Synthesis, X-ray Characterisation and Studies of the New Ionic Complex [Bis(pyridin-2-yl) disulfide] Triiodide, Obtained by Oxidation of 2-Mercaptopyridine with I_2 − Implications in the Mechanism of Action of Antithyroid Drugs

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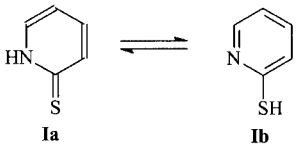
The reaction of 2-mercaptopyridine (C_5H_5NS or PYSH) with diiodine in a molar ratio of 1:2 in dichloromethane led to the oxidation and dimerization of the ligand and formation of $[(PYS–PYSH)^+\cdot I_3^-]$. The compound was characterised by elemental analysis, DTA-TG, FT-Raman, FT-IR, UV/Vis and ^1H NMR spectroscopy. The crystal structure of the complex has been determined by X-ray diffraction at 293(2) K. The compound $[(C_5H_4NS–SNC_5H_5)I_3]$ is monoclinic with the space group $P2_1$ and a = 8.230(2) Å, b = 35.708(7) Å, c = 11.369(2) Å, β = 91.86(3)° and Z = 8. The results are discussed in relation to the mechanism of action of antithyroid drugs. The easy oxidation of PYSH by I_2 to form the monocationic disulfide complex $[(PYS–PYSH)^+\cdot I_3^-]$ is similar to the case of the antithyroid drug methimazole (MMI) and may indicate that PYSH might also possess antithyroid properties similar to those of MMI.

Introduction

Because of the effective antithyroid activity of thioamides, their interaction with diiodine has been thoroughly studied in recent years.[1−3] These thioamides include the antithyroid drugs methimazole (MMI) and 6-*n*-propyl-2-thiouracil (PTU)[1−3] and studies have aimed at drawing conclusions about their mechanism of action. It has been proposed that both MMI and PTU display both irreversible and reversible inhibition depending on the relative concentrations of the drug and iodine.[4] Nakataka et.al.[5] reported that the inhibition of tyrosil iodination by antithyroid drugs should be different in the cases of PTU and MMI; du Mont et.al.[6a] and Berry et al.[6b,6c] proposed that drugs such as PTU should, rather, interfere either with the formation of the thyroid peroxidase (TPO)−iodonium complex[4] or inhibit the activity of the iodothyronine deiodinase type I (ID-1), an enzyme containing selenocysteine in its active site which is responsible for the monodeiodination of the T4 prohormone to the T3 hormone.[6] Isaia et al.[3] have shown that MMI is readily oxidised by the TPO system to form MMI disulfide [bis(1-methylimidazol-2-yl disulfide], while activated iodine is simultaneously reduced to the iodide anion. We also recently demonstrated that PTU forms weak charge transfer complexes (CT) with diiodine.[2c] Thus, although it has been concluded[1−4] that thioamides inhibit the formation of thyroid hormones by preventing the incorporation of oxidised iodides into tyrosine, the precise mechanism of this trapping is still a matter for further investigation.

The perturbation of the I−I bond by heterocycles such as 2-mercaptopyridine (PYSH; Figure 1) can lead to novel complexes containing polyiodides.[7] With the aim of studying the interfering mechanism of thioamides in TPO-catalysed iodination reactions of tyrosil residues of thyroglobuline, we report here the isolation and study of the oxidation product of an I_2 complex with 2-mercaptopyridine of formula $[(PYS−PYSH)^+\cdot I_3^-]$ (**1**).



Ia **Ib**

Figure 1. Tautomeric forms of 2-mercaptopyridine (**I**) (thione **Ia**, thiol **Ib**)

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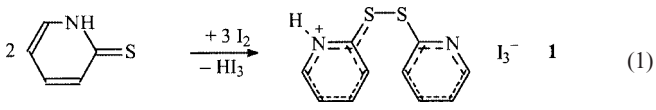
Results and Discussion

PYSH reacts with I_2 in a molar ratio of 1:2 oxidizing the ligand to disulfide [Equation (1)].



(1)

A thermal analysis in a flow of nitrogen showed that the compound decomposes in two stages. The TGA and DTA data curves show that the first stage of its decomposition (90−160 °C) is connected with an endothermic effect and involves a 42% mass loss consistent with the evolution of I_2 (calculated mass loss 42%). The second stage of its decomposition (204−234 °C) is connected with an endothermic effect and involves a 58% mass loss of (PYS−PYSH)I (calculated mass loss 58%). This indicates that I_3^- might be asymmetric of the $I^-\cdots I_2$ type[7b] which results in the easy breaking of this bond (see crystal structure).

