2.200 (3) and 2.191 (3) Å, respectively].

Introduction. Cu^I complexes of the type Cu*XL*, where *X* is bidentate and *L* monodentate, are almost invariably dimers or tetramers. Transition-metal complexes of the S_3N^- ligand have previously been prepared from S_4N_4 or $[(Ph_3P)_2N]^+[S_3N]^-$ (Herberhold, Haumaier & Schubert, 1981; Bojes, Chivers, Laidlaw & Trsic, 1982). We report here the preparation (by a new method) and X-ray structure determination of an unusual monomeric Cu^I complex.

Experimental. A solution of S_7NH (0.24 g, 1 mmol) in methanol (50 mL) was added to $[CuCl(PPh_3)_3]$ (0.88 g, 1 mmol) in methylene chloride (50 mL) and allowed to stand for 4 h at room temperature, giving a red solution. The solvent was removed under vacuum and the red

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residue washed with *n*-hexane (2 × 20 mL). Recrystallization from 1:1 CH_2Cl_2/C_2H_5OH gave red crystals of $[Cu(S_3N)(SPPh_3)]$ in low yield. The IR spectrum exhibits bands at 920, 740 and 600 cm⁻¹ assigned to the S_3N^- ligand and a band at 635 cm⁻¹ corresponding to $\nu(PS)$, together with PPh_3 bands. The UV/visible spectrum in ethanol shows λ_{max} 474 ($\varepsilon = 6130$), 335 (sh, $\varepsilon = 5844$) and 298 nm ($\varepsilon = 6500$).

Crystal 0.4 × 0.4 × 0.4 mm mounted in capillary. Stoe–Siemens four-circle diffractometer. Unit cell from 30 reflections, $20 < 2\theta < 25°$. Data collected for $\pm h$, $\pm k$, $+l$ to $2\theta = 50°$ with profile fitting (Clegg, 1981). No significant variation of three standard reflections. No absorption or extinction corrections applied. 4883 data merged ($R_{int} = 0.020$) to 3533 unique reflections; 2677 with $F > 4\sigma(F)$ used for all calculations. Structure solved by multisolution direct methods and refined on F with riding isotropic H [C–H 0.96 Å on external C–C–C bisectors, $U(H) = 1.2U_{eq}(C)$] and other atoms anisotropic to R 0.046, wR 0.046. 226 parameters. $w^{-1} = \sigma^2(F) + 0.0002F^2$. Slope of normal probability plot 1.52. Scattering factors from *International Tables for X-ray Crystallography* (1974). Max. $\Delta/\sigma = 0.015$, mean = 0.0004. Largest peak in final difference map 0.34 e Å⁻³, largest hole −0.49 e Å⁻³. All calculations performed with *SHELXTL* program (Sheldrick, 1983).

Table 1. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2 ×10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	5382 (1)	3269 (1)	10663 (1)	53 (1)
P	7322 (1)	4461 (1)	10895 (1)	33 (1)
N	5730 (5)	1994 (2)	9378 (5)	83 (2)
S(1)	5638 (1)	4226 (1)	11503 (1)	43 (1)
S(2)	3594 (1)	2729 (1)	10254 (2)	73 (1)
S(3)	4325 (2)	1967 (1)	9437 (2)	91 (1)
S(4)	6682 (2)	2585 (1)	9916 (2)	97 (1)
C(11)	7925 (4)	5135 (2)	11968 (4)	36 (1)
C(12)	7106 (4)	5631 (2)	11998 (4)	50 (1)
C(13)	7540 (6)	6156 (2)	12809 (5)	65 (2)
C(14)	8770 (6)	6175 (2)	13578 (5)	75 (2)
C(15)	9580 (5)	5685 (2)	13547 (5)	65 (2)
C(16)	9173 (4)	5162 (2)	12750 (4)	49 (1)
C(21)	8532 (3)	3869 (2)	11279 (4)	37 (1)
C(22)	8550 (4)	3500 (2)	12559 (4)	44 (1)
C(23)	9495 (4)	3061 (2)	12889 (5)	62 (2)
C(24)	10431 (4)	2990 (2)	11935 (5)	62 (2)
C(25)	10402 (4)	3348 (2)	10695 (5)	60 (2)
C(26)	9464 (4)	3793 (2)	10339 (5)	48 (1)
C(31)	7197 (3)	4668 (2)	8899 (4)	38 (1)
C(32)	7578 (4)	5237 (2)	8467 (4)	44 (1)
C(33)	7416 (4)	5407 (2)	6948 (4)	57 (2)
C(34)	6867 (4)	5008 (2)	5869 (4)	70 (2)
C(35)	6495 (5)	4438 (2)	6263 (5)	79 (2)
C(36)	6643 (4)	4265 (2)	7794 (4)	59 (2)

Table 2. Bond lengths (Å) and angles (°)

