still six significant peaks (0.7–1.0 e Å^{-3}) in a difference map, three each in the neighbourhood of C8 and C48 of the two independent molecules. Although considerable care *via* chromatography had been taken to try to ensure that the sample was a single isomer, it was soon realized that these additional peaks were consistent with a small amount of 2-ferrocenyl-6-nitro-3-phenylquinoxaline being present in addition to the major component, 3-ferrocenyl-6-nitro-2-phenylquinoxaline. The positions of these minor occupancy nitro groups also showed that the quinoxaline framework of the minor isomers did not overlap exactly the sites of the major isomer. Fortunately, we had previously determined the structure of 2-ferrocenyl-3-phenylquinoxaline (Glidewell *et al.*, 1996) and it was a relatively straightforward exercise to take the quinoxaline coordinates from that structure and use these as a template with the *FRAG* command available with *SHELXL*97 (Sheldrick, 1997) and appropriate *DFIX* restraints. Initially, the major and minor quinoxaline components were constrained using the *FRAG* command, but in the final rounds of refinement, these constraints were removed from the two major quinoxaline components. Refinement then proceeded smoothly with the atoms of each minor quinoxaline component allowed an overall isotropic displacement parameter [final values 0.055 (3) and 0.065 (3) Å^2]; the minor nitro-N atoms were assigned a U_{iso} value of 0.080 Å^2 and the minor nitro-O atoms were assigned the value 0.010 Å^2. The final occupancies of the two major/minor components refined to 0.813 (3)/0.187 (3) and 0.860 (3)/0.140 (3). All H atoms were treated as riding atoms (C—H 0.93 Å).

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX*96 *via* Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97. Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

We thank Dr J. F. Gallagher and Dublin City University for the funds to purchase the X-ray tube used in the data collections. While no direct support for the research described here was provided by NSERC (Canada), we do thank that organization for the partial funding of the 1992 upgrade of the CAD-4 diffractometer. SZA thanks the Committee of Vice-Chancellors and Principals (UK) and the University of St Andrews for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1223). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1842–1844

Polymeric Chloro(triphenyl trithiophosphite)copper(I)

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(*Received 11 May 1998; accepted 24 June 1998*)

Abstract

The title compound, *catena*-poly[copper(I)-μ-chloro-μ-[tris(phenylthio)phosphine-*P*:*S*]], [$CuCl(C_{18}H_{15}PS_3)]_n$, is polymeric. Only one of the S atoms acts as a donor to copper. Tetrahedrally coordinated Cu^I centres form spiro junctions between five-membered rings (–Cu—Cl—Cu—S—P–), thus forming a helical chain polymer in which the monomeric units are related by a 3_1 screw axis. Bond lengths at copper are Cu—P 2.2434 (16), Cu—Cl 2.3235 (16), Cu—Cl′ 2.3351 (15) and Cu—S3′ 2.3442 (15) Å.

Comment

Thiophosphites are versatile ligands in view of their diverse potential coordination sites. However, the corresponding coordination chemistry has not been in-

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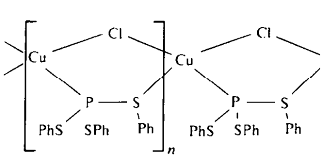
vestigated in depth. We present here the structure of polymeric chloro(triphenyl trithiophosphite)copper(I), [{(PhS)$_3$P}CuCl], (I).



(I)

The asymmetric unit of (I) consists of one formula unit. Formula units are connected *via* the 3_1 screw axis to form an infinite helical chain polymer (Figs. 1 and 2) of five-membered rings (-Cu—Cl—Cu—S—P-); the Cu atoms act as spiro junctions between the rings, which adopt a conformation with an approximate local twofold axis through chlorine and the midpoint of P—S3. The intra-annular Cu···Cu distance is 3.7940 (10) Å.