The conductimetric titration of PYSH with I_2 in acetonitrile is shown in Figure 2.

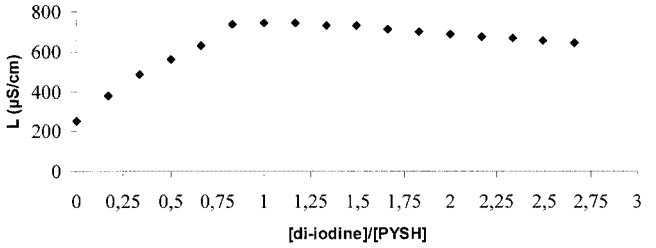


Figure 2. Conductivity titrations of PYSH (10^{-2} M) with I_2 in acetonitrile (T = 293 K)

At a zero I_2 concentration, the solution of PYSH in acetonitrile shows nonzero conductivity. Addition of I_2, increases the conductivity of the solution, with a maximum value attained at a molar ratio $[I_2]/[PYSH] = 0.83$, leading to a plateau in accordance with Equation (1).

Spectroscopy

(A) UV/Vis Spectroscopy

The UV/Vis spectra of dichloromethane solutions with constant concentrations of PYSH (10^{-4} M) and increasing quantities of diiodine are given in Figure 3. They exhibit one distinct absorption band at 495−505 nm which can be assigned to the "blue shift" band of I_2[2,8] occurring at 504 nm in free I_2 in CH_2Cl_2.[8e,8g]

The absorption band at 367 nm can be assigned to the I_3^- species (λ_{max} = 360 nm in free I_3^-).[9] I_3^- has one more absorption band at 295 nm, coinciding with the intra-ligand transition ($\pi^*\leftarrow\pi$) appearing at 292 nm in free PYSH.

No isosbestic points were observed, indicating that more than two species are present in solution (Figure 3). In the spectrophotometric titration curves of I_2/PYSH, the presence of the band at 367 nm, attributable to the I_3^- moiety, can be observed at low I_2/ligand ratios in accord with Equation (1) (see conductivity measurements).

(B) Vibrational Spectroscopy

The IR spectrum of the complex shows distinct vibrational bands at 1579 and 1452 cm^{-1} which can be assigned to ν(CN) vibrations (thioamide I and II bands) and at 1108 and 959 cm^{-1} attributable to the ν(CS) vibrations (thioamide III and IV bands). The new band appearing at 158 cm^{-1} in the FIR spectrum of the complex has been assigned to the ν(I−I) stretching vibration mode.[2a,2b,10]

Table 1 gives structural and Raman spectroscopic data of the complex and other complexes containing I_3^- in the region of 300−50 cm^{-1}.

Diiodine vapour gives a strong band at 216 cm^{-1} [ν(I−I)] which appears at 180 cm^{-1} in the solid state.[7b,11] This

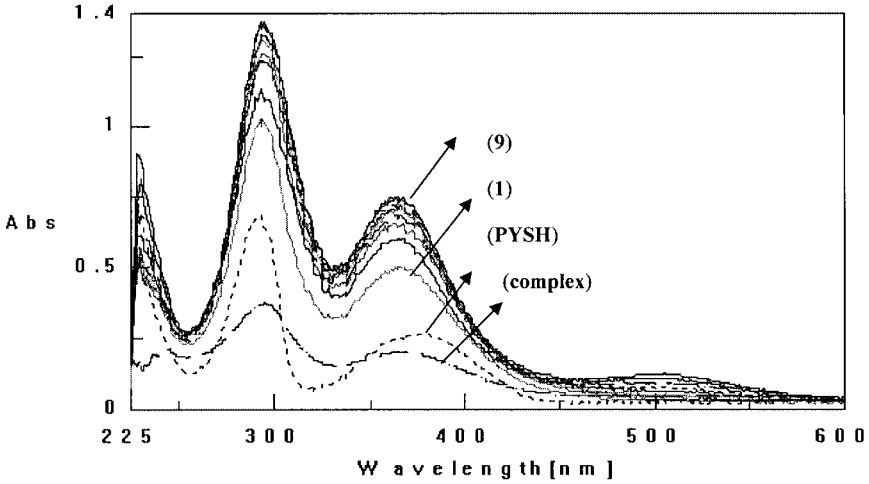


Figure 3. UV/Vis spectra of the complex (5×10^{-5} M) and the ligand (PYSH) (5×10^{-5} M) in dichloromethane; UV/Vis spectra of solutions with constant concentrations (10^{-4} M) of PYSH and increasing quantities of diiodine in dichloromethane ($[I_2]/[L]$: 1: 0.33; 2: 0.50; 3: 0.66; 4: 0.84; 5: 1.00; 6: 1.16; 7: 1.34; 8: 1.50; 9: 1.66)

