Crystal structure of bis(*N*-ethylpyridinium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)mercurate(II), $(C_7H_{10}N)_2[Hg(C_3S_5)_2]$

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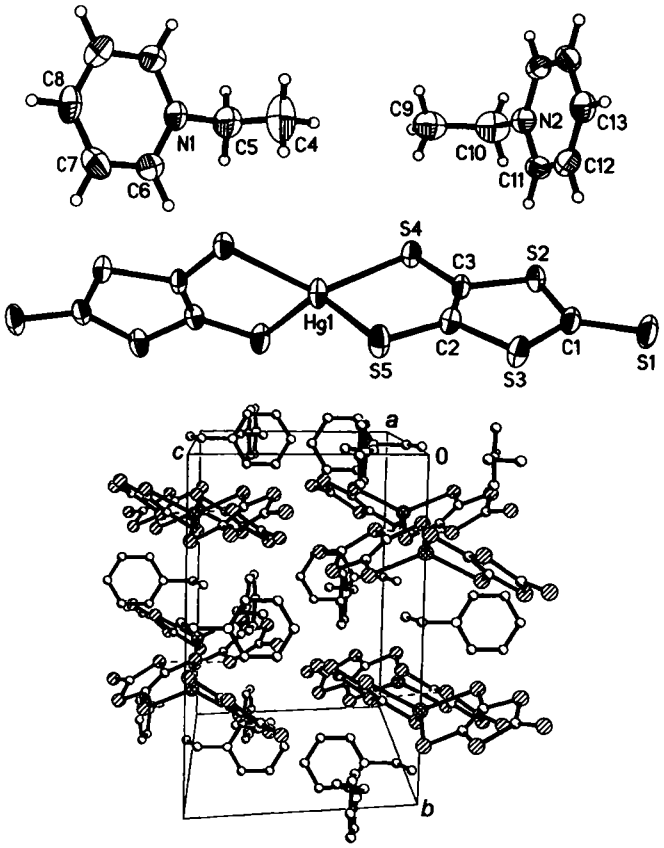

Abstract

$C_{20}H_{20}HgN_2S_{10}$, monoclinic, $C12/m1$ (no. 12), a = 20.286(4) Å, b = 14.598(3) Å, c = 10.007(2) Å, β = 104.964(3)°, V = 2862.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.034, $wR_{ref}(F^2)$ = 0.091, T = 293 K.

Source of material

The title complex was prepared according to the literature procedure [1]. The high optical-quality single crystals used for X-ray structure analysis were obtained by slow evaporation of an acetone solution held at approximately 277 K.

Discussion

Since 1979, metal bis(2-thioxo-1,3-dithiole-dithiolate) (dmit) complexes have attracted increasing attention owing to their potential applications as precursors for electrical conductors and superconductors [2]. Furthermore, many of these complexes have been reported as promising nonlinear optical materials [3,4]. In terms of their solid-state chemistry, these dmit complexes often display intermolecular contacts. It is well-known that the cation in the complexes influences the nature and extent of the S···S intermolecular contacts, and therefore the overall packing. For example, the S···S connectivity in $[Q]_2[Sn(dmit)_3]$ varies with the size of cation Q, i.e. from a three-dimensional arrangement to a chain and may even be absent [5]. Such an impact on the crystal structure has also been found in some Zn dmit complexes [6]. The title compound belongs to the transition metal dithiolene complexes. Amongst the metal-dmit complexes reported in the literature, only two crystal structures of mercury complexes of dmit have been determined to date. The first is bis(5-(1-(pyridin-2-yl)-vinylsulfanyl)-2-thioxo-1,3-dithiole-4-thiolato)mercury(II) [7], the second is bis(tetra-*n*-butylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)mercurate(II) [8]. More recently, the latter compound has been reported to possess fast third-order nonlinear optical response [9]. The title compound was synthesized to study the impact of cation on the intermolecular interactions in salts with the $[Hg(dmit)_2]^{2-}$ anion.

In the crystal structure, there are no distinguishing features from the other known structures of $[Zn(dmit)_2]^{2-}$ and mercury complexes of dmit in terms of ligand behavior and coordination characteristics of the metal ion [6-8]. The Hg—S bond lengths are 2.512(1) Å and 2.533(1) Å, which indicates the single-bond covalent interaction between Hg and S. These bond lengths are shorter than those in [8], showing stronger interactions between the transition metal and the ligand moiety. The S–Hg–S bond angles range from 89.21(4)° to 134.33(6)°, which is far from the typical tetrahedral angle, so that the HgS_4 core adopts a distorted tetrahedral geometry. The dihedral angle of between the two dmit rings is 77.0(3)°. The Hg ion deviates from the dmit best plane by 0.281(1) Å. The $[Hg(dmit)_2]^{2-}$ moiety is situated at the twofold rotation axis and the ethyl carbons, the nitrogen and its opposite ring carbon of the *N*-ethylpyridinium units lie on the mirror plane. There are weak intermolecular S···S contacts with distances of 3.555(2) Å for S2···S2(½–x,½–y,–z). For comparison, there are no short S···S interactions in [8], where Q = tetra-*n*-butylammonium being larger than the cation in the title compound.