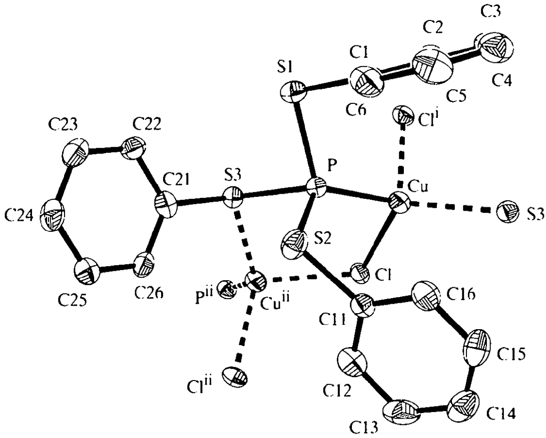


Fig. 1. Displacement ellipsoid plot (50% probability ellipsoids) of the title compound; H atoms have been omitted for clarity. The asymmetric unit (solid bonds) has been extended to complete the coordination sphere at copper and one five-membered ring. Symmetry operators are given in Table 1.

Only one of the ligand S atoms (S3) acts as a donor to copper; the other two SPh groups are exocyclic to the five-membered ring. The non-coordinating P—S distances [P—S2 2.103 (2) and P—S1 2.117 (2) Å] are, as expected, appreciably shorter than P—S3 [2.1745 (19) Å]; in the free ligand, which displays crystallographic threefold symmetry, the bond length is 2.127 (1) Å (Al'fonsov *et al.*, 1995).

The copper centres are tetrahedrally coordinated by one P, one S and two Cl atoms, with bond angles ranging from 100.40 (6)° for Cl^i—Cu—S3^i to 123.85 (6)° for P—Cu—S3^i, and bond lengths Cu—P 2.2434 (16), Cu—Cl 2.3235 (16), Cu—Cl^i 2.3351 (15) and Cu—S3^i 2.3442 (15) Å [symmetry code: (i) $-x+y$, $-x$, $z-\frac{1}{3}$].

The related materials [{(EtS)$_3$P}CuCl] and [{(^{i}PrS)$_3$P}-CuBr] also involve tetrahedral Cu^I, but the association of monomeric units is different (Kataeva *et al.*, 1995). In the ethyl derivative, spiro Cu atoms link alternating four- (-Cu—Cl—Cu—Cl-) and six-membered (-Cu—P—S—Cu—P—S-) rings, with distances Cu—Cl 2.373 (1) and 2.312 (1) (the reason for the large difference in these bond lengths is not clear), Cu—P 2.208 (1) and Cu—S 2.392 (1) Å. The isopropyl derivative is a dimer with a central Cu$_2$Br$_2$ ring and coordinated acetonitrile molecule; S atoms of the ligand do not coordinate to copper.

Experimental

The title compound was obtained directly from the ligand and copper(I) chloride in acetonitrile, and was recrystallized from

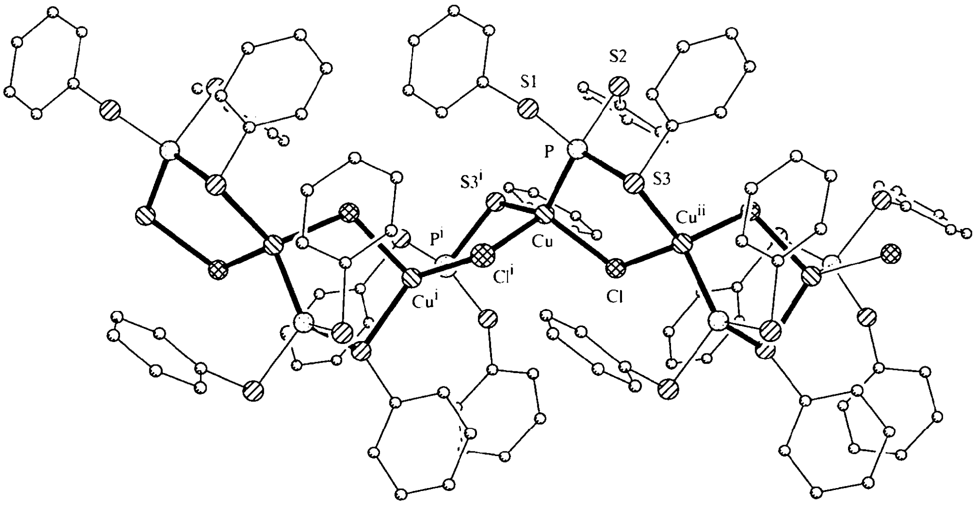


Fig. 2. A section of the chain polymer of the title compound (H atoms omitted) viewed parallel to the *b* axis. Atomic radii are arbitrary and the five-membered rings are drawn with thick bonds. Symmetry operators are given in Table 1.

the same solvent in a manner analogous to that used for related derivatives (Kataeva *et al.*, 1995).

