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Refinement of the crystal structure of tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate(II), $[C_{16}H_{36}N]_2[Zn(C_3S_5)_2]$, *at room temperature*

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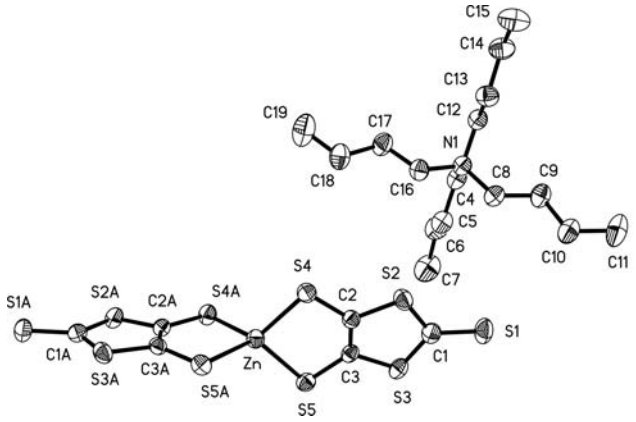

Abstract

$C_{38}H_{72}N_2S_{10}Zn$, monoclinic, *C*12/*c*1 (no. 15), $a = 18.5835(3)$ Å, $b = 8.8382(1)$ Å, $c = 31.4413(4)$ Å, $\beta = 101.967(1)°$, $V = 5051.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.1282$, $T = 295$ K.

Source of material

The synthesis of the title compound involved a modification of literature methods [1]. CS_2 (24 ml) was added to degassed dimethyl formamide (DMF, 48 ml), and the mixture was cooled to 273 K. Sodium (1.45 g) was added to the solution and the mixture was vigorously stirred under cooling until the reaction was completed. Several ml of MeOH were slowly added. To this solution, separate solutions of (i) $ZnCl_2 \cdot 2H_2O$ (2.13 g) dissolved in 25-28% NH_3 (40 ml) and (ii) Bu_4NBr (10.12 g) in water (30 ml) were added consecutively with stirring at room temperature. The mixture was stirred overnight. The product was isolated by filtration, washed with water and MeOH, and then solved in acetone. Single crystals of the title compound used for X-ray structure analysis were obtained by evaporation of acetone from the solution held at room temperature.

Experimental details

All H atoms were placed in geometrically calculated positions and refined using a riding model with $U_{iso}(H) = 1.2\ U_{eq}(C)$.

Discussion

Since their discovery nearly three decades ago [1], metal-bis(2-thioxo-1,3-dithiole-4,5-dithiolate) (dmit) complexes have attracted increasing attention owing to their potential applications as precursors for electrical conductors, superconductors [2] and for their optical and photoelectrical properties [3]. Furthermore, many of these complexes have been reported as promising nonlinear optical materials [4]. Zn complexes of dmit are promising organic optical materials, because the Zn complex anions effectively promote photoelectric properties and second harmonic generation by replacing the iodide in hemicyanine [5]. Furthermore, $[Zn(dmit)_2]^{2-}$ salts have received much attention for their use as stable dmit precursors in the syntheses of other metal-dmit salts [6,7]. The crystal structure of the title compound and related Zn-dmit complexes was previously reported [8,9]. However, the data in both of the published papers have smaller $N_{gt}/N(param)$ ratios and larger R values: $R = 0.057$ at RT [8] and $R = 0.049$ with two disordered tetrabutyl groups at 150 K [9].

The asymmetric unit of the title crystal structure is built up of one half of $[Zn(dmit)_2]^{2-}$ anion and one $(C_{16}H_{36}N)^+$ cation. The $[Zn(dmit)_2]^{2-}$ anion has C_2 symmetry with the Zn(II) ion located on the twofold axis. The dmit ligand shows its typical behaviour as a bidentate ligand and coordinates the Zn^{2+} ion through vicinal exocyclic sulfur atoms of two dmit molecules in a distorted tetrahedral manner. The bond lengths of dmit ligand show typical conjugation character. The C=S double bond (1.666(3) Å) is much longer than that of typical C=S (1.599 Å) [10]. The other C—S bonds span the range of 1.709(3) to 1.74 Å (1.819 Å) and are essentially single bonds with some double-bond character. The C=C bond lengths of the dmit ion are 1.359(3) Å and very close to the corresponding double-bond value of 1.34 Å. The S–Zn–S bond angles range from 95.12(2)° to 123.93(4)°. The Zn—S bond lengths are 2.3391(7) Å and 2.3435(7) Å, respectively.

