Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.9268 (1)	0.4736 (1)	0.1441 (1)	0.0519 (4)
N1	0.9270 (7)	0.6305 (7)	0.1446 (3)	0.058 (2)
C2	0.9241 (9)	0.678 (1)	0.1781 (4)	0.070 (3)
C3	0.9277 (9)	0.598 (1)	0.2129 (4)	0.076 (3)
N4	0.9265 (7)	0.496 (1)	0.2010 (4)	0.065 (3)
N5	0.9261 (7)	0.3171 (7)	0.1445 (3)	0.062 (2)
C6	0.9235 (9)	0.268 (1)	0.1099 (5)	0.075 (4)
C7	0.927 (1)	0.349 (1)	0.0742 (4)	0.079 (4)
N8	0.9268 (8)	0.450 (1)	0.0876 (4)	0.068 (3)
O9	0.9226 (7)	0.6886 (8)	0.1091 (3)	0.081 (2)
O10	0.9230 (7)	0.4128 (9)	0.2277 (3)	0.081 (2)
O11	0.9196 (7)	0.2529 (7)	0.1786 (3)	0.086 (3)
O12	0.9254 (7)	0.5331 (9)	0.0608 (3)	0.082 (2)
C13	0.921 (1)	0.801 (1)	0.1841 (6)	0.107 (5)
C14	0.924 (1)	0.634 (2)	0.2549 (5)	0.107 (5)
C15	0.917 (2)	0.143 (2)	0.1028 (7)	0.133 (7)
C16	0.927 (1)	0.312 (2)	0.0325 (5)	0.110 (5)
N17	0.7262 (6)	0.3726 (6)	0.1443 (3)	0.048 (2)
C18	0.6583 (9)	0.270 (1)	0.1683 (4)	0.066 (3)
C19	0.5262 (9)	0.196 (1)	0.1671 (4)	0.068 (3)
C20	0.4547 (8)	0.2243 (8)	0.1420 (3)	0.048 (2)
C21	0.5240 (8)	0.3332 (9)	0.1183 (3)	0.055 (2)
C22	0.6536 (9)	0.4009 (9)	0.1205 (3)	0.052 (2)
C23	0.3101 (8)	0.1421 (9)	0.1411 (4)	0.062 (2)
C24	0.2555 (6)	0.1437 (8)	0.1815 (3)	0.106 (5)
C25	0.2513 (6)	0.1804 (8)	0.1060 (3)	0.104 (5)
C26	0.2747 (6)	0.0009 (8)	0.1305 (3)	0.097 (4)
C27	1.1270 (7)	0.5797 (9)	0.1464 (4)	0.077 (3)
C28	1.1876 (7)	0.6655 (9)	0.1121 (4)	0.124 (7)
C29	1.189 (1)	0.520 (1)	0.1664 (5)	0.091 (4)
C30	1.330 (1)	0.588 (1)	0.1751 (5)	0.097 (4)
C31	1.388 (2)	0.532 (2)	0.1979 (7)	0.148 (8)
C32	1.503 (2)	0.569 (2)	0.209 (1)	0.19 (1)
C33	1.578 (2)	0.546 (2)	0.225 (1)	0.26 (2)

Table 2. *Selected geometric parameters* (Å, °)

Co—N5	1.877 (8)	C7—C16	1.44 (2)
Co—N8	1.88 (1)	N8—O12	1.34 (2)
Co—N1	1.885 (7)	N17—C22	1.34 (1)
Co—N4	1.89 (1)	N17—C18	1.34 (1)
Co—C27	2.086 (7)	C18—C19	1.38 (1)
Co—N17	2.088 (6)	C19—C20	1.35 (1)
N1—C2	1.25 (2)	C20—C21	1.39 (1)
N1—O9	1.37 (1)	C20—C23	1.51 (1)
C2—C13	1.51 (2)	C21—C22	1.35 (1)
C2—C3	1.51 (2)	C23—C24	1.49 (2)
C3—N4	1.28 (2)	C23—C25	1.54 (1)
C3—C14	1.46 (2)	C23—C26	1.57 (1)
N4—O10	1.32 (2)	C27—C29	1.43 (1)
N5—C6	1.28 (2)	C29—C30	1.49 (2)
N5—O11	1.34 (1)	C30—C31	1.41 (2)
C6—C15	1.47 (2)	C31—C32	1.27 (2)
C6—C7	1.51 (2)	C32—C33	1.20 (3)
C7—N8	1.30 (2)		
N5—Co—C27	92.2 (4)	C27—Co—N17	177.2 (4)
N8—Co—C27	92.3 (4)	C29—C27—C28	120.9 (6)
N1—Co—C27	88.0 (3)	C29—C27—Co	116.1 (7)
N4—Co—C27	87.8 (4)	C28—C27—Co	114.9 (3)