Table 1. Structural and Raman spectroscopic data of complex **1** and other known polyiodide adduct complexes

Compound	Iodine-containing counter part	Geometry	d(I−I) [Å]	n (bond order)	Raman data [cm^{-1}]	Ref.
[(PYS-PYSH)$^+$·I_3^-] [four molecules (**a**−**d**), see Figure 5)	I_3^-: I$^-$···I_2	linear asymmetric	**a**: 2.887(4), 2.944(3); **b**: 2.874(4), 2.957(3); **c**: 2.968(3), 2.862(4); **d**: 2.855(4), 2.927(3)	0.56, 0.48; 0.58, 0.46: 0.45, 0.59: 0.61, 0.50	162.4 vs, 154.7 vs	this work
[Et(NH$_2$)dtl] I_3^- [a]	I_3^-: I$^-$···I_2	linear asymmetric	2.74, 3.14	0.83, 0.28	167 s	[7b]
CsI_3	I_3^-: I$^-$···I_2	linear asymmetric	2.842, 3.038	0.63, 0.37	157 m, 148 s, 137 s, 102 s, 93 s	[7b]
UrBuI_3^- [b]	I_3^-: I$^-$−I$^+$−I$^-$	linear asymmetric	2.935, 2.889	0.49, 0.55	112 vs, 113 vs, 128 w	[7b]

[a] Et(NH$_2$)dtl = 3,5-bis(ethyllamino)-1,2-dithiolithium. [b] UrBu = *N*-butylurotropinium.

shifts to lower wavenumbers upon coordination to a donor atom, reflecting the reduction in the I−I bond order and the strengthening of the complex formed as well.[2,7b,8b,8c,12]

The Raman spectrum of the complex shows two strong bands at 162.4 and 154.7 cm^{-1}. It is worth mentioning that bands around 110 cm^{-1} are normally assigned to the ν_1 symmetric stretching of I_3^- which, being a symmetrical ion, normally exhibits only one Raman-active band.[2a,2b,7b] However, when a distortion of I_3^- occurs, the asymmetric stretching may become Raman-active and additional bands at higher (140−130 cm^{-1}) and at lower frequencies (80−70 cm^{-1}) can be observed[7b] and assigned to asymmetric stretching and deformation motions of asymmetric I_3^-, respectively.[7b,13] Thus, the complex should be a linear asymmetric I_3^- (I$^-$···I_2) complex (see crystal structure) (Table 1).[7b]

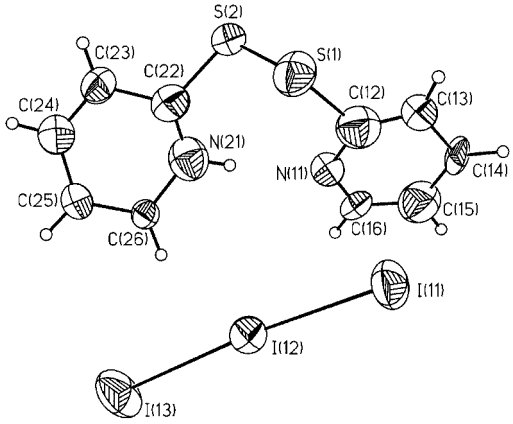


Figure 4. ORTEP diagram of the ionic components of compound **1** together with the atomic numbering scheme; thermal ellipsoids are shown at the 33% probability level, hydrogen atoms are depicted as the spheres of arbitrary radii; selected bond lengths are given in the text

Crystal and Molecular Structure of [(PYS−PYSH)$^+$·I_3^-]

Dark crystals of the complex suitable for a single-crystal X-ray analysis were grown by slow concentration of the filtrate obtained from the reaction of diiodine with the appropriate ligand in dichloromethane.

An ORTEP diagram of the compound is shown in Figure 4 with selected bond lengths and angles in Table 2. In the crystal there are four symmetry-independent cation/anion pairs (Figure 5). Figure 5 also shows the intermolecular or cation−anion interactions.

