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Organotin thiosemicarbazates. Crystal structure of triphenyltin 1-amino-4-(2-hydroxyphenyl)-2,3-diazapenta-(*E*)-1,(*E*)-3-dienyl-1-thiolate

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Abstract

Triphenyltin 1-amino-4-(2-hydroxyphenyl)-2,3-diazapenta-(*E*)-1,(*E*)-3-dienyl-1-thiolate, $[(C_6H_5)_3Sn\text{-}SC(\underline{N}^1H_2{=}\underline{N}^2\text{-}\underline{N}^3{=}C(CH_3)(C_6H_4\text{-}2\text{-}OH)]$, crystallizes in the triclinic space group $P\bar{1}$ with a 13.368(4), b 10.494(7), c 9.370(2) Å, α 96.16(4) β 96.57(2), γ 101.80(4)°; $Z = 2$. The crystal structure was determined from 3745 $I > 3\sigma(I)$ Mo-K_α reflections and refined to $R = 0.034$. The tin atom is in a distorted tetrahedral environment in which the $\underline{N}^2$ atom of the ligand is positioned at one face of the polyhedron at a distance of 2.872(4) Å from the metal atom. The Sn–S distance is 2.440(2) Å, and the S–C, C–N^2, N^2–N^3, N^3–C bond lengths are 1.741(4), 1.289(6), 1.412(5) and 1.283(6) Å, respectively. The otherwise planar thiosemicarbazate group is twisted (C–N^2–N^3–C torsional angle 43.9(5)°) in an apparent attempt to bring its $\underline{N}^3$ atom in a position to chelate. The free hemihydrated thiosemicarbazone acid (monoclinic, $C2/c$, a 14.385(2), b 14.733(2), c 10.855(3) Å, β 114.84(1)°; $Z = 8$ and $R = 0.036$ for 1464 observed reflections) $[\underline{N}^1H_2C({=}S)\underline{N}^2H\text{-}\underline{N}^3{=}C(CH_3)(C_6H_4\text{-}2\text{-}OH)] \cdot 0.5H_2O$, is a flat molecule (S–C 1.690(3), C–N^2 1.345(3), N^2–N^3 1.382(3), N^3–C 1.290(3) Å; C–N^2–N^3–C torsional angle 5.4(3)°). The phenolic proton in the thiosemicarbazate and in the uncomplexed thiosemicarbazone is hydrogen-bonded to the $\underline{N}^3$ atom.

Introduction

Carbonyl compounds ($R_2C{=}O$) condense with thiosemicarbazide $[NH_2C(S)\text{-}NHNH_2]$ to yield tautomeric [1–3] thiosemicarbazones, in which there can be

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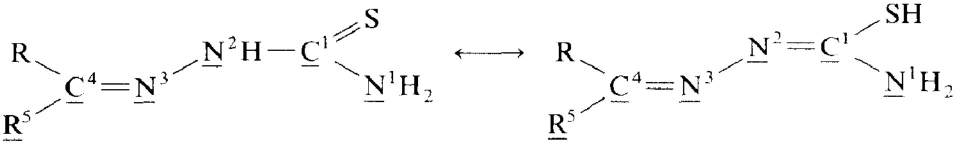
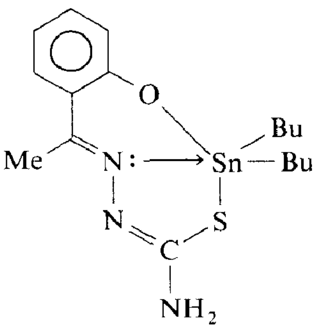
extended electron-delocalization when R is an aromatic group [4]:



