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Crystal structure of (morpholine-1-carbodithioato- κ^2 -*S,S'*)bis(triphenylphosphine- κ -*P*)gold(I), $C_{41}H_{38}AuNOP_2S_2$

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Abstract

$C_{41}H_{38}AuNOP_2S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 10.0821(2)$ Å, $b = 12.9409(2)$ Å, $c = 14.7183(3)$ Å, $\alpha = 76.207(1)^\circ$, $\beta = 80.444(1)^\circ$, $\gamma = 75.592(1)^\circ$, $V = 1794.63(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0170$, $wR_{ref}(F^2) = 0.0407$, $T = 150$ K.

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The molecular structure 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.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.28 × 0.23 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.34 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.0°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	29308, 8549, 0.022
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 8165
$N(param)_{refined}$:	434
Programs:	Bruker [1], SHELX [2, 3], Mercury [4]

Source of material

Au(tht)Cl (tht = tetrahydrothiophene; 0.32 g, 1 mmol) dissolved in 10 mL acetonitrile was added to a stirring acetonitrile solution of sodium morpholinecarbodithioate, [Na(S₂CNC₄H₈O)] (0.19 g, 1 mmol) and triphenylphosphine (0.52 g, 2 mmol) and the mixture was stirred for 2 h. The resulting white precipitate was filtered and washed with water:ethanol (50:50) and dried under vacuum. Colourless block crystals were obtained by vapour diffusion of hexane into dichloromethane. Yield = 0.69 g (78%); m.p. = 168–169 °C; FT-IR ν_{max} (cm⁻¹): 2846(s), 1477(w), 1453(m), 1432(s), 1412(s), 1260(m), 1212(s), 1098(m), 689(s), 493(m), 422(m) ¹H NMR (400 MHz, DMSO-d₆) δ 7.49 (th, $J = 4.3, 1.9$ Hz, 18H), 7.45–7.38 (m, 12H), 4.09 (t, $J = 4.9$ Hz, 4H), 3.62 (t, $J = 4.8$ Hz, 4H).

Experimental details

The structure was solved by the direct method using the SHELXS [2] program and refined. The visual crystal structure information was performed using Mercury [4] system software.

Comment

Dithiocarbamates (R₂NCS₂⁻) are very versatile monoanionic ligands which form stable metal complexes with all classes

