Crystal structure of trichloro(1′-isopropyl-8-methoxy-3′,3′-dimethyl-6-nitro-1′,3′-dihydrospiro[chromene-2,2′-indole])antimony(III), $SbCl_3(C_{22}H_{24}N_2O_4)$

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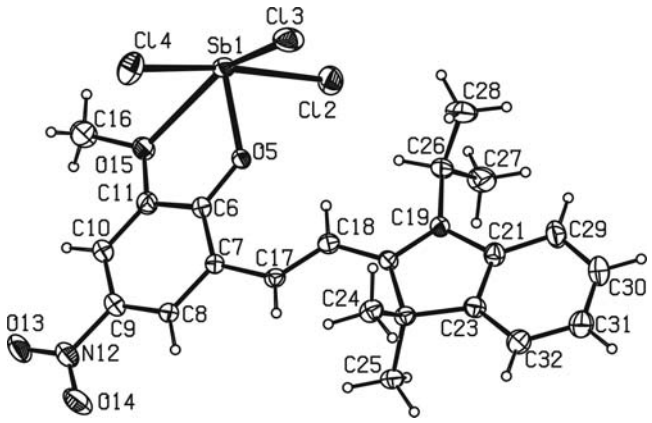

Abstract

$C_{22}H_{24}Cl_3N_2O_4Sb$, monoclinic, $P2_1/n$ (no. 14), a = 9.2391(1) Å, b = 16.6888(3) Å, c = 17.7113(4) Å, β = 101.6743(6)°, V = 2674.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.136, T = 293 K.

Source of material

The 1′-isopropyl-8-methoxy-3′,3′-dimethyl-6-nitro-1′,3′-dihydrospiro[chromene-2,2′-indole] (spiropyran, SP) was prepared from 2,3,3-trimethylindolenine and 3-nitro-5-methoxysalicylaldehyde as described elswhere [1]. The addition of antimony trichloride (0.125 g) to the SP (0.035 g) in 10 % acetone solution of IXAN (3 ml) solution shifted the equilibrium to the open merocyanine form due to the formation of yellow colored complex with the metal ion. After thirty days at room temperature yellow crystals were obtained.

Discussion

Since the discovery of the photochromic reactions of spiropyrans in 1952 by Fisher and Hirshberg [2,3] this class of molecules have been extensively applied in the field of optical filters and optical recording. The performance of such systems is based on the reversible conversion between the spiropyran form and a highly colored merocyanine form upon UV irradiation. This reversible cleavage of a C/O bond occurs in the some spiropyrans also upon complexation with metal ions resulting in the increase in their photostability [4]. The metal-ion complexing ability of the spiropyrane is enhanced by the interaction between the phenolate anion of its merocyanine form and a metal ion and can be influenced by the substituents [5-7]. Up to the present time, the existence of merocyanine form of spiropyrans has only been assumed in solutions, for example, illustrated by the basicity of the donor oxygen atom [8,9]. However no X-ray crystallographic investigations of open forms of spiropyrans were presented to date.

The molecular structure of the title compound indicates that the open forms is induced by the stabilization of the oxo anion by the bond formed between oxygen atom (O5) of the chromene and the antimony atom (Sb1), the corresponding distance being 2.017Å. The molecule is not planar as attested by the central (C7–C17–C18–C19) torsion angle value of 173.1°. A quasi co-planarity is observed between NO_2 group and phenyl ring (C6-C11), the corresponding torsion angle value being 178°, while the methyl group C16 is out of the ring plan as indicated by the torsion angle C6–C11–O15–C16 which value is 168°. The antimony is in a deformed square-pyramide, the oxygen atom O5 occupying the apical position, bond values between Sb1 and Cl2, Cl3, Cl4 are: 2.646, 2.399 and 2.5 Å, respectively. The Atom O15 is located in the region of the 4th basis-plane position, its distance to Sb1 is 2.676 Å.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.2 × 0.2 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.60 cm^{-1}
Diffractometer, scan mode:	Kappa CDD, φ
$2\theta_{max}$:	57.44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20254, 6652
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4256
$N(param)_{refined}$:	304
Programs:	SHELXS-97, SHELXL-97 [10], ORTEP-III [11], PLATON [12], SIR97 [13]