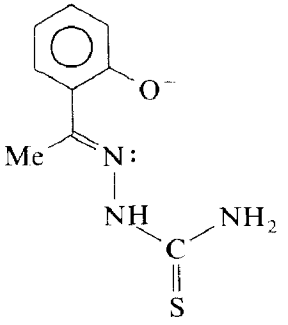
thione thiol

Thiosemicarbazones coordinate to metals through the sulfur or imino nitrogen in the neutral thione form, but through the negatively-charged sulfur end if deprotonated [5]. Many thiosemicarbazones are known to possess medicinal properties [3,5], and their transition metal complexes are fungitoxic [6,7]. Acetone thiosemicarbazone has commanded much study: the ligand exhibits both mono- and bi-dentate behavior towards transition [3] and organotransition metal [8] compounds. Relatively little information has been reported on main group metal thiosemicarbazates; for tin in particular, some inorganic tin(II) [9,10] and tin(IV) [11,12], and organotin(IV) [13–16] derivatives have been described, and the chelating ability of the thiosemicarbazate group has been documented in the thiosemicarbazone derivative of chlorotin(II) pyruvate [10].

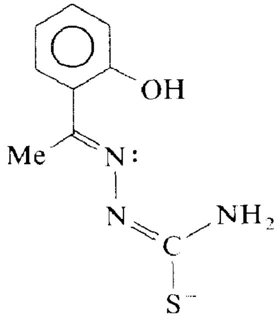
The dibasic thiosemicarbazone derivative of 2-hydroxyacetophenone has been condensed with di-n-butyltin oxide to give a monomeric compound (I) [15]. In its derivatives with triorganotin hydroxides, the ligand may be expected to bond to tin through either the phenoxide (II) or the mercaptide (III) ends, depending on whether the thione or thiol form dominates. We have chosen the triphenyltin unit to bind with this ligand for this first structural study of an organotin thiosemicarbazate.



(I)



(II)



(III)

Experimental

Heating of a solution of 2-hydroxyacetophenone and thiosemicarbazide in ethanol yielded 2-hydroxyacetophenonethiosemicarbazone (cf. ref 17). Yellow crystals of the organotin derivative, m.p. 143–144° C, were obtained by slow evaporation of an ethanol solution containing triphenyltin hydroxide and the thiosemicarbazone in a 1/1 molar ratio. Anal.: Found: C, 58.05; H, 4.44; N, 7.39. $C_{27}H_{25}N_3OSSn$ calcd.:

C, 57.98; H, 4.68; N, 7.51%. A crystal measuring 0.38 × 0.32 × 0.20 mm was used in the study. Intensity data were collected at 295 K on a CAD4 four-circle diffractometer using a $2\theta/\theta$ scan mode to $2\theta_{\max} = 50°$ (monochromatic Mo-K_α radiation, λ 0.71069 Å). The 3745 observed reflections with $I > 3\sigma(I)$ were used in the full matrix least-squares refinement after Gaussian absorption correction and solution of the structure by vector methods, with the non-H atom thermal parameters refined anisotropically. H-atoms were placed at estimated positions. The XTAL program system on a Perkin–Elmer 3240 computer [18] was used in the calculations. Atomic coordinates are listed in Tables 1 and 2 and the molecular structure is depicted in Fig. 1.

For comparison, the structure of the free ligand, 2-hydroxyacetophenone thiosemicarbazone, as the hemihydrate, m.p. 180–181° C, was also determined; 1464 $I > 3\sigma(I)$ reflections were refined to $R = 0.036$. The 2-[1-(2-hydroxyphenyl)ethylidene]hydrazinecarbothioamide molecule is shown in Fig. 2, along with bond

Table 1

Atomic coordinates for triphenyltin 1-amino-4-(2-hydroxyphenyl)-2,3-diazapenta-1,3-dienylthiolate

