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The crystal structure of bis[μ_2 -(*N,N*-diethylcarbamodithioato- $\kappa S:\kappa S,\kappa S'$)]bis[1'-(diphenylphosphino- κP)-1-cyanoferrocene]disilver(I), $C_{56}H_{56}Ag_2Fe_2N_4P_2S_4$

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Abstract

$C_{56}H_{56}Ag_2Fe_2N_4P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.5058(2)$ Å, $b = 10.8362(2)$ Å, $c = 14.3325(3)$ Å, $\alpha = 72.400(1)^\circ$, $\beta = 75.241(1)^\circ$, $\gamma = 77.132(1)^\circ$, $V = 1343.71(5)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0191$, $wR_{ref}(F^2) = 0.0443$, $T = 150(2)$ K.

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The molecular structure of the title complex is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

1'-(Diphenylphosphino)-1-cyanoferrocene (*L*; 20 mg, 51 μmol) [5] and silver(I) *N,N'*-diethylcarbamodithioate (Sigma-Aldrich; 13 mg, 51 μmol) were mixed in chloroform (2 mL). The resulting mixture was stirred for 60 min and then

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Table 1: Data collection and handling.

Crystal:	Orange prism
Size:	0.30 × 0.17 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.50 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	20417, 6185, 0.020
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5705
$N(param)_{refined}$:	318
Programs:	Bruker [1], SHELX [2, 3], PLATON [4]

evaporated under vacuum. The orange-brown residue was crystallized from ethyl acetate-hexane (2 + 10 mL) to afford the title compound as rusty orange, prismatic crystals (13 mg, 38%).

Characterization data: ¹H NMR (400 MHz, CDCl₃): δ 1.30 (t, ³ $J_{HH} = 7.1$ Hz, 6 H, CH₃), 3.99 (q, ³ $J_{HH} = 7.1$ Hz, 4 H, CH₂), 4.47 (apparent q, $J' = 1.9$ Hz, 2 H, C₅H₄), 4.51 (apparent t, $J' = 1.9$ Hz, 2 H, C₅H₄), 4.52 (apparent t, $J' = 1.8$ Hz, 2 H, C₅H₄), 4.63 (apparent t, $J' = 1.8$ Hz, 2 H, C₅H₄), 7.33–7.45 (m, 6 H, PPh₂), 7.48–7.55 (m, 4 H, PPh₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 1.9 (br s). ESI+ MS: m/z 502 ([Ag(L)]⁺). IR (Nujol, cm^{−1}): ν_{max} 3103 w, 3087 w, 3068 w, 2226 s, 1586 w, 1478 s, 1421 s, 1267 s, 1230 w, 1207 m, 1170 m, 1136 m, 1096 m, 1073 m, 1049 w, 985 m, 911 m, 842 m, 810 w, 776 w, 749 m, 744 m, 704 m, 695 s, 563 w, 532 w, 509 s, 482 s, 474 m, 459 m. Anal. Calc. for $C_{56}H_{56}Ag_2Fe_2N_4P_2S_4 \times 0.2$ CHCl₃ (663.3): C 50.88, H 4.27, N 4.22%. Found C 50.64, H 4.17, N 3.99% (sample from chloroform).

Experimental details

The structure was solved by direct methods using SHELXS [2] and refined by full-matrix least-squares based on F^2 with SHELXL [3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in their calculated positions and refined as riding atoms [3] with U_{iso} set to a multiple of U_{eq} of their bonding carbon atoms.