Data reduction: *REDU*4 (Stoe & Cie, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON*93 (Spek, 1993). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Branchaud, B. P., Meier, M. S. & Malekzadeh, M. N. (1987). *J. Org. Chem.* **52**, 212–217.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Giese, B. & Hartung, J. (1992). *Chem. Ber.* **125**, 1777–1779.
Halpern, J. (1985). *Science*, **227**, 869–875.
Hartung, J., Hertel, B. & Trach, F. (1993). *Chem. Ber.* **126**, 1187–1191.
Marzilli, L. G., Toscano, P. J., Randaccio, L., Bresciani-Pahor, N. & Calligaris, M. (1979). *J. Am. Chem. Soc.* **101**, 6754–6756.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Spek, A. L. (1993). *PLUTON*93. *Program for the Display and Analysis of Crystal and Molecular Structures*. Utrecht Univ., The Netherlands.
Stoe & Cie (1992). *REDU*4. *Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.

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Tetraethylammonium (2-Thioxo-1,3-dithiole-4,5-dithiolato-S^4, S^5)triphenylphosphinecopper(I)

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Abstract

The structure of the title compound, $(C_8H_{20}N)[Cu(C_3S_5)(C_{18}H_{15}P)]$, has been determined. There are two independent formula units. The Cu atom is tricoordi-

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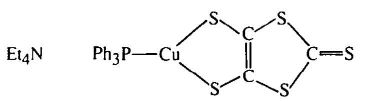
nated by two S atoms from the 2-thioxo-1,3-dithiole-4,5-dithiolate ligand and the P atom from the triphenylphosphine ligand. The bond lengths Cu—P and Cu—S are 2.181 (2) (×2), and 2.238 (2) and 2.248 (2) Å, respectively.

Comment

The chemistry of compounds involving dmit (dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate) has attracted much attention in recent years (Valade *et al.*, 1991; Olk, Olk, Dietzsch, Kirmse & Hoyer, 1992) because of the good electrical conductivity of many planar bis(dmit)–metal complexes (metal = Ni, Pd, Pt, Au) (Bousseau *et al.*, 1986; Matsubayashi & Yokozawa, 1990). A series of homoleptic complexes have been obtained (Matsubayashi, Akiba & Tanaka, 1988). A new compound, (I), containing dmit and PPh_3 ligands is reported here.



(I)

The crystal structure of the title compound contains four formula units per unit cell and the bond lengths and angles of the two independent anions are essentially similar. Selected geometric parameters of one anion of the title compound are given in Table 2. The structure of the compound is essentially planar. In the anion, the Cu atom is coordinated in a triangular manner by two S atoms from the dmit ligand and the P atom of the PPh_3 ligand. The Cu—P bond length of 2.181 (2) Å is shorter than the mean Cu—P bond length found in $[CuBr(Ph_3P)_2]$ [2.272 (8) Å; Davis, Beiford & Paul, 1973]. The mean Cu—S bond length of 2.237 (2) Å is shorter than that observed in both $(epy)_2[Cu(dmit)_2]$ (epy is the *N*-ethylpyridinium cation) [2.271 (8) Å; Matsubayashi, Takahashi & Tanaka, 1988], in which the Cu atom is coordinated to two dmit ligands, and $(mpy)_2[Cu_4(dmit)_3]$ (mpy is the *N*-methylpyridinium cation) [2.305 (2) Å; Matsubayashi & Yokozawa, 1991].

