Crystal structure of bis(tetra-*n*-butylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)mercurate(II), $[(C_4H_9)_4N]_2[Hg(C_3S_5)_2]$

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Received February 2, 2005, accepted and available on-line March 1, 2005; CCDC no. 1267/1476

Abstract

$C_{38}H_{72}HgN_2S_{10}$, monoclinic, $P1c1$ (no. 7), $a = 10.151(1)$ Å, $b = 28.659(4)$ Å, $c = 9.286(2)$ Å, $\beta = 110.18(1)^\circ$, $V = 2535.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.073$, $wR_{\text{ref}}(F^2) = 0.194$, $T = 293$ K.

Source of material

Two methods were used to prepare $[(C_4H_9)_4N]_2[Hg(C_3S_5)_2]$ (abbreviated as BMDT) crystals. The first is a modification according to literature method [1]. To degassed dimethyl formamide (DMF, 48 ml), CS_2 (24 ml) was added and the mixture was cooled to 0 °C. Sodium (1.45 g) was added to the solution and the mixture was vigorously stirred with cooling until the reaction was com-

pleted. An adequate volume of MeOH was slowly added. To this solution, separate solutions of $HgCl_2$ (4.24 g) dissolved in acetone (10 ml) and Bu_4NBr (10.12 g) in water (30 ml) were added consecutively with stirring at room temperature. The mixture was stirred overnight, then the product was isolated by filtration and washed with water and MeOH, to afford BMDT crystals. In the second, a very simple method, BMDT was obtained by the metathetical reaction of $[(C_4H_9)_4N]_2[Zn(C_3S_5)_2]$ (9.44 g) and $HgCl_2$ (2.72 g) in acetone (55 ml). The dark red single crystals used for X-ray structure analysis were obtained by slow evaporation of an acetone solution.

Experimental details

The C14 atom was split into two positions, which were treated as a disorder model and their fractional site occupancies were refined to 0.78(9)/0.22. Other C atoms only tend to disorder. The little high R values are attributed to the poor quality of the crystal. The absolute structure is confirmed by a Flack parameter [2] of $-0.01(2)$.

Discussion

Over the past two decades, an enormous amount of research has gone into the synthesis and characterization of 1,3-dithiole-2-thione-4,5-dithiolate (dmit) ligand complexes and related selenium and oxygen substituted isologs. They are generally used as important building blocks for organic, organometallic and coordination complex electrical conductors and superconductors [3]. Recently, these complexes have been reported as possessing nonlinear optical properties [4–6].

The title complex, $[(C_4H_9)_4N]_2[Hg(C_3S_5)_2]$, is also a novel nonlinear optical crystal. In this structure, the Hg^{2+} is coordinated with the four S (dmit) atoms forming a tetrahedral environment. The Hg—S bond lengths range from 2.525(7) Å to 2.540(6) Å with an average value of 2.530 Å. It is nearly the same as the sum of single-bond covalent radii of Hg—S, i.e. 2.51 Å [7], which indicates that a strong single-bond covalent interaction is formed between Hg and S. The S—Hg—S bond angles ranging from 88.5(2)° to 128.4(3)° (average value of 110.2°) are far from the typical tetrahedral angle. The most striking features are the structure characteristics of Hg-dmit complexes: possessing an extended electronically delocalized core comprising the central Hg, four S and the C=C units. The S atoms compose part of the delocalized core. The inclusion of Hg improve the delocalization. This delocalization will greatly enhance the hyperpolarizability and the nonlinear susceptibility, and lead to the large third order nonlinear optical (TONLO) properties. These TONLO properties were investigated with femtosecond optical Kerr effect at 800 nm wavelength and found to exhibit efficient TONLO susceptibility and second hyperpolarizability, and the TONLO response is very fast.

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Table 1. Data collection and handling.