Crystal data

[CuCl($C_{18}H_{15}PS_3$)]
$M_r = 457.44$
Trigonal
$P3_1$
$a = 12.519\,(2)$ Å
$c = 10.257\,(3)$ Å
$V = 1392.2\,(5)$ Å^3
$Z = 3$
$D_x = 1.637$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 10.0–12.5°$
$\mu = 1.741$ mm^{-1}
$T = 173\,(2)$ K
Prism
0.40 × 0.14 × 0.12 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.757$, $T_{\max} = 0.811$
4566 measured reflections
3620 independent reflections
2777 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.035$
$\theta_{\max} = 27.56°$
$h = -11 \rightarrow 16$
$k = -16 \rightarrow 13$
$l = -13 \rightarrow 11$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.097$
$S = 1.018$
3620 reflections
217 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 1.1312P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.054 (19)

Table 1. *Selected geometric parameters (Å, °)*

Cu—P	2.2434 (16)	P—S1	2.117 (2)
Cu—Cl	2.3235 (16)	P—S3	2.1745 (19)
Cu—Cl$^{\rm i}$	2.3351 (15)	S1—C1	1.776 (6)
Cu—S3$^{\rm i}$	2.3442 (15)	S2—C11	1.795 (6)
P—S2	2.103 (2)	S3—C21	1.796 (6)
P—Cu—Cl	101.22 (6)	S2—P—Cu	124.41 (8)
P—Cu—Cl$^{\rm i}$	104.53 (6)	S1—P—Cu	119.77 (8)
Cl—Cu—Cl$^{\rm i}$	107.13 (3)	S3—P—Cu	106.89 (7)
P—Cu—S3$^{\rm i}$	123.85 (6)	Cu—Cl—Cu$^{\rm ii}$	109.06 (5)
Cl—Cu—S3$^{\rm i}$	118.09 (6)	C1—S1—P	97.56 (19)
Cl$^{\rm i}$—Cu—S3$^{\rm i}$	100.40 (6)	C11—S2—P	102.23 (19)
S2—P—S1	100.64 (8)	C21—S3—P	102.27 (19)
S2—P—S3	104.41 (8)	C21—S3—Cu$^{\rm ii}$	115.5 (2)
S1—P—S3	96.40 (8)	P—S3—Cu$^{\rm ii}$	103.85 (7)
Cl—Cu—P—S3	−36.04 (8)	Cu—Cl—Cu$^{\rm ii}$—S3	11.82 (7)
P—Cu—Cl—Cu$^{\rm ii}$	13.21 (7)	Cu—P—S3—Cu$^{\rm ii}$	45.34 (8)
P—S3—Cu$^{\rm ii}$—Cl	−33.66 (7)		

Symmetry codes: (i) $-x + y, -x, z - \frac{1}{3}$; (ii) $-y, x - y, \frac{1}{3} + z$.

The absolute structure was determined on the basis of 1478 Friedel pairs. The origin was fixed according to the method of Flack & Schwarzenbach (1988). H atoms were refined using a riding model starting from calculated positions.

Data collection: *P*3 *Software* (Nicolet, 1987). Cell refinement: *P*3 *Software*. Data reduction: *XDISK* in *P*3 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

LF acknowledges the award of a postdoctoral fellowship by the Deutscher Akademischer Austauschdienst. We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1265). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1844–1846

Iodo(phthalocyaninato)vanadium(III)

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(*Received 5 March 1998; accepted 9 June 1998*)

Abstract

A new vanadium phthalocyanine complex with the formula [VI($C_{32}H_{16}N_8$)], or PcVI (Pc = $C_{32}H_{16}N_8$), has been obtained by the reaction of pure V powder with