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Key indicators

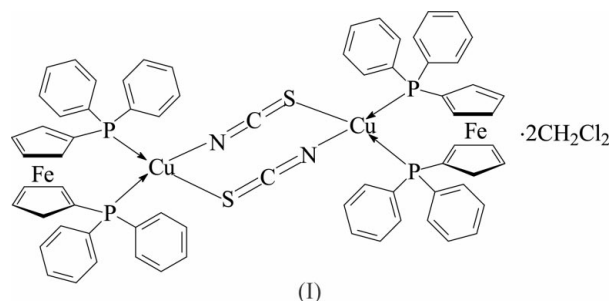
Single-crystal X-ray study
 $T = 123$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
Disorder in solvent or counterion
 R factor = 0.056
 wR factor = 0.166
Data-to-parameter ratio = 17.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Di- μ -thiocyanato-bis{[1,1'-bis(diphenylphosphino)-
ferrocene- κ^2P,P']copper(I)} dichloromethane
disolvateThe 1,1'-bis(diphenylphosphino)ferrocene ligand chelates to the Cu^{I} atom forming the centrosymmetric title dimer $[\text{Cu}_2(\text{NCS})_2(\text{C}_{34}\text{H}_{28}\text{P}_2)_2] \cdot 2\text{CH}_2\text{Cl}_2$. The thiocyanate ions bridge the Cu atoms, which show tetrahedral coordination. The solvent molecules are disordered over twofold rotation axes.

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Comment

Our studies of the phosphine complexes of copper(I) salts (Li *et al.*, 2004*a,b*) have been extended to the study of the copper(I) thiocyanate complex of 1,1'-bis(diphenylphosphino)ferrocene, a bidentate diphosphine. The ligand has been used in the synthesis of binuclear adducts of copper(I) halides (Díez *et al.*, 2001; Neo *et al.*, 1994); in the adducts, the ligand functions as a chelate. In the nitrate and formate derivatives, the anions bridge the metal atoms (Neo *et al.*, 1994).

The molecular structure of the title compound, (I), is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The complex molecule is centrosymmetric, and the diphosphine ligand coordinates in a chelating mode. The bite angle of $112.13(4)^\circ$ is only marginally larger than those found in the chloride [$111.26(4)^\circ$; Díez *et al.*, 2001] and iodide [$111.2(4)^\circ$; Neo *et al.*, 1994] derivatives. These values are, however, much smaller than that in the nitrate derivative [$117.8(1)^\circ$; Neo *et al.*, 1994], which is claimed to have the largest bite angle in complexes of this ligand. The Cu^{I} atom in these complexes exists in tetrahedral environments. On the other hand, the centrosymmetric copper(I) thiocyanate complex with the diphosphine, 1,2-bis(diphenylphosphino)ethane, has a 2:3 stoichiometry. One of the Cu^{I} atoms is chelated by the donor ligand, but the bite angle is even smaller [$89.72(4)^\circ$; Saravanabharathi *et al.*, 2002]. Other adducts of copper(I) thiocyanate are known, some of the best studied being *N*-heterocyclic complexes (Näther & Jeß, 2004). Complexes of 1,1'-bis(diphenylphosphino)ferrocene as a chelating and bridging ligand have also been mentioned by Díez *et al.* (1999).

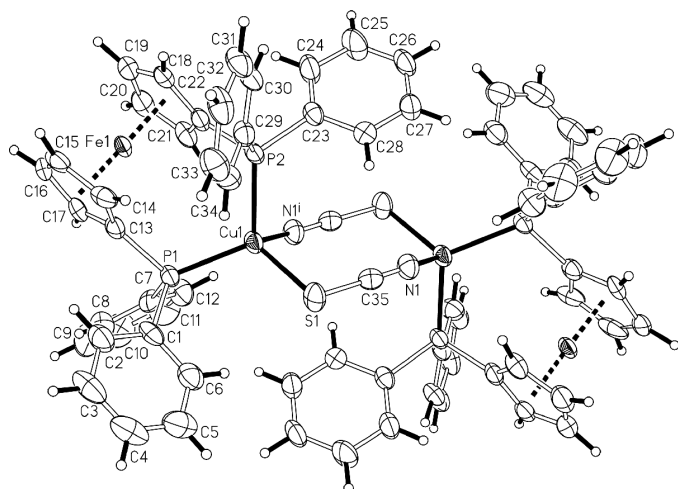


Figure 1
ORTEP (Johnson, 1976) plot of (I), with displacement ellipsoids shown at the 75% probability level. H atoms are drawn as spheres of arbitrary radii. The solvent molecules have been omitted for clarity. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

Experimental

A dichloromethane solution (5 ml) of 1,1'-bis(diphenylphosphino)-ferrocene (0.055 g, 0.1 mmol) was placed in a glass tube and an aqueous solution of sodium thiocyanate, containing cuprous thiocyanate (0.012 g, 0.1 mmol), was added dropwise. The resulting solution was allowed to stand at room temperature for several days. Orange prisms deposited on the walls of the tube in about 50% yield. The crystals turned opaque after a day.