Crystal:	dark red prism, size 0.17 × 0.31 × 0.32 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	34.74 cm ⁻¹
Diffraction, scan mode:	Bruker P4, ω
$2\theta_{\max}$:	52°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6177, 5937
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2473
$N(\text{param})_{\text{refined}}$:	460
Programs:	SIR92 [8], SHELXTL [9], PLATON [10]

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(18C)	2a		-0.7050	0.9186	0.2397	0.282
H(19A)	2a		-0.3409	0.8184	0.2032	0.081
H(19B)	2a		-0.2061	0.8051	0.1670	0.081
H(20A)	2a		-0.3287	0.8109	-0.0929	0.121
H(20B)	2a		-0.4639	0.8267	-0.0598	0.121
H(21A)	2a		-0.3351	0.7376	0.0338	0.131
H(21B)	2a		-0.4762	0.7533	0.0529	0.131
H(22A)	2a		-0.5273	0.7045	-0.1584	0.210
H(22B)	2a		-0.4432	0.7369	-0.2319	0.210
H(22C)	2a		-0.5837	0.7545	-0.2158	0.210
H(23A)	2a		0.7699	0.5639	0.5317	0.099
H(23B)	2a		0.8666	0.6052	0.5202	0.099
H(24A)	2a		0.8277	0.5747	0.7894	0.147
H(24B)	2a		0.9080	0.6212	0.7835	0.147
H(25A)	2a		0.9938	0.5340	0.6978	0.142
H(25B)	2a		1.0801	0.5806	0.7210	0.142
H(26A)	2a		1.1770	0.5337	0.9340	0.259
H(26B)	2a		1.0321	0.5307	0.9587	0.259
H(26C)	2a		1.1134	0.5782	0.9836	0.259
H(27A)	2a		0.5075	0.6374	0.5923	0.100
H(27B)	2a		0.6393	0.6188	0.7243	0.100
H(28A)	2a		0.4585	0.5609	0.4848	0.140
H(28B)	2a		0.5956	0.5416	0.6114	0.140
H(29A)	2a		0.5034	0.5706	0.8070	0.179
H(29B)	2a		0.3624	0.5828	0.6750	0.179
H(30A)	2a		0.3412	0.5117	0.7847	0.348
H(30B)	2a		0.4677	0.4918	0.7438	0.348
H(30C)	2a		0.3265	0.5041	0.6127	0.348
H(31A)	2a		0.6699	0.6282	0.3033	0.110
H(31B)	2a		0.5752	0.5892	0.3344	0.110
H(32A)	2a		0.5007	0.6843	0.2963	0.111
H(32B)	2a		0.4058	0.6454	0.3297	0.111
H(33A)	2a		0.4848	0.6467	0.0651	0.114
H(33B)	2a		0.3913	0.6076	0.0985	0.114
H(34A)	2a		0.2497	0.6601	-0.0778	0.170
H(34B)	2a		0.3069	0.7013	0.0382	0.170
H(34C)	2a		0.2136	0.6624	0.0731	0.170
H(35A)	2a		0.7779	0.6775	0.6800	0.108
H(35B)	2a		0.6441	0.6970	0.5528	0.108
H(36A)	2a		0.9027	0.6793	0.5070	0.135
H(36B)	2a		0.7680	0.6972	0.3761	0.135
H(37A)	2a		0.9089	0.7623	0.4748	0.178
H(37B)	2a		0.7752	0.7669	0.5224	0.178
H(38A)	2a		0.9728	0.7810	0.7367	0.397
H(38B)	2a		1.0366	0.7327	0.7162	0.397
H(38C)	2a		0.9029	0.7346	0.7639	0.397