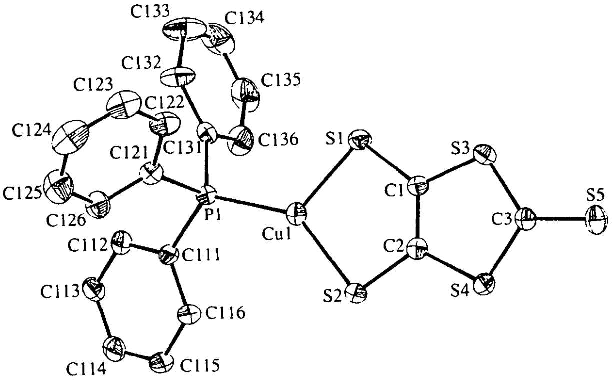


Fig. 1. *ORTEP*II (Johnson, 1976) view of the title compound. Displacement ellipsoids are shown at the 30% probability level.

Experimental

The title compound was obtained from 4,5-bis(benzoylthio)-1,3-dithiol-2-thione, $[Cu(PPh_3)(NO_3)]$ and Et_4NBr, and crystallized from CH_3OH, CH_2Cl_2 and $(C_2H_5)_2O$.

Crystal data

$(C_8H_{20}N)[Cu(C_3S_5)(C_{18}H_{15}P)]$
$M_r = 652.44$
Triclinic
$P\bar{1}$
$a = 13.372\ (1)$ Å
$b = 15.427\ (2)$ Å
$c = 16.627\ (6)$ Å
$\alpha = 104.79\ (2)°$
$\beta = 77.32\ (2)°$
$\gamma = 104.40\ (1)°$
$V = 3167.3$ Å^3
$Z = 4$
$D_x = 1.368$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.25–13.49°$
$\mu = 1.08$ mm^{-1}
$T = 296$ K
Prism
0.25 × 0.17 × 0.13 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
22 449 measured reflections
11 127 independent reflections

6632 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.033$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = -18 \rightarrow 18$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 300 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.069$
$wR = 0.089$
$S = 1.58$
6632 reflections
667 parameters
H atoms positioned geometrically (C—H = 0.95 Å) and not refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu1	0.32873 (7)	0.25261 (6)	0.63608 (6)	3.29 (2)
Cu2	0.16205 (7)	0.74379 (6)	0.86085 (6)	3.31 (2)
S1	0.3131 (2)	0.3992 (1)	0.6731 (1)	3.52 (4)
S2	0.4770 (2)	0.2688 (1)	0.6841 (1)	3.47 (5)
S3	0.4612 (2)	0.5555 (1)	0.7624 (1)	3.30 (4)