Comment

Dithiocarbamates have attracted attention as readily accessible and structurally changeable ligands for transition metal ions and have even found manifold practical use [6–8].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ag	0.11162(2)	0.90051(2)	0.57463(2)	0.01796(4)
Fe	−0.11330(2)	0.76206(2)	0.89548(2)	0.01302(5)
N1	−0.55587(17)	0.81998(16)	1.01630(12)	0.0322(3)
P	0.20444(4)	0.84529(4)	0.72532(3)	0.01268(8)
C1	−0.31474(17)	0.70951(15)	0.92414(11)	0.0174(3)
C2	−0.21470(17)	0.60197(15)	0.97083(12)	0.0185(3)
H2	−0.225079	0.560309	1.040281	0.022*
C3	−0.09777(18)	0.56976(15)	0.89391(12)	0.0197(3)
H3	−0.015583	0.502193	0.902921	0.024*
C4	−0.12438(18)	0.65605(15)	0.80056(12)	0.0192(3)
H4	−0.062907	0.655392	0.736990	0.023*
C5	−0.25747(18)	0.74263(16)	0.81851(11)	0.0189(3)
H5	−0.300972	0.810322	0.769580	0.023*
C6	0.06622(16)	0.85481(14)	0.83626(11)	0.0141(3)
C7	−0.06676(17)	0.94850(15)	0.83569(12)	0.0182(3)
H7	−0.096908	1.009202	0.778195	0.022*
C8	−0.14568(19)	0.93495(16)	0.93588(13)	0.0231(3)
H8	−0.237493	0.985089	0.957038	0.028*
C9	−0.06328(18)	0.83338(17)	0.99877(12)	0.0223(3)
H9	−0.090934	0.803563	1.069391	0.027*
C10	0.06746(17)	0.78377(16)	0.93847(11)	0.0176(3)
H10	0.142495	0.715603	0.961657	0.021*
C11	−0.44800(18)	0.77258(16)	0.97521(12)	0.0217(3)
C12	0.33119(16)	0.94766(14)	0.72864(11)	0.0137(3)
C13	0.30902(19)	1.00941(16)	0.80477(12)	0.0213(3)
H13	0.225832	0.998089	0.858058	0.026*
C14	0.4082(2)	1.08761(17)	0.80307(13)	0.0264(4)
H14	0.392983	1.128623	0.855557	0.032*
C15	0.52867(18)	1.10577(16)	0.72537(13)	0.0242(4)
H15	0.596224	1.159155	0.724309	0.029*
C16	0.55046(18)	1.04574(16)	0.64902(14)	0.0243(4)
H16	0.632686	1.058881	0.595182	0.029*
C17	0.45319(17)	0.96666(15)	0.65059(12)	0.0194(3)
H17	0.469708	0.925176	0.598228	0.023*
C18	0.31212(16)	0.68113(14)	0.75418(11)	0.0147(3)
C19	0.29954(19)	0.58892(16)	0.70804(12)	0.0233(3)
H19	0.230458	0.609739	0.665801	0.028*
C20	0.3877(2)	0.46670(17)	0.72365(14)	0.0306(4)
H20	0.378133	0.403974	0.692450	0.037*
C21	0.4895(2)	0.43578(16)	0.78438(13)	0.0258(4)
H21	0.550325	0.352402	0.794213	0.031*
C22	0.50246(18)	0.52642(16)	0.83077(12)	0.0224(3)
H22	0.571957	0.505200	0.872747	0.027*
C23	0.41401(17)	0.64825(15)	0.81598(12)	0.0185(3)
H23	0.422945	0.709985	0.848323	0.022*
S1	0.15840(4)	0.74405(4)	0.45708(3)	0.02175(9)
S2	−0.14019(4)	0.86410(4)	0.54578(3)	0.01738(8)
N2	−0.09257(16)	0.69922(13)	0.43191(10)	0.0207(3)
C31	−0.02935(17)	0.76270(14)	0.47264(11)	0.0159(3)
C32	−0.0051(2)	0.60689(17)	0.37386(13)	0.0276(4)
H32A	−0.062628	0.537271	0.381990	0.033*
H32B	0.085572	0.564777	0.400230	0.033*
C33	0.0368(3)	0.6748(2)	0.26368(14)	0.0504(6)
H33A	−0.052664	0.717882	0.237603	0.076*
H33B	0.091680	0.609855	0.227208	0.076*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H33C	0.098406	0.740456	0.255054	0.076*
C34	−0.2521(2)	0.72491(17)	0.43508(14)	0.0292(4)
H34A	−0.268958	0.718279	0.371518	0.035*
H34B	−0.290881	0.815838	0.440153	0.035*
C35	−0.3375(2)	0.6321(2)	0.52105(18)	0.0415(5)
H35A	−0.301375	0.541901	0.515918	0.062*
H35B	−0.442365	0.654562	0.518397	0.062*
H35C	−0.323975	0.639895	0.584475	0.062*