Atom	*x*	*y*	*z*
Sn	0.22193(3)	0.04789(3)	0.41755(3)
S(1)	0.3736(1)	0.0440(1)	0.2962(1)
C(2)	0.4585(4)	0.1527(4)	0.4317(5)
N(2)	0.5591(3)	0.1748(5)	0.4167(5)
N(3)	0.4205(3)	0.2113(4)	0.5336(4)
N(4)	0.4966(3)	0.2867(4)	0.6444(4)
C(5)	0.4852(3)	0.4016(4)	0.6911(5)
C(50)	0.4037(4)	0.4641(5)	0.6239(6)
C(51)	0.5596(4)	0.4762(5)	0.8148(5)
C(52)	0.6320(4)	0.4191(6)	0.8908(5)
O(52)	0.6398(3)	0.2951(4)	0.8531(4)
C(53)	0.6992(4)	0.4938(7)	1.0075(6)
C(54)	0.6970(5)	0.6194(7)	1.0508(6)
C(55)	0.6272(6)	0.6768(6)	0.9782(7)
C(56)	0.5589(4)	0.6067(5)	0.8619(5)
C(11)	0.1124(4)	−0.0937(4)	0.2626(5)
C(12)	0.0254(4)	−0.0605(5)	0.1943(6)
C(13)	−0.0441(4)	−0.1509(6)	0.0927(6)
C(14)	−0.0271(5)	−0.2735(6)	0.0576(6)
C(15)	0.0575(5)	−0.3081(5)	0.1234(6)
C(16)	0.1277(4)	−0.2178(5)	0.2245(6)
C(21)	0.1786(3)	0.2312(4)	0.4291(4)
C(22)	0.1990(4)	0.3143(5)	0.3271(5)
C(23)	0.1774(4)	0.4392(5)	0.3415(6)
C(24)	0.1317(5)	0.4777(5)	0.4573(7)
C(25)	0.1093(4)	0.3952(5)	0.5603(6)
C(26)	0.1321(4)	0.2733(5)	0.5446(5)
C(31)	0.2287(4)	−0.0310(4)	0.6157(4)
C(32)	0.1540(5)	−0.1447(5)	0.6266(6)
C(33)	0.1524(6)	−0.2018(6)	0.7507(7)
C(34)	0.2256(7)	−0.1488(7)	0.8687(7)
C(35)	0.2983(6)	−0.0400(6)	0.8629(6)
C(36)	0.2983(5)	0.0210(5)	0.7367(5)