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(7A)	2a		-0.2157	0.8763	-0.0633	0.100
H(7B)	2a		-0.1306	0.9143	0.0512	0.100
H(8A)	2a		-0.0488	0.8207	0.0677	0.094
H(8B)	2a		0.0383	0.8603	0.1748	0.094
H(9A)	2a		0.0768	0.8955	-0.0319	0.115
H(9B)	2a		-0.0156	0.8576	-0.1430	0.115
H(10A)	2a		0.2218	0.8407	-0.0848	0.195
H(10B)	2a		0.1498	0.8006	-0.0242	0.195
H(10C)	2a		0.2416	0.8379	0.0901	0.195
H(11A)	2a		-0.2123	0.8777	0.3686	0.089
H(11B)	2a		-0.0815	0.8620	0.3300	0.089
H(12A)	2a		-0.1645	0.9553	0.3062	0.153
H(12B)	2a		-0.0189	0.9359	0.3073	0.153
H(13A)	2a		-0.1232	0.9279	0.5486	0.214
H(13B)	2a		0.0110	0.9029	0.5502	0.214
C(14)	2a	0.22(9)	0.05(1)	0.963(6)	0.66(2)	0.14(8)
H(14A)	2a	0.22	0.0133	0.9594	0.7417	0.208
H(14B)	2a	0.22	0.0406	0.9947	0.6262	0.208
H(14C)	2a	0.22	0.1445	0.9531	0.6910	0.208
C(14')	2a	0.78	0.008(6)	0.983(1)	0.55(1)	0.20(3)
H(14D)	2a	0.78	0.0528	0.9896	0.6522	0.294
H(14E)	2a	0.78	-0.0723	1.0027	0.5032	0.294
H(14F)	2a	0.78	0.0731	0.9884	0.4923	0.294
H(15A)	2a		-0.3322	0.9406	0.0866	0.105
H(15B)	2a		-0.4285	0.9024	-0.0191	0.105
H(16A)	2a		-0.4078	0.9207	0.2858	0.114
H(16B)	2a		-0.4935	0.8784	0.1918	0.114
H(17A)	2a		-0.5577	0.9718	0.0912	0.102
H(17B)	2a		-0.6500	0.9282	0.0183	0.102
H(18A)	2a		-0.7487	0.9687	0.1727	0.282
H(18B)	2a		-0.6110	0.9616	0.3145	0.282