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

Atom	Site	x	y	z	U_{iso}
H(81)	4*e*	0.5241	0.2136	0.5170	0.050
H(101)	4*e*	0.2985	0.3542	0.6370	0.070
H(161)	4*e*	–0.0821	0.3861	0.6172	0.080
H(162)	4*e*	0.0600	0.4237	0.5960	0.080
H(163)	4*e*	0.0743	0.3652	0.6663	0.080
H(171)	4*e*	0.4023	0.1241	0.4184	0.060
H(181)	4*e*	0.1016	0.1016	0.4026	0.060
H(241)	4*e*	0.4663	0.0138	0.2464	0.070
H(242)	4*e*	0.4569	0.0845	0.3035	0.070
H(243)	4*e*	0.3208	0.0642	0.2378	0.070
H(251)	4*e*	0.5352	–0.0737	0.3801	0.070
H(252)	4*e*	0.4212	–0.0665	0.4344	0.070

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(253)	4*e*	0.5140	0.0084	0.4196	0.070
H(261)	4*e*	–0.0574	0.0337	0.3687	0.060
H(271)	4*e*	–0.1796	–0.0628	0.4150	0.080
H(272)	4*e*	–0.0208	–0.0999	0.4260	0.080
H(273)	4*e*	–0.1447	–0.1271	0.3566	0.080
H(281)	4*e*	–0.1139	0.0210	0.2275	0.080

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(282)	4*e*	–0.2423	0.0341	0.2721	0.080
H(283)	4*e*	–0.2093	–0.0520	0.2445	0.080
H(291)	4*e*	–0.0523	–0.1627	0.2524	0.070
H(301)	4*e*	0.0660	–0.2595	0.1912	0.110
H(311)	4*e*	0.3129	–0.2538	0.1945	0.110
H(321)	4*e*	0.4493	–0.1429	0.2449	0.070