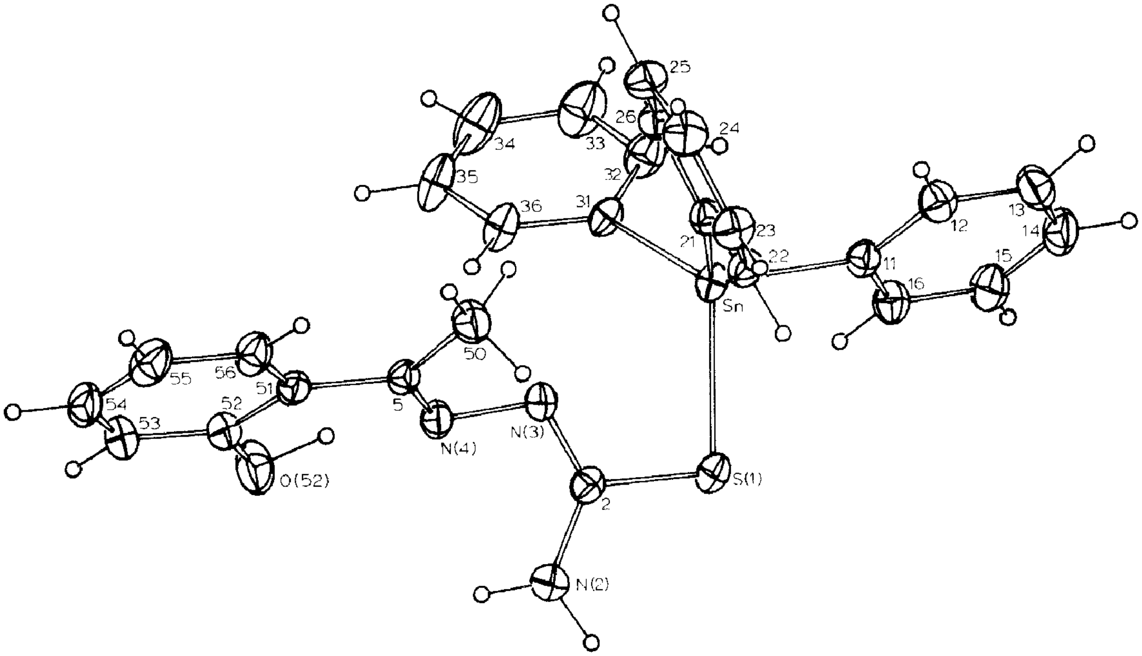


Fig. 1. Selected bond distances and angles in triphenyltin 1-amino-4-(2-hydroxyphenyl)-2,3-diazapenta-1,3-dienyl-1-thiolate: Sn–S(1) 2.440(2), Sn–C(11) 2.150(4), Sn–C(21) 2.115(5), Sn–C(31) 2.113(4) Å; S(1)–Sn–C(11) 97.6(1), S(1)–Sn–C(21) 113.3(1), S(1)–Sn–C(31) 113.6(1), C(11)–Sn–C(21) 109.7(2), C(11)–Sn–C(31) 107.0(2), C(21)–Sn–C(31) 114.2(2)°. Thermal ellipsoids of the non-hydrogen atoms here and elsewhere are at the 20% probability level; hydrogen atoms have arbitrary radii of 0.1 Å. Crystallographic non-hydrogen atom labeling is shown.

Table 2

Atomic coordinates for 2-[1-(2-hydroxyphenyl)ethylidene]hydrazinecarbothioamide

Atom	*x*	*y*	*z*
S(1)	0.21209(5)	0.38617(4)	−0.03976(7)
C(2)	0.1622(2)	0.3797(1)	0.0758(2)
N(2)	0.1195(2)	0.4505(1)	0.1057(2)
N(3)	0.1645(1)	0.3001(1)	0.1377(2)
N(4)	0.1422(1)	0.2947(1)	0.2495(2)
C(5)	0.1382(1)	0.2150(1)	0.2963(2)
C(50)	0.1479(3)	0.1292(2)	0.2284(4)
C(51)	0.1244(2)	0.2089(1)	0.4214(2)
C(52)	0.1066(2)	0.2854(1)	0.4877(2)
O(52)	0.1068(1)	0.3711(1)	0.4431(2)
C(53)	0.0911(2)	0.2762(2)	0.6043(2)
C(54)	0.0924(2)	0.1929(2)	0.6597(3)
C(55)	0.1103(2)	0.1170(2)	0.5998(3)
C(56)	0.1251(2)	0.1247(2)	0.4827(3)
O	0	0.4823(2)	0.7500
H(2A)	0.086(2)	0.446(2)	0.159(2)
H(2B)	0.114(2)	0.499(2)	0.061(2)
H(3)	0.192(2)	0.257(2)	0.115(2)
H(50A)	0.116(2)	0.135(2)	0.129(4)
H(50B)	0.211(3)	0.113(2)	0.258(3)
H(50C)	0.108(2)	0.083(2)	0.243(3)
H(52)	0.116(2)	0.370(2)	0.377(3)
H(53)	0.079(2)	0.327(2)	0.645(2)
H(54)	0.083(2)	0.189(2)	0.741(3)
H(55)	0.114(2)	0.061(2)	0.635(3)
H(56)	0.138(2)	0.070(2)	0.441(3)
H	0.050(2)	0.447(2)	0.800(3)

dimensions; non-H atomic coordinates are given in Table 2. H atoms were refined in (x, y, z).

Discussion *

The structure of triphenyltin 1-amino-4-(2-hydroxyphenyl)-2,3-diazapenta-1,3-dienyl-1-thiolate, depicted in Fig. 1, confirms the transformation of the thiosemicarbazone free acid from the thioamide to the thiolimine form upon condensation with the organotin hydroxide. The 2,3-diazapentadienyl-1-thiol fragment has the following bond lengths: S–C 1.741(4), C–N^2 1.289(6), N^2–N^3 1.412(5), N^3–C 1.283(6) Å, compared to the distances of 1.690(3), 1.345(3), 1.382(3) and 1.290(3) Å, respectively, in the uncomplexed hemihydrate ligand. The tin atom is essentially four-coordinate, and is bonded to the sulfur atom (Sn–S 2.440(2) Å) of the ligand whose $\underline{N}^2$ atom approaches the tin atom at a distance of 2.872(4) Å. This tin–nitrogen distance is too long to be regarded as a bond, however, and the N–Sn–S bite angle is too small for the nitrogen and sulfur atoms to occupy the

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* In the discussion the atom numbering is that shown in the introduction above, not that in Figs. 1 and 2.