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(1)	2a	0.2124(2)	0.74900(4)	0.3974(3)	0.0693(4)	0.0864(5)	0.0983(6)	0.0015(5)	0.0161(4)	-0.0114(7)
C(1)	2a	-0.127(3)	0.588(1)	0.168(4)	0.08(2)	0.09(2)	0.09(2)	0.00(2)	0.03(2)	-0.00(2)
C(2)	2a	-0.017(2)	0.6730(8)	0.213(3)	0.06(1)	0.07(2)	0.10(2)	0.02(1)	0.04(2)	-0.02(2)
C(3)	2a	0.064(2)	0.6460(7)	0.326(3)	0.05(1)	0.07(1)	0.08(2)	0.01(1)	0.03(1)	0.01(1)
C(4)	2a	0.351(2)	0.8447(7)	0.556(3)	0.07(1)	0.06(1)	0.06(2)	-0.01(1)	0.01(1)	0.01(1)
C(5)	2a	0.455(2)	0.8260(9)	0.505(3)	0.06(1)	0.09(2)	0.06(2)	-0.02(1)	-0.01(1)	0.00(2)
C(6)	2a	0.560(3)	0.9069(8)	0.646(3)	0.10(2)	0.06(2)	0.08(2)	0.01(1)	-0.00(2)	0.04(2)
S(1)	2a	-0.236(1)	0.5448(3)	0.100(1)	0.119(7)	0.092(6)	0.17(1)	-0.028(5)	0.038(7)	-0.032(7)
S(2)	2a	-0.1599(6)	0.6440(2)	0.0818(8)	0.082(4)	0.082(4)	0.082(5)	0.001(3)	0.019(4)	-0.014(4)
S(3)	2a	0.0197(7)	0.5887(2)	0.3241(8)	0.097(4)	0.070(4)	0.103(5)	0.016(3)	0.046(4)	0.014(4)
S(4)	2a	-0.0044(6)	0.7313(2)	0.1688(8)	0.086(4)	0.070(4)	0.084(5)	0.008(3)	0.000(4)	0.002(4)
S(5)	2a	0.2066(6)	0.6656(2)	0.4872(8)	0.072(4)	0.093(4)	0.083(5)	0.011(3)	0.015(4)	0.013(4)
S(6)	2a	0.1882(6)	0.8226(2)	0.5361(8)	0.061(3)	0.093(4)	0.101(5)	0.008(3)	0.019(4)	-0.022(4)
S(7)	2a	0.4486(6)	0.7775(3)	0.4000(9)	0.069(4)	0.104(5)	0.108(6)	0.008(3)	0.033(4)	-0.012(5)
S(8)	2a	0.3914(6)	0.8998(2)	0.6473(9)	0.077(4)	0.076(4)	0.106(6)	0.009(3)	0.019(4)	-0.002(4)
S(9)	2a	0.6078(6)	0.8604(2)	0.5587(9)	0.065(4)	0.083(4)	0.100(6)	0.003(3)	0.027(4)	0.015(4)
S(10)	2a	0.6575(9)	0.9542(3)	0.711(1)	0.115(6)	0.080(5)	0.132(8)	-0.010(5)	0.015(6)	0.030(6)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(1)	2a	-0.249(2)	0.8736(7)	0.144(3)	0.08(1)	0.07(1)	0.09(2)	-0.01(1)	0.03(1)	0.02(1)
C(7)	2a	-0.157(3)	0.8816(7)	0.043(3)	0.11(2)	0.03(1)	0.10(2)	-0.02(1)	0.02(2)	-0.00(1)
C(8)	2a	-0.025(2)	0.8536(7)	0.072(3)	0.09(2)	0.06(1)	0.09(2)	0.01(1)	0.04(2)	-0.01(1)
C(9)	2a	0.049(2)	0.8630(9)	-0.040(3)	0.09(2)	0.13(2)	0.08(2)	0.02(2)	0.03(2)	0.03(2)
C(10)	2a	0.177(3)	0.8328(9)	-0.012(4)	0.11(2)	0.12(2)	0.18(4)	-0.00(2)	0.07(2)	-0.04(2)
C(11)	2a	-0.158(2)	0.8843(8)	0.303(3)	0.06(1)	0.09(2)	0.05(2)	0.01(1)	-0.01(1)	-0.03(1)
C(12)	2a	-0.095(3)	0.931(1)	0.347(3)	0.09(2)	0.17(3)	0.12(3)	0.00(2)	0.02(2)	-0.05(3)
C(13)	2a	-0.038(4)	0.9325(9)	0.525(4)	0.20(4)	0.08(2)	0.22(5)	0.02(2)	0.03(4)	-0.08(3)
C(15)	2a	-0.371(2)	0.9097(7)	0.086(3)	0.05(1)	0.07(2)	0.12(2)	0.00(1)	-0.00(2)	0.04(2)