In the crystal packing of the compound, the intermolecular contacts are consistent with a van der Waals type of packing and the structure displays no sizable intermolecular voids. The packing is formed by channels of cations and anions viewing along [010].

Table 1. Data collection and handling.

Crystal:	purple-red block, size 0.17 × 0.25 × 0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.26 cm^{-1}
Diffractometer, scan mode:	Bruker APEX2 CCD, φ/ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23713, 5785
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3875
$N(param)_{refined}$:	236
Programs:	SHELXTL [11], SIR-97 [12], PLATON [13], ORTEP-III [14], WinGX [15]

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

Atom	Site	x	y	z	U_{iso}
H(4A)	8*f*	0.2502	–0.0905	0.5988	0.077
H(4B)	8*f*	0.1888	–0.0310	0.5608	0.077
H(5A)	8*f*	0.2927	0.1590	0.6129	0.088
H(5B)	8*f*	0.2328	0.2146	0.5732	0.088
H(6A)	8*f*	0.3496	0.0167	0.5674	0.115
H(6B)	8*f*	0.2869	0.0557	0.5274	0.115
H(7A)	8*f*	0.3249	0.3067	0.5309	0.181
H(7B)	8*f*	0.3903	0.2008	0.5259	0.181
H(7C)	8*f*	0.3871	0.2692	0.5715	0.181
H(8A)	8*f*	0.0832	0.1517	0.6297	0.071
H(8B)	8*f*	0.1406	0.2320	0.6075	0.071
H(9A)	8*f*	0.0263	0.0442	0.5644	0.089
H(9B)	8*f*	0.0868	0.1109	0.5415	0.089
H(10A)	8*f*	–0.0078	0.2953	0.5789	0.102
H(10B)	8*f*	0.0490	0.3561	0.5524	0.102
H(11A)	8*f*	–0.0199	0.2504	0.4890	0.180
H(11B)	8*f*	–0.0697	0.3598	0.5096	0.180
H(11C)	8*f*	–0.0758	0.1844	0.5152	0.180

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12A)	8*f*	0.1017	–0.1607	0.5894	0.075
H(12B)	8*f*	0.1625	–0.2189	0.6279	0.075
H(13A)	8*f*	0.0303	–0.0821	0.6380	0.087
H(13B)	8*f*	0.0918	–0.1363	0.6772	0.087
H(14A)	8*f*	0.0152	–0.3336	0.6125	0.107
H(14B)	8*f*	0.0758	–0.3869	0.6520	0.107
H(15A)	8*f*	–0.0017	–0.3129	0.6992	0.169
H(15B)	8*f*	–0.0373	–0.4412	0.6672	0.169
H(15C)	8*f*	–0.0629	–0.2731	0.6584	0.169
H(16A)	8*f*	0.2306	0.1436	0.6655	0.073
H(16B)	8*f*	0.1713	0.0575	0.6847	0.073
H(17A)	8*f*	0.2987	–0.0828	0.6691	0.093
H(17B)	8*f*	0.2408	–0.1597	0.6923	0.093
H(18A)	8*f*	0.3308	0.0933	0.7266	0.103
H(18B)	8*f*	0.2681	0.0324	0.7487	0.103
H(19A)	8*f*	0.3307	–0.1974	0.7593	0.186
H(19B)	8*f*	0.3735	–0.0629	0.7856	0.186
H(19C)	8*f*	0.3958	–0.1196	0.7429	0.186