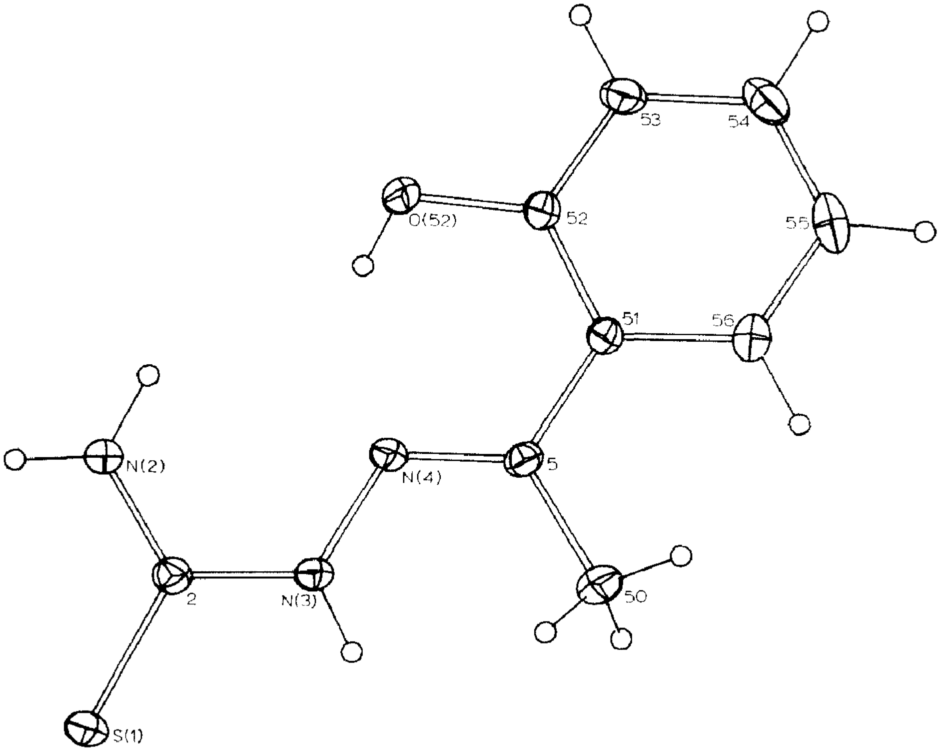

Fig. 2(a). Plot of 2-[1-(2-hydroxyphenyl)ethylidene]hydrazinecarbothioamide hemihydrate (water molecule not shown): S(1)–C(2) 1.690(3), C(2)–N(2) 1.317(3), C(2)–N(3) 1.345(3), N(3)–N(4) 1.382(3), N(4)–C(5) 1.290(3), C(5)–C(50) 1.499(4), C(5)–C(51) 1.471(3), C(51)–C(52) 1.406(3), C(51)–C(56) 1.401(3), C(52)–O(52) 1.353(3) C(52)–C(53) 1.381(4), C(53)–C(54) 1.364(4), C(54)–C(55) 1.372(5), C(55)–C(56) 1.378(5) Å; S(1)–C(2)-N(2) 121.7(2), S(1)–C(2)–N(3) 119.4(2), N(2)–C(2)–N(3) 119.0(2), C(2)–N(3)–N(4) 121.4(2), N(3)–N(4)–C(5) 117.5(2), N(4)–C(5)–C(50) 123.1(3), N(4)–C(5)–C(51) 117.9(2), C(50)–C(5)–C(51) 119.0(2), C(5)–C(51)–C(52) 123.0(2), C(5)–C(51)–C(56) 120.6(2), C(52)–C(51)–C(56) 116.4(2), C(51)–C(52)–O(52) 122.7(2), C(51)–C(52)–C(53) 120.9(2), O(52)–C(52)–C(53) 116.4(2), C(52)–C(53)–C(54) 121.0(3), C(53)–C(54)–C(55) 119.6(3), C(51)–C(56)–C(55) 121.8(3)°.