Crystal data

[Cu₂(NCS)₂(C₃₄H₂₈P₂)₂]·2CH₂Cl₂ *D_m* measured by flotation in
M_r = 1521.80 CH₃OH/CCl₄
 Monoclinic, *C*2/*c* Mo *K*α radiation
a = 27.253 (2) Å Cell parameters from 3724
b = 16.662 (1) Å reflections
c = 17.179 (1) Å *θ* = 2.4–26.4°
β = 114.429 (1)° *μ* = 1.33 mm⁻¹
V = 7102.6 (7) Å³ *T* = 123 (2) K
Z = 4 Block, orange
D_x = 1.423 Mg m⁻³ 0.42 × 0.39 × 0.34 mm
D_m = 1.460 Mg m⁻³

Data collection

Bruker SMART APEX area- 7360 independent reflections
 detector diffractometer 6058 reflections with *I* > 2σ(*I*)
φ and *ω* scans *R_{int}* = 0.039
 Absorption correction: multi-scan *θ_{max}* = 26.5°
 (SADABS; Bruker, 2002) *h* = -34 → 33
T_{min} = 0.312, *T_{max}* = 0.636 *k* = -20 → 20
 20 031 measured reflections *l* = -21 → 15

Refinement

Refinement on *F*² *w* = 1/[σ²(*F_o*²) + (0.0898*P*)²
R[*F*² > 2σ(*F*²)] = 0.056 + 19.286*P*]
wR(*F*²) = 0.166 where *P* = (*F_o*² + 2*F_c*²)/3
S = 1.05 (Δ/σ)_{max} = 0.001
 7360 reflections Δ*ρ*_{max} = 1.10 e Å⁻³
 412 parameters Δ*ρ*_{min} = -1.01 e Å⁻³
 H-atom parameters constrained

Table 1
Selected geometric parameters (Å, °).

Cu1—N1 ⁱ	2.013 (3)	Fe1—C16	2.029 (4)
Cu1—P1	2.247 (1)	Fe1—C17	2.034 (4)
Cu1—P2	2.289 (1)	Fe1—C18	2.039 (4)
Cu1—S1	2.383 (1)	Fe1—C19	2.053 (4)
Fe1—C13	2.050 (4)	Fe1—C20	2.064 (4)
Fe1—C14	2.052 (4)	Fe1—C21	2.041 (4)
Fe1—C15	2.070 (4)	Fe1—C22	2.030 (4)
N1 ⁱ —Cu1—P1	118.4 (1)	C15—Fe1—C19	113.6 (2)
N1 ⁱ —Cu1—P2	97.8 (1)	C15—Fe1—C20	142.5 (2)
N1 ⁱ —Cu1—S1	103.6 (1)	C15—Fe1—C21	176.7 (2)
P1—Cu1—P2	112.13 (4)	C15—Fe1—C22	136.5 (2)
P1—Cu1—S1	113.21 (4)	C16—Fe1—C17	41.0 (2)
P2—Cu1—S1	110.37 (4)	C16—Fe1—C18	135.1 (2)
C13—Fe1—C14	41.1 (2)	C16—Fe1—C19	109.2 (2)
C13—Fe1—C15	68.3 (2)	C16—Fe1—C20	112.2 (2)
C13—Fe1—C16	68.8 (2)	C16—Fe1—C21	142.1 (2)
C13—Fe1—C17	40.9 (2)	C16—Fe1—C22	175.8 (2)
C13—Fe1—C18	144.3 (2)	C17—Fe1—C18	174.6 (2)
C13—Fe1—C19	174.6 (2)	C17—Fe1—C19	134.5 (2)
C13—Fe1—C21	110.0 (2)	C17—Fe1—C20	109.0 (2)
C13—Fe1—C22	113.6 (2)	C17—Fe1—C21	112.4 (2)
C14—Fe1—C15	40.2 (2)	C17—Fe1—C22	143.0 (2)
C14—Fe1—C16	68.3 (2)	C18—Fe1—C20	68.2 (2)
C14—Fe1—C17	68.8 (2)	C18—Fe1—C21	68.7 (2)
C14—Fe1—C18	114.3 (2)	C18—Fe1—C22	41.1 (2)
C14—Fe1—C19	143.4 (2)	C18—Fe1—C19	40.5 (2)
C13—Fe1—C20	135.2 (2)	C19—Fe1—C20	40.3 (2)
C14—Fe1—C20	176.2 (2)	C19—Fe1—C21	68.3 (2)
C14—Fe1—C21	136.8 (2)	C19—Fe1—C22	68.7 (2)
C14—Fe1—C22	111.0 (2)	C20—Fe1—C21	40.6 (2)
C15—Fe1—C16	40.4 (2)	C20—Fe1—C22	68.8 (2)
C15—Fe1—C17	68.3 (2)	C21—Fe1—C22	41.1 (2)
C15—Fe1—C18	110.9 (2)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

The two dichloromethane molecules are disordered about twofold axes and were allowed to refine over the axes. The C—Cl distance was restrained to 1.79 (1) Å and the Cl···Cl distance to 2.93 (2) Å; in each molecule, the displacement parameters of the Cl atoms were constrained to be equal. The refinement converged satisfactorily, but the difference Fourier map indicated the presence of a peak of 2 e Å⁻³ ca 3 Å from the Cl atoms of the disordered solvent molecules. The excess electron density was then accounted for by using the SQUEEZE option (Sluis & Spek, 1990) in PLATON (Spek, 2003). The final difference map showed the largest peak about 1 e Å⁻³ from atom C14 and the deepest hole about 0.5 e Å⁻³ from atom C11, but was otherwise featureless. The void in the crystal structure amounted to 5% of the cell volume. H atoms were placed in calculated positions and were included in the refinement in the riding model approximation; C—H = 0.95 Å for the phenyl atoms, C—H = 1.00 Å for the cyclopentadienyl atoms and C—H = 0.99 Å for the methylene atoms, with *U* = 1.2*U_{eq}*(parent C atoms).

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP II (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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