From a structural viewpoint, they are versatile donors than can coordinate as terminal and bridging ligands. The flexible coordination of dithiocarbamates can be demonstrated in their silver(I) complexes [8]. For instance, homoleptic Ag(I)-dithiocarbamate complexes, typically forming complicated polymeric coordination assemblies in the solid state, can be cleaved into smaller discrete species by addition of other ligands. The coordination of phosphine ligands to the polymeric Ag(I) dithiocarbamates gives rise to dimeric species with bridging dithiocarbamate ligands analogous to the title compound [9–13] or even to mononuclear complexes of the type [(R₃P)₂Ag(S₂CNR₂-κ²S,S')] [10, 14, 15], depending on the amount and type of the auxiliary ligand.

Having recently demonstrated that 1'-(diphenylphosphino)-1-cyanoferrocene [1] can be accommodated in Ag(I) complexes as a *P*-monodentate (terminal), *P,N*-bridging and even *P,N*-chelating ligand [16, 17], we decided to extend our investigations further toward Ag(I) complexes containing a supporting dithiocarbamate ligand.

The reaction between equimolar quantities of the phosphinoferrocene nitrile Ph₂PfcCN (fc = ferrocene-1,1'-diyl) and silver(I) *N,N*-diethylcarbamodithioate in chloroform produced the orange complex [Ag(Ph₂PfcCN-κ*P*)(μ-Et₂NCS₂-κ*S*:κ*S*,κ*S*')]₂. The compound crystallizes with the symmetry of the triclinic space group *P* $\bar{1}$ and with the complex molecule lying around the crystallographic inversion centres (*Z* = 1). Formally, the structure consists of two equivalent Ag(Ph₂PfcCN-κ*P*)(Et₂NCS₂-κ*S*:κ*S*') fragments symmetrically interlinked into a dimeric assembly by a pair of additional Ag–S interactions. This gives rise to identical PS₃ donor sets around the chemically identical Ag(I) centres. Expectedly, the Ag–S bonds involving the bridging sulfur atom S2 (Ag–S2 = 2.6608(5) Å, Ag–S2' = 2.6394(4) Å) are slightly but statistically longer than the bonds involving the terminally coordinated sulfur atom S1 (Ag–S1 = 2.6308(4) Å), and this asymmetry is reflected also in the C–S distances (C31–S1 = 1.715(2) Å, C31–S2 = 1.742(2) Å). The central Ag₂S₂ ring, rather regular in terms of bond distances, is compressed along the Ag···Ag' axis (*cf.* S2–Ag–S2' = 101.63(1)°, Ag–S2–Ag' = 78.37(1)°). Notably, the Ag···Ag' distance of 3.3488(3) Å

exceeds by far the sum the of covalent radii (2.9 Å) but still falls below the threshold of the van der Waals contacts (3.44 Å).

The coordination spheres around the silver atoms are severely distorted as evidenced by the dihedral angle of the {Ag,S2,S2'} and {Ag,P,S1} planes of 65.42(2)° that departs substantially from the 90° expected for a regular tetrahedron. The chelating dithiocarbamate ligand is associated with the smallest interligand angle of 68.55(1)° (S1–Ag–S2), and the P–Ag–S angles, ranging from 116.34(1)° for P–Ag–S2' to 130.20(2) for P–Ag–S2, compensate for this closure.

The ferrocene ligands coordinate as simple phosphine donors. Hence, their nitrile substituents are rotated away from the Ag(I) centres. The torsion angle C1–Cg1–Cg2–C6, where Cg1 and Cg2 are the centroids of the cyclopentadienyl rings C(1–5) and C(6–10), respectively, is –157.8(1)°. The ferrocene moiety shows similar Fe–C distances (2.026(2)–2.063(2) Å) and, accordingly, a tilt angle of only 2.1(1)°. The P–Ag distance of 2.3990(5) Å in the title compound compares well with the value reported for the analogous triphenylphosphine complex (2.4125(4) Å) [10].

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