axial–equatorial positions of a trigonal bipyramid. The tin–carbon distances are normal, and the three phenyl groups subtend angles of 107.0(2), 109.7(2) and 114.2(2)° at the tin atom. The overall geometry is distorted tetrahedral, a geometry also adopted by other triorganotin mercaptides such as $(C_6H_5)_3SnS$–C(=E)-NR_2 (E = O, S) [19,20] and $(C_6H_5)_3SnS$–C(=S)-OR [21,22]. There are no examples of four-membered 'chelate' Sn–S–C–N rings among triorganotin compounds; the tin–nitrogen distance in four-coordinated tricyclohexyltin mercaptobenzthiazole is 3.055(8) Å [25]. Five-membered chelate rings with nitrogen and sulfur donor ends are less strained, but for triphenyltin 2-aminophenylsulfide, the tin–nitrogen distance * exceeds 4 Å [26], whereas it is 2.893(3) Å in the 2-dimethylaminophenylsulfide [27] analogue.

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* The tin–nitrogen bond in di-n-butyltin bis-5-nitropyridyl-2-sulfide is 2.77 Å [23]; a four-membered Sn–S–C–N chelate ring is allowed in the six-coordinated, skew-trapezoidal bipyramidal [24] polytope.

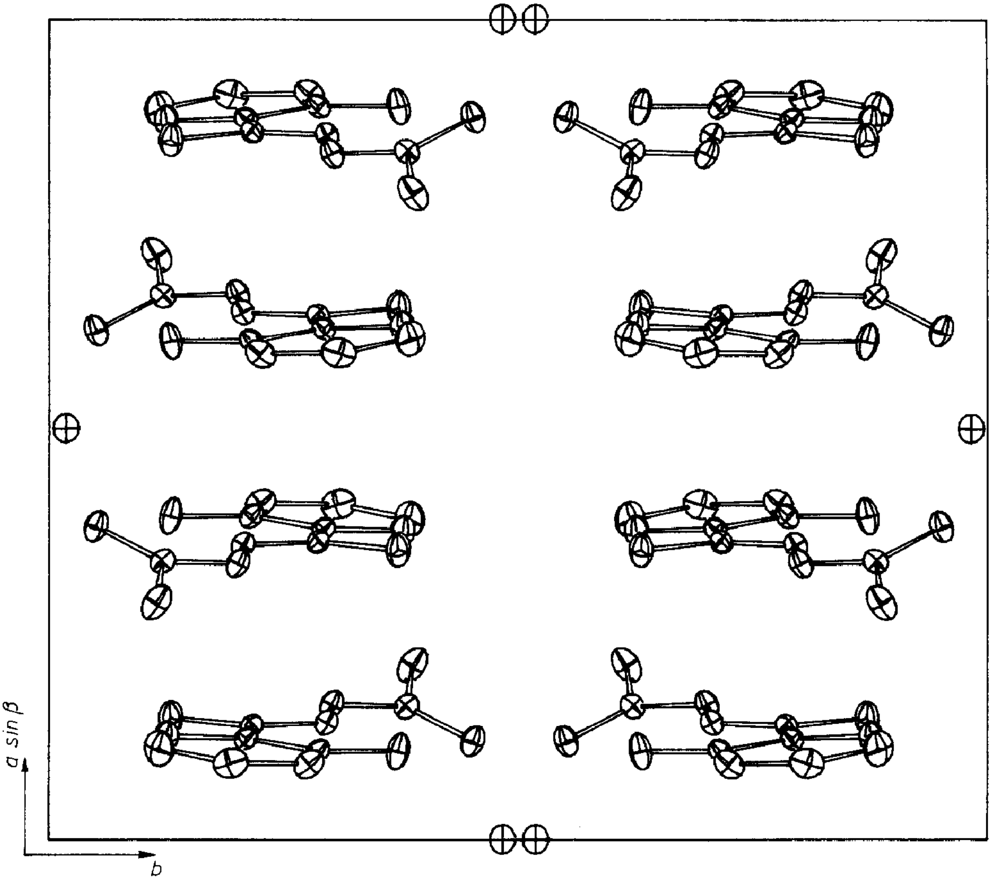

Fig. 2(b)(i). The unit cell, plotted down *c*, showing the parallel packing of the molecules and the hydrogen bonding about the water molecule.