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}
Sb(1)	4*e*	–0.15781(5)	0.26922(3)	0.43471(3)	0.0417(3)	0.0582(4)	0.0634(4)	0.0088(2)	0.0093(2)	–0.0084(2)
Cl(2)	4*e*	–0.2490(2)	0.1234(1)	0.4608(2)	0.064(1)	0.072(1)	0.128(2)	–0.016(1)	0.039(1)	–0.011(1)
Cl(3)	4*e*	–0.1983(3)	0.2315(2)	0.3014(1)	0.079(2)	0.111(2)	0.064(1)	0.024(1)	–0.008(1)	–0.013(1)
Cl(4)	4*e*	–0.0405(3)	0.3954(1)	0.4003(2)	0.120(2)	0.062(1)	0.106(2)	–0.000(1)	0.038(2)	0.008(1)
O(5)	4*e*	0.0384(5)	0.2121(3)	0.4501(3)	0.035(2)	0.048(2)	0.064(3)	0.001(2)	0.005(2)	–0.020(2)
C(6)	4*e*	0.1663(7)	0.2345(3)	0.4932(4)	0.044(3)	0.043(3)	0.046(3)	0.000(2)	0.005(2)	–0.006(2)
C(7)	4*e*	0.2992(6)	0.2021(3)	0.4813(3)	0.040(3)	0.038(2)	0.035(3)	–0.001(2)	0.008(2)	0.001(2)
C(8)	4*e*	0.4340(7)	0.2323(3)	0.5256(4)	0.039(3)	0.040(3)	0.057(4)	0.000(2)	0.004(3)	0.000(2)
C(9)	4*e*	0.4299(8)	0.2887(5)	0.5806(4)	0.048(4)	0.057(4)	0.057(4)	–0.010(3)	0.002(3)	–0.008(3)
C(10)	4*e*	0.2981(8)	0.3174(4)	0.5976(4)	0.051(3)	0.054(3)	0.060(4)	–0.004(3)	0.004(3)	–0.009(3)
C(11)	4*e*	0.1676(7)	0.2892(4)	0.5538(4)	0.046(3)	0.048(3)	0.060(4)	–0.004(3)	0.014(3)	–0.003(3)
N(12)	4*e*	0.5693(7)	0.3206(4)	0.6249(4)	0.058(4)	0.072(4)	0.066(4)	–0.014(3)	–0.001(3)	–0.008(3)
O(13)	4*e*	0.5656(7)	0.3696(4)	0.6754(4)	0.071(3)	0.098(4)	0.090(4)	–0.014(3)	–0.006(3)	–0.045(4)
O(14)	4*e*	0.6851(7)	0.2958(5)	0.6077(4)	0.050(3)	0.123(5)	0.094(5)	–0.016(4)	0.000(3)	–0.028(4)
O(15)	4*e*	0.0303(5)	0.3091(3)	0.5649(3)	0.047(2)	0.066(3)	0.065(3)	–0.001(2)	0.013(2)	–0.022(2)
C(16)	4*e*	0.020(1)	0.3768(7)	0.6154(7)	0.065(5)	0.104(7)	0.101(7)	0.007(5)	0.020(5)	–0.044(6)
C(17)	4*e*	0.3101(6)	0.1349(3)	0.4294(3)	0.038(3)	0.039(3)	0.051(3)	0.002(2)	0.012(2)	0.008(2)
C(18)	4*e*	0.1956(7)	0.0872(4)	0.3962(4)	0.040(3)	0.051(3)	0.052(3)	0.003(3)	0.015(2)	–0.003(3)
C(19)	4*e*	0.2080(6)	0.0175(3)	0.3526(3)	0.038(3)	0.043(3)	0.041(3)	–0.002(2)	0.006(2)	–0.002(2)
N(20)	4*e*	0.0921(5)	–0.0295(3)	0.3267(3)	0.041(2)	0.042(2)	0.052(3)	–0.003(2)	0.009(2)	–0.003(2)
C(21)	4*e*	0.1348(7)	–0.0972(4)	0.2856(4)	0.054(3)	0.048(3)	0.055(4)	–0.005(3)	0.017(3)	–0.004(3)
C(22)	4*e*	0.2831(7)	–0.0904(4)	0.2862(4)	0.046(3)	0.057(3)	0.043(3)	0.003(3)	0.008(2)	–0.006(3)
C(23)	4*e*	0.3448(6)	–0.0161(4)	0.3282(4)	0.040(3)	0.044(3)	0.048(3)	0.003(2)	0.011(2)	0.003(2)
C(24)	4*e*	0.4026(8)	0.0420(4)	0.2739(4)	0.056(4)	0.052(3)	0.061(4)	0.002(3)	0.019(3)	0.009(3)
C(25)	4*e*	0.4649(7)	–0.0391(4)	0.3969(4)	0.045(3)	0.058(4)	0.061(4)	0.010(3)	0.004(3)	–0.003(3)
C(26)	4*e*	–0.0602(7)	–0.0159(4)	0.3389(5)	0.034(3)	0.060(4)	0.082(5)	0.001(3)	0.012(3)	–0.013(3)
C(27)	4*e*	–0.106(1)	–0.0827(6)	0.3888(7)	0.053(4)	0.081(5)	0.115(8)	–0.006(4)	0.027(4)	0.013(5)
C(28)	4*e*	–0.166(1)	–0.0019(7)	0.2640(6)	0.052(4)	0.097(6)	0.100(7)	0.006(4)	–0.002(4)	0.028(6)
C(29)	4*e*	0.048(1)	–0.1593(5)	0.2516(5)	0.068(5)	0.062(4)	0.083(5)	–0.013(4)	0.011(4)	–0.029(4)
C(30)	4*e*	0.120(1)	–0.2167(6)	0.2161(6)	0.092(7)	0.064(5)	0.086(6)	–0.010(4)	0.006(5)	–0.028(4)
C(31)	4*e*	0.268(1)	–0.2125(6)	0.2163(6)	0.084(6)	0.074(5)	0.073(6)	0.008(5)	0.010(4)	–0.021(4)
C(32)	4*e*	0.3506(9)	–0.1479(5)	0.2485(5)	0.061(4)	0.067(4)	0.066(4)	0.004(3)	0.018(3)	–0.011(4)

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