Refinement of the crystal structure of bis[bis(*N,N*-diethyldithiocarbamato)mercury(II)], [Hg(S₂CNEt₂)₂]₂

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Abstract

C₂₀H₄₀Hg₂N₄S₈, monoclinic, *P*1₂/n1 (No. 14), *a* = 9.6048(7) Å, *b* = 10.9119(8) Å, *c* = 15.798(1) Å, β = 102.375(2)°, *V* = 1617.3 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.031, *wR*_{ref}(*F*²) = 0.061, *T* = 183 K.

Source of material

The title compound, a known species [1], was isolated as yellow blocks from the slow evaporation of an acetonitrile/chloroform (1/1) solution of the compound.

Experimental details

The H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation.

Discussion

The zinc-triad 1,1-dithiolates (e.g. dithiocarbamate, [−]S₂CNR₂; xanthate, [−]S₂COR) are known to adopt a wide variety of structural motifs [2]. The diversity in structures is tantalising and an attempt has been made, based on qualitative arguments, to rationalise the appearance of different aggregates and arrays for the binary mercury dithiocarbamates [3]. Difficulties in the field are evident when one considers the appearance of both a monomeric [1, 4] and a dimeric form of Hg(S₂CNEt₂)₂ [1]. In the desire to acquire high quality geometric parameters to enable valence bond sum calculations to be conducted, a new refinement for the monomeric form of Hg(S₂CNEt₂)₂ has been undertaken as the original studies were performed using photographic methods [1, 4].

The centrosymmetric molecule of [Hg(S₂CNEt₂)₂]₂ is illustrated in the figure. The coordination environment is defined by a two S atoms of a chelating ligand and two S atoms derived from bridging dithiocarbamate ligands. The Hg atom exists in a distorted tetrahedral geometry (range of S–Hg–S angles: 70.40(3)°, for the chelate angle, to 144.88(3)°). The key bond distances are *d*(Hg–S1, S2, S3 & S4) of 2.518(1) Å, 2.6408(9) Å, 2.6724(9) Å and 2.422(1) Å, respectively for symmetry operation *i*: −*x*, −*y*, 1−*z*. Finally, there is a transannular Hg⋯S3' contact amounting to 3.1305(9) Å.

Table 1. Data collection and handling.

Crystal:	block yellow, size 0.21 × 0.21 × 0.23 mm
Wavelength:	Mo <i>K</i> _α radiation (0.7107 Å)
μ:	100.16 cm ^{−1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, ω
2θ _{max} :	60°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	13353, 4719
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 3782
<i>N</i> (<i>param</i>) _{refined} :	154
Programs:	teXsan [5], SHELXL-97 [6], ORTEPII [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2a)	4e	−0.0501	0.3182	0.1056	0.039
H(2b)	4e	−0.0874	0.1968	0.1532	0.039
H(3a)	4e	−0.0109	0.1439	0.0260	0.064
H(3b)	4e	0.0999	0.0916	0.1085	0.064
H(3c)	4e	0.1373	0.2129	0.0609	0.064
H(4a)	4e	0.2738	0.3815	0.2429	0.043
H(4b)	4e	0.1771	0.4085	0.1489	0.043
H(5a)	4e	0.1647	0.5743	0.2417	0.057

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(5b)	4e	0.1075	0.4853	0.3073	0.057
H(5c)	4e	0.0108	0.5122	0.2133	0.057
H(7a)	4e	-0.1721	0.4257	0.3376	0.032
H(7b)	4e	-0.0508	0.3737	0.4150	0.032
H(8a)	4e	-0.1338	0.5633	0.4550	0.062
H(8b)	4e	-0.1715	0.4581	0.5171	0.062

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(8c)	4e	-0.2926	0.5102	0.4397	0.062
H(9a)	4e	-0.4177	0.3625	0.3353	0.031
H(9b)	4e	-0.4404	0.2217	0.3576	0.031
H(10a)	4e	-0.4555	0.2448	0.2074	0.066
H(10b)	4e	-0.3215	0.1604	0.2479	0.066
H(10c)	4e	-0.2980	0.3010	0.2258	0.066

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Hg	4e	0.14009(2)	0.07156(1)	0.451596(9)	0.0340(1)	0.02577(8)	0.02347(8)	0.00548(7)	0.00407(6)	0.00909(6)
S(1)	4e	0.0144(1)	0.08427(8)	0.29464(6)	0.0272(5)	0.0206(4)	0.0206(4)	-0.0039(4)	0.0026(4)	0.0011(3)
S(2)	4e	0.2385(1)	0.26060(8)	0.37795(6)	0.0245(5)	0.0244(5)	0.0240(5)	-0.0043(4)	0.0018(4)	0.0026(3)
S(3)	4e	-0.0367(1)	0.19669(8)	0.52920(6)	0.0229(5)	0.0243(4)	0.0159(4)	-0.0008(4)	-0.0025(4)	-0.0021(3)
S(4)	4e	-0.2921(1)	0.05344(8)	0.43974(7)	0.0307(6)	0.0197(5)	0.0322(5)	-0.0044(4)	-0.0104(4)	0.0072(4)
N(1)	4e	0.0936(4)	0.2795(3)	0.2157(2)	0.031(2)	0.026(2)	0.024(2)	-0.003(2)	0.005(2)	0.005(1)
N(2)	4e	-0.2366(3)	0.2793(3)	0.3984(2)	0.022(2)	0.019(1)	0.016(1)	-0.002(1)	0.001(1)	0.004(1)
C(1)	4e	0.1137(4)	0.2155(3)	0.2884(2)	0.021(2)	0.022(2)	0.020(2)	0.002(2)	0.006(2)	0.001(1)
C(2)	4e	-0.0088(5)	0.2437(4)	0.1370(2)	0.033(2)	0.035(2)	0.027(2)	-0.005(2)	0.002(2)	0.005(2)
C(3)	4e	0.0605(5)	0.1661(4)	0.0779(3)	0.045(3)	0.058(3)	0.025(2)	-0.008(2)	0.009(2)	-0.003(2)
C(4)	4e	0.1745(5)	0.3924(4)	0.2102(3)	0.043(3)	0.034(2)	0.031(2)	-0.008(2)	0.011(2)	0.013(2)
C(5)	4e	0.1086(5)	0.5005(4)	0.2463(3)	0.041(3)	0.025(2)	0.044(3)	-0.007(2)	-0.002(2)	0.012(2)
C(6)	4e	-0.1900(4)	0.1865(3)	0.4505(2)	0.021(2)	0.016(2)	0.015(2)	0.004(1)	0.003(1)	0.001(1)
C(7)	4e	-0.1537(4)	0.3928(3)	0.3974(2)	0.025(2)	0.025(2)	0.029(2)	-0.003(2)	0.001(2)	0.009(2)
C(8)	4e	-0.1912(5)	0.4897(4)	0.4576(3)	0.042(3)	0.017(2)	0.063(3)	-0.003(2)	0.007(2)	-0.005(2)
C(9)	4e	-0.3753(4)	0.2796(3)	0.3371(2)	0.022(2)	0.028(2)	0.022(2)	0.001(2)	-0.004(2)	0.009(2)
C(10)	4e	-0.3613(5)	0.2432(4)	0.2465(2)	0.043(3)	0.063(3)	0.020(2)	-0.004(2)	-0.008(2)	0.010(2)

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