The structure of the title compound is better understood when it is contrasted with the structure of the free acid hemihydrate (Fig. 2) (the first crystal structure reported of a potentially tridentate free ligand of this type). The thiosemicarbazate fragment in the organotin compound is twisted ($C-N^2-N^3-C$ torsional angle 43.9(5)°), whereas this fragment is relatively flat in the uncomplexed thiosemicarbazone hemihydrate (torsional angle 5.4(3)°). The planarity of the organic molecule suggests dominance of conjugative over steric effects, and this is supported by the observation of a shorter nitrogen–nitrogen (1.382(3) Å) bond, whose carbon substituents are in a *trans* disposition. This bond is lengthened (1.412(5) Å) in the tin complex. The carbon–sulfur bond (1.690(3) Å) in the ligand is similarly lengthened (1.741(4) Å) in the organotin complex.

The most conspicuous feature in the lattice array of the ligand is the (quasi-)parallel packing of the ligand planes (Fig. 2), related by inversion centers and two-fold axes with spacings (ca. 3.6–3.8 Å), suggestive of charge-transfer interactions. In addition, significant hydrogen-bonding interactions are found in the lattice. The intramolecular H(52) ··· N(4) contact is 1.92(3) Å; Intermolecular hydrogen bonds are also present; the water molecule, located on a two-fold axis, contacts a pair of symmetry-related sulfur atoms (H ··· S 2.42(3) Å), with a four-coordinate oxygen environment resulting from O · · · H contacts to symmetry-related amine hydrogen atom H(2A) at 2.15(3) Å; the other amine hydrogen atom H(2B) interacts with more distant phenolic oxygen atoms at 2.29(3) Å. In the tin derivative, none of the ligand hydrogen atoms approach neighboring sulfur, nitrogen or oxygen atoms at distances less than 2.6 Å.

The atomic coordinates of 2-[1-(2-hydroxyphenyl)ethylidene]hydrazinecarbothioamide are listed in Table 2.

Acknowledgement

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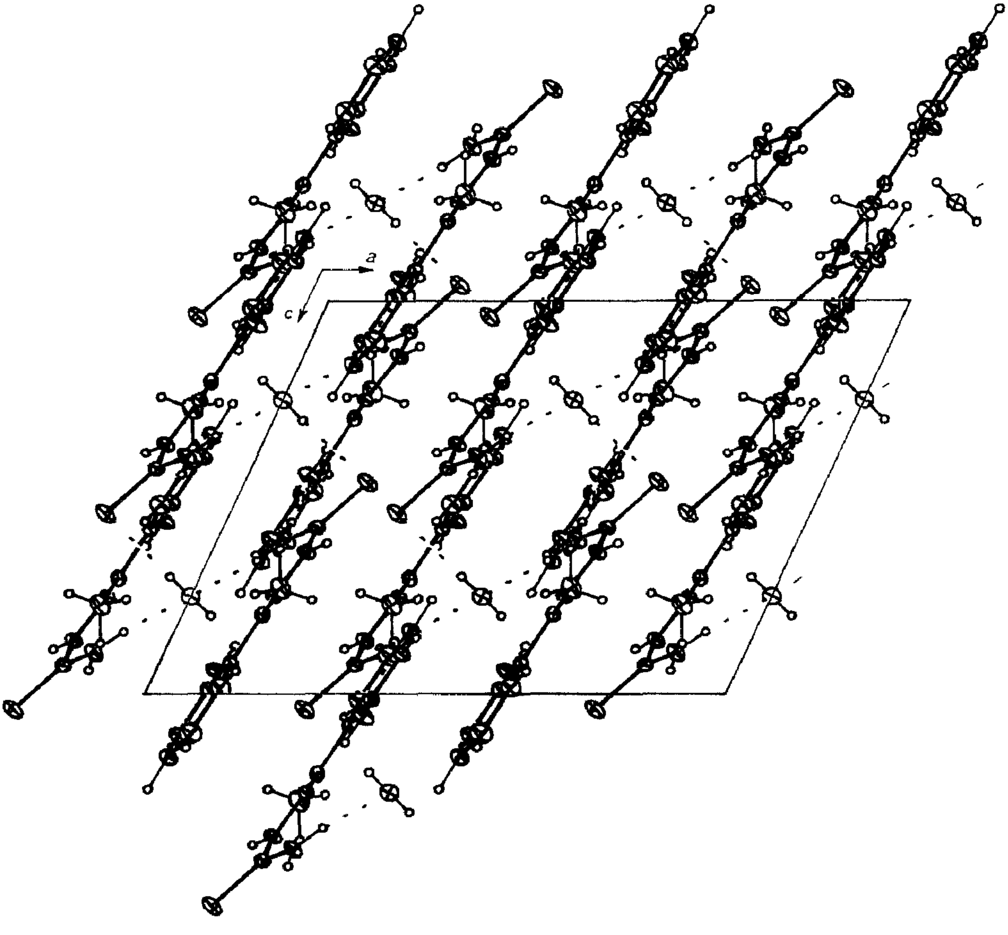