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Au1	0.64088 (2)	0.26803 (2)	0.73120 (2)	0.01499 (3)
S1	0.63931 (5)	0.16917 (4)	0.92629 (3)	0.01988 (10)
S2	0.41445 (5)	0.21271 (4)	0.80661 (3)	0.01885 (9)
P1	0.65331 (5)	0.44360 (4)	0.73709 (3)	0.01417 (9)
P2	0.77641 (5)	0.14261 (4)	0.64549 (3)	0.01415 (9)
O1	0.18867 (19)	0.19981 (14)	1.13309 (11)	0.0338 (4)
N1	0.38944 (18)	0.12828 (14)	0.98998 (11)	0.0192 (3)
C1	0.4736 (2)	0.16656 (15)	0.91561 (13)	0.0166 (4)
C2	0.4212 (2)	0.10509 (16)	1.08751 (13)	0.0223 (4)
H2A	0.519565	0.103742	1.088554	0.027*
H2B	0.403173	0.033117	1.121123	0.027*
C3	0.3307 (3)	0.19372 (18)	1.13468 (15)	0.0282 (5)
H3A	0.350241	0.179367	1.200821	0.034*
H3B	0.352985	0.264696	1.102242	0.034*
C4	0.1570 (3)	0.22056 (19)	1.03879 (15)	0.0302 (5)
H4A	0.174174	0.292778	1.005112	0.036*
H4B	0.058132	0.222494	1.039330	0.036*
C5	0.2433 (2)	0.13382 (17)	0.98696 (14)	0.0227 (4)
H5A	0.220933	0.062251	1.016994	0.027*
H5B	0.222972	0.152094	0.920749	0.027*
C6	0.5157 (2)	0.52151 (15)	0.80716 (13)	0.0172 (4)
C7	0.4818 (2)	0.63551 (16)	0.78968 (15)	0.0238 (4)
H7	0.527541	0.676288	0.736819	0.029*
C8	0.3813 (2)	0.68920 (18)	0.84959 (16)	0.0286 (5)
H8	0.358758	0.766641	0.837317	0.034*
C9	0.3139 (2)	0.63129 (19)	0.92663 (16)	0.0299 (5)
H9	0.246423	0.668521	0.967871	0.036*
C10	0.3453 (3)	0.5185 (2)	0.94341 (16)	0.0312 (5)
H10	0.297734	0.478272	0.995616	0.037*
C11	0.4461 (2)	0.46364 (17)	0.88434 (14)	0.0239 (4)
H11	0.467495	0.386194	0.896758	0.029*
C12	0.8117 (2)	0.44214 (15)	0.78215 (13)	0.0169 (4)
C13	0.9213 (2)	0.35228 (17)	0.77880 (15)	0.0240 (4)
H13	0.908720	0.290074	0.760513	0.029*
C14	1.0490 (2)	0.35337 (18)	0.80210 (16)	0.0284 (5)
H14	1.123827	0.292606	0.798390	0.034*
C15	1.0672 (2)	0.4432 (2)	0.83080 (15)	0.0289 (5)
H15	1.154584	0.444088	0.846410	0.035*
C16	0.9579 (2)	0.53108 (19)	0.83656 (15)	0.0277 (5)
H16	0.969653	0.591712	0.857799	0.033*
C17	0.8314 (2)	0.53132 (17)	0.81152 (14)	0.0221 (4)
H17	0.757351	0.592849	0.814407	0.027*
C18	0.6681 (2)	0.53402 (14)	0.62149 (13)	0.0164 (4)
C19	0.7941 (2)	0.55653 (15)	0.57689 (14)	0.0190 (4)
H19	0.873378	0.531312	0.609748	0.023*
C20	0.8046 (2)	0.61571 (16)	0.48452 (14)	0.0237 (4)
H20	0.890878	0.630428	0.454536	0.028*
C21	0.6889 (3)	0.65315 (17)	0.43633 (14)	0.0261 (5)
H21	0.696217	0.692975	0.373193	0.031*
C22	0.5630 (2)	0.63252 (17)	0.48017 (15)	0.0255 (4)
H22	0.483737	0.659042	0.447340	0.031*
C23	0.5521 (2)	0.57307 (16)	0.57219 (14)	0.0204 (4)
H23	0.465488	0.558841	0.601806	0.024*
C24	0.8049 (2)	0.20231 (15)	0.51993 (13)	0.0170 (4)
C25	0.7990 (2)	0.14800 (16)	0.44985 (14)	0.0210 (4)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
H25	0.786098	0.075303	0.466648	0.025*
C26	0.8120 (2)	0.19984 (18)	0.35563 (14)	0.0258 (4)
H26	0.806596	0.162703	0.308387	0.031*
C27	0.8327 (2)	0.30515 (18)	0.33012 (15)	0.0270 (5)
H27	0.841257	0.340253	0.265589	0.032*
C28	0.8410 (2)	0.35927 (17)	0.39895 (15)	0.0252 (4)
H28	0.857369	0.430970	0.381538	0.030*
C29	0.8255 (2)	0.30879 (16)	0.49339 (14)	0.0212 (4)
H29	0.828843	0.346985	0.540355	0.025*
C30	0.7240 (2)	0.01856 (15)	0.64220 (13)	0.0163 (4)
C31	0.5861 (2)	0.02495 (16)	0.63533 (14)	0.0213 (4)
H31	0.519014	0.088982	0.643868	0.026*
C32	0.5464 (2)	−0.06263 (17)	0.61592 (15)	0.0247 (4)
H32	0.452506	−0.057514	0.609767	0.030*
C33	0.6437 (2)	−0.15726 (16)	0.60556 (14)	0.0224 (4)
H33	0.616950	−0.216089	0.590612	0.027*
C34	0.7795 (2)	−0.16579 (16)	0.61700 (14)	0.0227 (4)
H34	0.845175	−0.231754	0.612585	0.027*
C35	0.8207 (2)	−0.07816 (16)	0.63499 (14)	0.0202 (4)
H35	0.914318	−0.084219	0.642336	0.024*
C36	0.9469 (2)	0.09476 (15)	0.68573 (13)	0.0171 (4)
C37	1.0651 (2)	0.11945 (16)	0.63032 (15)	0.0230 (4)
H37	1.060649	0.156551	0.566528	0.028*
C38	1.1898 (2)	0.08991 (18)	0.66819 (18)	0.0296 (5)
H38	1.270186	0.107493	0.630142	0.035*
C39	1.1981 (2)	0.03521 (18)	0.76062 (18)	0.0306 (5)
H39	1.283532	0.015740	0.786266	0.037*
C40	1.0812 (3)	0.00906 (19)	0.81546 (17)	0.0311 (5)
H40	1.086930	−0.029983	0.878630	0.037*
C41	0.9557 (2)	0.03920 (18)	0.77922 (15)	0.0267 (4)
H41	0.875482	0.022127	0.817889	0.032*

of metal. It is the most common class of monoanionic 1,1-dithiolate ligands. Other classes include carbamates, xanthates, dithiophosphates, dithiophosphonates, among others [5]. The upsurge in the number of dithiocarbamate derivatives prepared so far stems from the ability to vary the substituents on the nitrogen atom [6]. The ease of synthesis and ability to modify the ligand has made this ligand prominent in coordination chemistry. The DTC ligand is capable of bonding to low-valent metals and has diverse coordination modes. There are nine possible coordination modes observed for DTC, but only six are prominent in the literature [7]. DTC can act as a monodentate as well as a bidentate in a monometallic system. In the bidentate system, (the most common coordination mode) the ligand coordinates to the metal via its two sulfur atoms forming two approximately equivalent metal-sulfur bonds with the metal-sulfur distance ranging from 2.25–2.55 Å and a small bite angle (S–M–S) in the range 60–80°. The chemistry of

gold dithiocarbamate complexes has been extensively studied [5–8] owing to their antitumor/anticancer properties [9–14], as precursors for gold nanoparticle synthesis [15, 16]. Several structures of gold dithiocarbamate complexes have been reported to date but only a few have been reported with triphenylphosphine [17–20].

The crystal structure of the title compound has one molecular unit consisting of a bidentate morpholinecarbodithioate unit, two triphenylphosphine moieties and Au(I) centre. The metal centre's coordination environment is occupied by two sulfur and two phosphorous atoms of the morpholinecarbodithioate and triphenylphosphine ligands, respectively. Furthermore, the Au(I) centre adopts a distorted tetrahedral geometry with bond angles around the Au(I) atom ranging from $66.16(2)$ to $132.12(2)^\circ$. All bond distances are comparable to those of closely related compounds in literature [17–20]. Interestingly, the title compound is isostructural to the (piperidine-1-carbodithioato-S,S') derivative [17] with a calculated root mean squared deviation of $1.604 \text{ \AA}$ for their crystal packing similarity. Intermolecular C—H $\cdots\pi$ interactions exist between the hydrogen atoms of the morpholinyl unit and the phenyl rings.

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