S4	0.6048 (1)	0.4476 (1)	0.7658 (1)	3.11 (4)
S5	0.6554 (2)	0.6498 (2)	0.8340 (1)	4.37 (5)
S6	0.1753 (2)	0.5962 (1)	0.8320 (1)	3.33 (4)
S7	0.0158 (2)	0.7246 (1)	0.8089 (1)	3.25 (4)
S8	0.0307 (2)	0.4371 (1)	0.7419 (1)	3.14 (4)
S9	−0.1077 (1)	0.5441 (1)	0.7265 (1)	3.17 (4)
S10	−0.1551 (2)	0.3414 (2)	0.6602 (2)	4.67 (6)
P1	0.2129 (2)	0.1470 (1)	0.5724 (1)	2.94 (4)
P2	0.2781 (2)	0.8528 (1)	0.9209 (1)	3.17 (5)
N1	0.7005 (5)	0.3778 (4)	0.4499 (4)	3.1 (1)
N2	0.1867 (5)	0.3562 (4)	0.9507 (4)	3.9 (2)
C1	0.4266 (5)	0.4395 (5)	0.7170 (4)	2.7 (2)
C2	0.4946 (5)	0.3869 (5)	0.7205 (4)	2.6 (2)
C3	0.5779 (6)	0.5566 (5)	0.7907 (4)	3.0 (2)
C4	0.0648 (5)	0.5548 (5)	0.7841 (4)	2.6 (2)
C5	0.0005 (5)	0.6058 (4)	0.7747 (4)	2.4 (1)
C6	−0.0817 (6)	0.4356 (5)	0.7065 (5)	3.2 (2)
C11	0.6267 (6)	0.3612 (6)	0.3870 (5)	4.5 (2)
C12	0.5196 (7)	0.2978 (7)	0.4100 (7)	6.0 (3)
C21	0.7195 (6)	0.2883 (5)	0.4608 (5)	4.0 (2)
C22	0.7632 (9)	0.2260 (7)	0.3788 (7)	6.5 (3)
C31	0.6571 (7)	0.4246 (6)	0.5372 (5)	4.1 (2)
C32	0.6410 (9)	0.5221 (7)	0.5438 (7)	6.8 (3)
C41	0.8008 (6)	0.4359 (6)	0.4106 (5)	4.2 (2)
C42	0.8858 (7)	0.4675 (8)	0.4683 (6)	6.7 (3)
C51	0.2895 (7)	0.3990 (6)	0.9020 (5)	5.1 (2)
C52	0.3833 (8)	0.4140 (9)	0.9468 (6)	7.2 (3)
C61	0.1876 (8)	0.2615 (6)	0.9616 (6)	5.7 (3)
C62	0.203 (1)	0.1918 (7)	0.8769 (7)	8.0 (3)
C71	0.1039 (7)	0.3545 (6)	0.8990 (5)	4.7 (2)
C72	−0.0089 (8)	0.3119 (8)	0.9363 (7)	6.4 (3)
C81	0.1643 (7)	0.4111 (6)	1.0406 (5)	4.6 (2)
C82	0.1606 (9)	0.5121 (7)	1.0466 (7)	6.5 (3)
C111	0.2515 (5)	0.0402 (5)	0.5102 (5)	2.9 (2)
C112	0.1976 (6)	−0.0186 (5)	0.4486 (5)	3.7 (2)
C113	0.2282 (6)	−0.0995 (5)	0.4034 (5)	3.9 (2)
C114	0.3162 (7)	−0.1205 (5)	0.4208 (6)	4.4 (2)
C115	0.3718 (6)	−0.0634 (6)	0.4807 (6)	4.4 (2)
C116	0.3380 (6)	0.0193 (5)	0.5288 (5)	3.9 (2)
C121	0.0935 (6)	0.1109 (5)	0.6456 (4)	3.3 (2)
C122	0.0391 (7)	0.1775 (6)	0.6935 (6)	4.7 (2)
C123	−0.0526 (7)	0.1527 (7)	0.7474 (6)	5.6 (3)
C124	−0.0874 (8)	0.0612 (9)	0.7566 (6)	6.7 (3)
C125	−0.0314 (9)	−0.0034 (7)	0.7105 (7)	6.4 (3)
C126	0.0585 (7)	0.0194 (6)	0.6531 (6)	4.7 (2)
C131	0.1682 (6)	0.1861 (5)	0.4941 (5)	3.2 (2)
C132	0.0651 (7)	0.1983 (7)	0.5036 (6)	5.9 (2)
C133	0.0413 (8)	0.2352 (8)	0.4405 (7)	7.9 (3)
C134	0.1168 (9)	0.2553 (7)	0.3722 (6)	7.1 (3)
C135	0.2171 (9)	0.2420 (6)	0.3647 (6)	6.3 (3)
C136	0.2412 (7)	0.2084 (6)	0.4262 (6)	5.0 (2)
C211	0.3909 (7)	0.8921 (6)	0.8438 (5)	4.2 (2)
C212	0.3711 (9)	0.9410 (7)	0.7898 (6)	6.3 (3)
C213	0.455 (1)	0.9710 (8)	0.7269 (7)	8.0 (4)
C214	0.552 (1)	0.9505 (9)	0.7181 (8)	8.1 (4)
C215	0.5699 (9)	0.9023 (9)	0.7719 (8)	7.8 (4)
C216	0.4897 (7)	0.8710 (7)	0.8340 (6)	5.7 (3)
C221	0.3358 (6)	0.8159 (5)	0.9935 (5)	3.4 (2)
C222	0.3678 (7)	0.7306 (6)	0.9628 (6)	5.4 (2)
C223	0.4097 (9)	0.6981 (7)	1.0176 (7)	7.1 (3)
C224	0.4172 (9)	0.7466 (7)	1.0995 (7)	6.9 (3)
C225	0.385 (1)	0.8292 (8)	1.1280 (7)	7.8 (3)
C226	0.3449 (8)	0.8638 (7)	1.0730 (6)	6.0 (3)
C231	0.2424 (6)	0.9588 (5)	0.9823 (5)	3.6 (2)
C232	0.3182 (7)	1.0382 (6)	1.0033 (6)	4.9 (2)
C233	0.2884 (8)	1.1168 (6)	1.0552 (6)	5.4 (2)
C234	0.1811 (8)	1.1159 (6)	1.0897 (6)	5.6 (2)
C235	0.1068 (8)	1.0392 (6)	1.0675 (6)	5.3 (2)
C236	0.1361 (7)	0.9593 (6)	1.0149 (5)	4.4 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—S1	2.238 (2)	S3—C1	1.744 (6)
Cu1—S2	2.231 (2)	S3—C3	1.721 (6)
Cu1—P1	2.181 (2)	S4—C2	1.750 (6)
S1—C1	1.735 (6)	S4—C3	1.736 (7)
S2—C2	1.740 (7)	S5—C3	1.648 (6)
S1—Cu1—S2	98.41 (6)	S1—C1—S3	119.5 (4)
S1—Cu1—P1	121.08 (7)	S1—C1—C2	125.5 (5)
S2—Cu1—P1	140.51 (7)	S3—C1—C2	114.9 (4)
Cu1—S1—C1	95.5 (2)	S2—C2—S4	120.0 (4)
Cu1—S2—C2	95.7 (3)	S2—C2—C1	124.9 (5)
Cu1—P1—C111	118.5 (3)	S4—C2—C1	115.1 (4)
Cu1—P1—C121	112.6 (2)	S3—C3—S4	111.5 (3)
Cu1—P1—C131	112.3 (3)	S3—C3—S5	124.3 (4)
C1—S3—C3	99.6 (3)	S4—C3—S5	124.3 (4)
C2—S4—C3	99.0 (3)		