Fig. 2(b)(ii). The unit cell, plotted down *b*, showing the parallel packing of the molecules, and the hydrogen bonding about the water molecule.

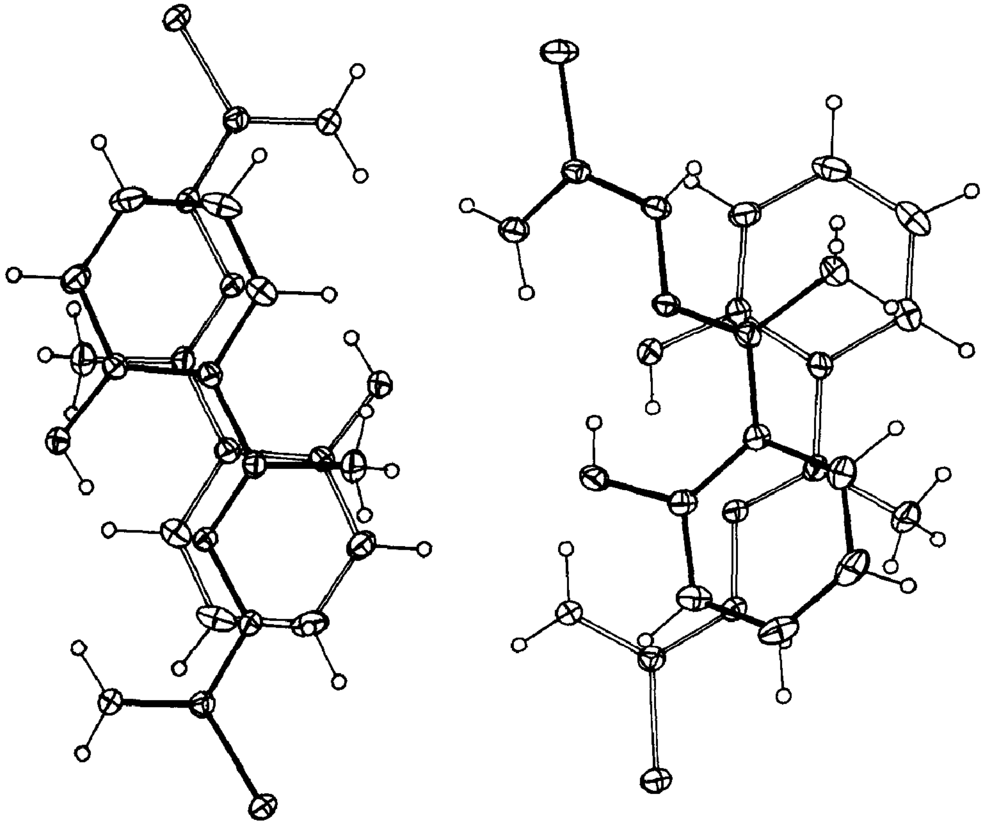

Fig. 2(c). Successive molecular 'charge-transfer' overlaps, projected normal to the ligand plane; related molecules are generated by $(0.5-x,\ 0.5-y,\ 1-z)$ and $(\bar{x},\ y,\ 0.5-z)$, respectively.

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