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*f*	0.2732(2)	0.5603(3)	0.60654(9)	0.074(2)	0.063(2)	0.059(2)	0.012(1)	0.008(1)	–0.011(1)
C(2)	8*f*	0.3583(1)	0.5255(3)	0.68382(8)	0.055(1)	0.053(1)	0.049(1)	0.000(1)	0.010(1)	–0.003(1)
C(3)	8*f*	0.3958(1)	0.6208(3)	0.66238(8)	0.059(2)	0.051(1)	0.046(1)	0.011(1)	0.010(1)	0.001(1)
C(4)	8*f*	0.2177(2)	–0.0058(3)	0.58931(8)	0.074(2)	0.076(2)	0.046(1)	0.020(2)	0.019(1)	–0.004(1)
C(5)	8*f*	0.2642(2)	0.1302(4)	0.58463(9)	0.076(2)	0.088(2)	0.062(2)	0.015(2)	0.030(2)	–0.000(2)
C(6)	8*f*	0.3154(2)	0.0950(4)	0.5545(1)	0.105(3)	0.117(3)	0.079(2)	0.028(2)	0.052(2)	0.008(2)
C(7)	8*f*	0.3583(2)	0.2301(6)	0.5448(1)	0.105(3)	0.160(4)	0.113(3)	0.016(3)	0.060(3)	0.037(3)
C(8)	8*f*	0.1119(2)	0.1402(3)	0.60749(8)	0.067(2)	0.058(2)	0.057(2)	0.012(1)	0.019(1)	–0.001(1)
C(9)	8*f*	0.0595(2)	0.1288(4)	0.56414(9)	0.077(2)	0.083(2)	0.062(2)	0.012(2)	0.012(2)	0.003(2)
C(10)	8*f*	0.0156(2)	0.2735(4)	0.5547(1)	0.075(2)	0.100(2)	0.082(2)	0.018(2)	0.017(2)	0.020(2)
C(11)	8*f*	–0.0428(2)	0.2664(6)	0.5134(1)	0.091(3)	0.171(4)	0.090(3)	0.035(3)	0.002(2)	0.029(3)
C(12)	8*f*	0.1257(2)	–0.1407(3)	0.61930(8)	0.076(2)	0.057(2)	0.051(1)	0.008(1)	0.007(1)	–0.009(1)
C(13)	8*f*	0.0691(2)	–0.1560(3)	0.6471(1)	0.088(2)	0.063(2)	0.067(2)	–0.004(2)	0.020(2)	–0.009(1)
C(14)	8*f*	0.0366(2)	–0.3141(4)	0.6428(1)	0.104(3)	0.066(2)	0.100(2)	0.002(2)	0.028(2)	–0.000(2)
C(15)	8*f*	–0.0216(2)	–0.3374(4)	0.6693(2)	0.130(3)	0.081(3)	0.139(4)	–0.019(2)	0.052(3)	0.000(2)
C(16)	8*f*	0.2069(2)	0.0463(3)	0.66633(8)	0.069(2)	0.069(2)	0.046(1)	0.003(1)	0.013(1)	–0.009(1)
C(17)	8*f*	0.2638(2)	–0.0644(4)	0.6876(1)	0.090(2)	0.084(2)	0.057(2)	0.010(2)	0.007(2)	0.003(2)
C(18)	8*f*	0.3043(2)	0.0030(5)	0.7320(1)	0.082(2)	0.107(3)	0.065(2)	0.008(2)	0.009(2)	–0.005(2)
C(19)	8*f*	0.3554(3)	–0.1031(5)	0.7571(1)	0.127(3)	0.145(4)	0.088(3)	0.045(3)	–0.004(3)	–0.012(3)
N(1)	8*f*	0.1652(1)	0.0097(2)	0.62061(6)	0.066(1)	0.058(1)	0.044(1)	0.007(1)	0.014(1)	–0.0060(9)
S(1)	8*f*	0.20507(5)	0.5517(1)	0.56281(3)	0.0921(6)	0.0997(7)	0.0660(5)	0.0189(5)	–0.0143(4)	–0.0155(4)
S(2)	8*f*	0.27151(4)	0.47272(9)	0.65480(2)	0.0690(5)	0.0741(5)	0.0590(4)	–0.0112(4)	0.0058(3)	–0.0077(3)
S(3)	8*f*	0.35305(4)	0.66049(9)	0.60874(2)	0.0752(5)	0.0734(5)	0.0503(4)	0.0149(4)	0.0129(3)	0.0096(3)
S(4)	8*f*	0.38694(4)	0.45501(8)	0.73598(2)	0.0690(4)	0.0695(4)	0.0507(4)	–0.0131(3)	0.0112(3)	0.0071(3)
S(5)	8*f*	0.48045(4)	0.70596(8)	0.68279(2)	0.0589(4)	0.0617(4)	0.0592(4)	–0.0005(3)	0.0187(3)	0.0093(3)
Zn	4*e*	½	0.58134(5)	¾	0.0569(3)	0.0593(3)	0.0496(2)	0	0.0122(2)	0

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