C(16)	2a	-0.462(2)	0.9099(8)	0.183(3)	0.08(2)	0.08(2)	0.10(2)	0.00(1)	0.01(2)	-0.03(2)
C(17)	2a	-0.589(2)	0.9416(8)	0.114(3)	0.07(2)	0.07(2)	0.09(2)	0.02(1)	-0.01(2)	0.01(2)
C(18)	2a	-0.671(3)	0.948(1)	0.220(4)	0.11(2)	0.25(4)	0.20(4)	0.08(3)	0.05(3)	-0.05(4)
C(19)	2a	-0.291(2)	0.8240(7)	0.133(3)	0.08(2)	0.05(1)	0.09(2)	-0.00(1)	0.05(2)	0.01(1)
C(20)	2a	-0.380(3)	0.8077(8)	-0.022(3)	0.11(2)	0.08(2)	0.12(3)	-0.01(2)	0.05(2)	0.00(2)
C(21)	2a	-0.420(3)	0.7558(7)	-0.012(3)	0.08(2)	0.08(2)	0.15(3)	-0.01(1)	0.02(2)	-0.01(2)
C(22)	2a	-0.501(4)	0.7361(9)	-0.169(3)	0.20(3)	0.10(2)	0.13(3)	-0.05(2)	0.07(3)	-0.04(2)
N(2)	2a	0.675(2)	0.6281(6)	0.525(2)	0.06(1)	0.08(1)	0.07(2)	0.01(1)	0.04(1)	-0.02(1)
C(23)	2a	0.803(3)	0.5948(8)	0.571(3)	0.09(2)	0.07(2)	0.10(2)	0.01(1)	0.05(2)	0.02(2)
C(24)	2a	0.884(3)	0.591(1)	0.738(4)	0.06(2)	0.16(3)	0.13(3)	0.04(2)	0.03(2)	0.01(2)
C(25)	2a	1.018(3)	0.562(1)	0.758(4)	0.12(2)	0.12(2)	0.11(3)	-0.01(2)	0.02(2)	0.00(2)
C(26)	2a	1.092(3)	0.550(1)	0.924(4)	0.12(3)	0.21(4)	0.21(5)	-0.01(3)	0.08(3)	0.04(4)
C(27)	2a	0.585(3)	0.6154(9)	0.616(3)	0.09(2)	0.09(2)	0.07(2)	0.01(2)	0.03(2)	0.00(2)
C(28)	2a	0.522(3)	0.565(1)	0.589(4)	0.09(2)	0.14(3)	0.14(3)	0.01(2)	0.07(2)	0.06(2)
C(29)	2a	0.441(3)	0.561(1)	0.706(5)	0.12(3)	0.12(2)	0.19(4)	0.04(2)	0.04(3)	0.07(3)
C(30)	2a	0.390(4)	0.513(1)	0.712(6)	0.20(4)	0.26(5)	0.22(5)	0.00(4)	0.06(4)	0.13(5)
C(31)	2a	0.603(3)	0.6217(8)	0.354(3)	0.11(2)	0.08(2)	0.09(2)	-0.00(2)	0.03(2)	-0.01(2)
C(32)	2a	0.475(2)	0.6516(8)	0.282(3)	0.08(2)	0.09(2)	0.10(2)	0.01(1)	0.01(2)	-0.04(2)
C(33)	2a	0.414(2)	0.6406(8)	0.111(3)	0.10(2)	0.09(2)	0.09(2)	-0.02(2)	0.02(2)	-0.01(2)
C(34)	2a	0.284(2)	0.6686(9)	0.029(3)	0.11(2)	0.12(2)	0.12(2)	0.03(2)	0.04(2)	0.01(2)
C(35)	2a	0.725(2)	0.6771(8)	0.571(3)	0.08(2)	0.06(2)	0.12(2)	0.01(1)	0.02(2)	-0.03(2)
C(36)	2a	0.818(3)	0.6980(8)	0.486(3)	0.12(2)	0.11(2)	0.13(3)	-0.01(2)	0.06(2)	0.02(2)
C(37)	2a	0.859(3)	0.7486(9)	0.537(5)	0.11(2)	0.14(3)	0.22(5)	-0.06(2)	0.09(3)	-0.06(3)
C(38)	2a	0.951(5)	0.749(1)	0.704(6)	0.19(5)	0.27(6)	0.29(8)	-0.10(4)	0.02(5)	-0.09(5)

Acknowledgments. This work is supported by an '863' grant of the National Advanced Materials Committee of China (NAMCC, no. 2002AA313070) and grants of National Natural Science Foundation of China (NNSFC, nos. 60476020, 50272037, 60377016 and 50323006).

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