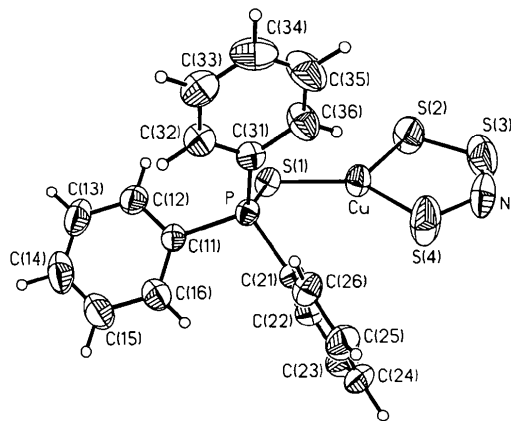|			
Cu—S(1)	2·214 (2)	Cu—S(2)	2·200 (3)
Cu—S(4)	2·191 (3)	P—S(1)	1·996 (2)
P—C(11)	1·810 (4)	P—C(21)	1·807 (4)
P—C(31)	1·813 (4)	N—S(3)	1·489 (6)
N—S(4)	1·655 (5)	S(2)—S(3)	2·007 (3)
C(11)—C(12)	1·383 (6)	C(11)—C(16)	1·390 (5)
C(12)—C(13)	1·390 (6)	C(13)—C(14)	1·369 (8)
C(14)—C(15)	1·367 (8)	C(15)—C(16)	1·374 (6)
C(21)—C(22)	1·389 (5)	C(21)—C(26)	1·391 (6)
C(22)—C(23)	1·376 (6)	C(23)—C(24)	1·402 (7)
C(24)—C(25)	1·345 (6)	C(25)—C(26)	1·384 (6)
C(31)—C(32)	1·375 (5)	C(31)—C(36)	1·376 (5)
C(32)—C(33)	1·384 (5)	C(33)—C(34)	1·355 (6)
C(34)—C(35)	1·362 (7)	C(35)—C(36)	1·396 (6)
S(1)—Cu—S(2)	127·9 (1)	S(1)—Cu—S(4)	133·7 (1)
S(2)—Cu—S(4)	98·4 (1)	S(1)—P—C(11)	108·7 (1)
S(1)—P—C(21)	113·3 (1)	C(11)—P—C(21)	107·3 (2)
S(1)—P—C(31)	113·1 (1)	C(11)—P—C(31)	106·4 (2)
C(21)—P—C(31)	107·8 (2)	S(3)—N—S(4)	125·5 (3)
Cu—S(1)—P	102·6 (1)	Cu—S(2)—S(3)	97·8 (1)
N—S(3)—S(2)	114·7 (2)	Cu—S(4)—N	103·7 (2)
P—C(11)—C(12)	118·2 (3)	P—C(11)—C(16)	121·7 (3)
C(12)—C(11)—C(16)	120·2 (3)	C(11)—C(12)—C(13)	119·6 (4)
C(12)—C(13)—C(14)	119·6 (4)	C(13)—C(14)—C(15)	120·8 (4)
C(14)—C(15)—C(16)	120·6 (5)	C(11)—C(16)—C(15)	119·2 (4)
P—C(21)—C(22)	119·2 (3)	P—C(21)—C(26)	120·8 (3)
C(22)—C(21)—C(26)	120·0 (3)	C(21)—C(22)—C(23)	119·6 (4)
C(22)—C(23)—C(24)	119·9 (4)	C(23)—C(24)—C(25)	120·0 (4)
C(24)—C(25)—C(26)	121·2 (4)	C(21)—C(26)—C(25)	119·3 (4)
P—C(31)—C(32)	121·0 (3)	P—C(31)—C(36)	120·0 (3)
C(32)—C(31)—C(36)	119·0 (3)	C(31)—C(32)—C(33)	120·9 (4)
C(32)—C(33)—C(34)	119·7 (4)	C(33)—C(34)—C(35)	120·6 (4)
C(34)—C(35)—C(36)	120·1 (4)	C(31)—C(36)—C(35)	119·7 (4)

Fig. 1. The [Cu(S$_3$N)(SPPh$_3$)] complex, showing 50% probability thermal ellipsoids and the names of the non-hydrogen atoms. H atoms have been drawn as spheres of arbitrary radius 0·12 Å.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular structure is shown in Fig. 1. The Cu atom is trigonally coordinated by three S atoms with Cu—S(1) 2·214 (2), Cu—S(2) 2·200 (3) and Cu—S(4) 2·191 (3) Å. These bonds are significantly longer than in tris(ethylenethiourea)copper(I) tetrafluoroborate [2·27 (1) Å;

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39490 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Weininger, Hunt & Amma, 1972] where the Cu atom is also trigonally coordinated by three S atoms. The N—S distances are 1·489 (6) and 1·655 (5) Å, with the longer bond to the S attached to Cu. Similar differences have been reported in [Pd(S$_3$N)$_2$] (Weiss & Neubert, 1966) and [Co(NO)$_2$(S$_3$N)] (Herberhold et al., 1981), but in [Cu(S$_3$N)(PPh$_3$)$_2$] and [Cu(S$_3$N)$_2$]$^-$ the opposite effect was found (Bojes, Chivers & Codding, 1981).

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