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983). The heavy atom (Cu) was located in the *E* map and the remaining non-H atoms were located using *DIRDIF* (Beurskens, 1984). The structure was refined by a full-matrix least-squares technique with anisotropic displacement parameters for all atoms. All calculations were performed on a VAX 785 computer using the *TEXSAN* (Molecular Structure Corporation, 1987) package. The view of the molecule was produced using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors.* Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Bousseau, M., Valade, L., Legros, J.-P., Cassoux, P., Garbauskas, M. & Interrante, L. V. (1986). *J. Am. Chem. Soc.* **108**, 1908–1916, and references therein.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Davis, P. H., Beiford, R. L. & Paul, I. C. (1973). *Inorg. Chem.* **12**, 213–218.

Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, Univ. of Glasgow, Scotland.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Matsubayashi, G., Akiba, K. & Tanaka, T. (1988). *Inorg. Chem.* **27**, 4744–4749, and references therein.

Matsubayashi, G., Takahashi, K. & Tanaka, T. (1988). *J. Chem. Soc. Dalton Trans.* pp. 967–972.

Matsubayashi, G. & Yokozawa, A. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3535–3539.

Matsubayashi, G. & Yokozawa, A. (1991). *J. Chem. Soc. Chem. Commun.* pp. 68–69.

Molecular Structure Corporation (1987). *TEXSAN. TEXRAY Structure Analysis Package.* Version 2.1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Olk, R.-M., Olk, B., Dietzsch, W., Kirmse, R. & Hoyer, E. (1992). *Coord. Chem. Rev.* **117**, 99–131.

Valade, L., Legros, J.-P., Tejel, C., Pomarede, B., Garreau, B., Bruniquel, M. F. & Cassoux, P. (1991). *Synth. Met.* pp. 41–43, 2268.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.