Table 1. Data collection and handling.

Crystal:	red plate, size 0.07 × 0.14 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	61.20 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7144, 2609
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2268
$N(param)_{refined}$:	162
Programs:	SHELXTL [10], PLATON [11], ORTEP-3 [12]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(4A)	4*i*	0.7494	½	0.3039	0.209
H(4B)	8*j*	0.7038	0.4463	0.3822	0.209
H(5A)	8*j*	0.6567	0.4461	0.1559	0.115
H(6A)	8*j*	0.5793	0.3649	0.2628	0.076
H(7A)	8*j*	0.4728	0.3632	0.2968	0.087
H(8A)	4*i*	0.419	½	0.3128	0.102
H(9A)	4*i*	0.7816	½	–0.1343	0.141
H(9B)	8*j*	0.7738	0.5537	–0.0036	0.141
H(10A)	8*j*	0.8891	0.4462	–0.0097	0.106
H(11A)	8*j*	0.8902	0.3648	0.1979	0.068
H(12A)	8*j*	0.9123	0.3646	0.4338	0.074
H(13A)	4*i*	0.9221	½	0.5534	0.078

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	8*j*	0.7730(2)	0.1899(4)	0.3256(5)	0.033(2)	0.060(3)	0.050(3)	0.008(2)	0.004(2)	–0.009(2)
C(2)	8*j*	0.6395(2)	0.1859(3)	0.2329(5)	0.035(2)	0.058(3)	0.038(2)	0.006(2)	0.008(2)	0.002(2)
C(3)	8*j*	0.6612(2)	0.2394(3)	0.1412(5)	0.025(2)	0.053(2)	0.044(3)	0.003(2)	0.004(2)	–0.004(2)
C(4)	4*i*	0.7067(6)	½	0.329(1)	0.075(8)	0.19(1)	0.14(1)	0	–0.003(8)	0
C(5)	4*i*	0.6541(5)	½	0.211(1)	0.067(6)	0.082(6)	0.138(9)	0	0.027(7)	0
C(6)	8*j*	0.5567(3)	0.4197(4)	0.2682(6)	0.061(3)	0.056(3)	0.073(4)	0.001(3)	0.018(3)	0.000(3)
C(7)	8*j*	0.4943(3)	0.4185(4)	0.2891(6)	0.064(4)	0.076(4)	0.081(4)	–0.023(3)	0.023(3)	–0.010(3)
C(8)	4*i*	0.4626(4)	½	0.299(1)	0.042(5)	0.107(7)	0.112(8)	0	0.033(5)	0
C(9)	4*i*	0.7926(6)	½	–0.035(1)	0.130(9)	0.082(6)	0.059(5)	0	0.004(6)	0
C(10)	4*i*	0.8698(6)	½	0.0226(9)	0.120(9)	0.098(7)	0.054(5)	0	0.036(6)	0
C(11)	8*j*	0.8943(2)	0.4201(3)	0.2456(6)	0.049(3)	0.048(3)	0.078(4)	–0.002(2)	0.025(3)	–0.009(3)
C(12)	8*j*	0.9075(3)	0.4199(4)	0.3862(6)	0.052(3)	0.062(3)	0.073(4)	0.007(3)	0.018(3)	0.016(3)
C(13)	4*i*	0.9138(4)	½	0.4575(9)	0.050(5)	0.081(6)	0.065(5)	0	0.016(4)	0
Hg(1)	4*g*	½	0.22526(2)	0	0.0293(2)	0.0808(2)	0.0538(2)	0	0.0017(1)	0
N(1)	4*i*	0.5871(3)	½	0.2547(8)	0.041(3)	0.069(4)	0.085(5)	0	0.018(3)	0
N(2)	4*i*	0.8870(3)	½	0.1750(6)	0.049(3)	0.061(4)	0.058(4)	0	0.024(3)	0
S(1)	8*j*	0.85348(7)	0.1759(1)	0.4146(2)	0.0332(7)	0.091(1)	0.079(1)	0.0131(7)	–0.0017(7)	0.0010(9)
S(2)	8*j*	0.74907(6)	0.25517(9)	0.1770(2)	0.0287(6)	0.0650(7)	0.0554(8)	–0.0019(5)	0.0087(6)	0.0004(6)
S(3)	8*j*	0.70454(6)	0.1427(1)	0.3682(1)	0.0372(6)	0.0774(8)	0.0506(7)	0.0089(6)	0.0053(6)	0.0142(6)
S(4)	8*j*	0.61294(6)	0.29203(9)	–0.0086(1)	0.0355(6)	0.0641(7)	0.0451(7)	–0.0012(5)	0.0064(5)	0.0095(6)
S(5)	8*j*	0.55711(6)	0.1533(1)	0.2312(2)	0.0348(6)	0.0900(9)	0.0617(8)	–0.0047(6)	0.0099(6)	0.0243(7)

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