The structure of the compound consists of two residues, one cationic (PYS−PYSH)$^+$ containing the S−S bond linking the two 2-mercaptopyridine molecules, one of which is protonated, and one I_3^- counter anion. There are only a few crystal structures reported in the literature containing open-chain stable cations of DS−SD dimers. These include the monocation [{($C_4H_6N_2S$−$SN_2C_4H_5$)$_2$}$^{2+}$·(I_3^-)·(I_5^-)][3] ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione) and dications such as [{($C_4H_6N_2S$−)$_2$}$^{2+}$·2I_3^-·I_2][3] ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione), [{(*i*Pr$_2$timdt)$_2$}$^{2+}$·(IBr$_2^-$)$_2$][14a] (*i*Pr$_2$timdt = 1,3-diisopropylimidazolidine-2,4,5-trithione), and [{(H$_2$N)$_2$C−S−S−C(NH$_2$)$_2$}$^{2+}$·(2I$^-$)][14b] [(H$_2$N)$_2$C=S = thiourea], [(L)$_2^{2+}$·2(I_3^-)][14c] (L = 1,3-diisopropyl-4,5-dimethylimidazoldithiocarboxylate).

The mean value of the S−S bond length measured in the four symmetry-independent cation/anion pairs found in the structure is 2.032 Å [the individual bonds are S(1)−S(2) = 2.003(12) Å (**a**), S(3)−S(4) = 2.010(15) Å (**b**), S(5)−S(6) = 2.052(14) Å (**c**) and S(7)−S(8) = 2.062(14) (**d**), respectively] (Figure 5). These are among the shortest bonds of this type.[3,14] Examples include the monocation [{($C_4H_6N_2S$−$SN_2C_4H_5$)$_2$}$^{2+}$·(I_3^-)·(I_5^-)] ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione) with S−S = 2.094(3) Å[3] and the dications, [{($C_4H_6N_2S$−)$_2$}$^{2+}$·2I_3^-·I_2] ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione) with S−S = 2.085(2) Å,[3] [{(*i*Pr$_2$timdt)$_2$}$^{2+}$·(IBr$_2^-$)$_2$], (*i*Pr$_2$timdt = 1,3-diisopropylimidazolidine-2,4,5-trithione) with S−S = 2.071(7) Å,[18] [{(H$_2$N)$_2$C−S−S−C(NH$_2$)$_2$}$^{2+}$·(2I$^-$)] [(H$_2$N)$_2$C=S = thiourea] with S−S = 2.044 Å,[14b] and [(L)$_2^{2+}$·2(I_3^-)] (L = 1,3-diisopropyl-4,5-dimethylimidazoldithiocarboxylate) with S−S= 2.024(5) Å.[14c]

The two C−S bond lengths in the four symmetry-independent cation/anion pairs of the complex are unequal due to the monoprotonation of the aromatic ring of the disulfide [S(1)−C(12) = 1.85(3) and S(2)−C(22) = 1.77(3) Å (**a**), S(4)−C(42) = 1.78(3) and S(3)−C(32) = 1.75(3) Å (**b**), S(6)−C(62) = 1.65(2) and S(5)−C(52) = 1.77(3) Å (**c**), S(7)−C(72) = 1.71(2) and S(8)−C(82) = 1.69(3) Å (**d**), respectively] (Figure 5). The longer C−S distance corre-

Table 2. Selected bond lengths [Å] and angles [°] for **1**

Bond lengths [Å]			
I(11)−I(12)	2.892(4)	S(3)−S(4)	2.010(15)
I(12)−I(13)	2.943(3)	S(3)−C(32)	1.78(3)
I(21)−I(22)	2.880(4)	S(4)−C(42)	1.75(3)
I(22)−I(23)	2.960(3)	S(5)−S(6)	2.052(14)
I(31)−I(32)	2.860(4)	S(5)−C(52)	1.65(2)
I(32)−I(33)	2.963(3)	S(6)−C(62)	1.77(3)
I(41)−I(42)	2.855(4)	S(7)−S(8)	2.062(14)
I(42)−I(43)	2.928(3)	S(7)−C(72)	1.71(2)
S(1)−S(2)	2.003(15)	S(8)−C(82)	1.69(3)
S(1)−C(12)	1.85(3)		
S(2)−C(22)	1.77(3)		
Angles [°]			
I(11)−I(12)−I(13)	174.92(12)	I(33)−I(32)−I(31)	176.17(11)
I(21)−I(22)−I(23)\tab	174.96(11)	I(41)−I(42)−I(43)	175.58(11)
C(12)−S(1)−S(2)−C(22)	90.4(15)	C(52)−S(5)−S(6)−C(62)	83.5(13)
C(32)−S(3)−S(4)−C(42)	−89.7(14)	C(72)−S(7)−S(8)−C(82)	−86.8(13)

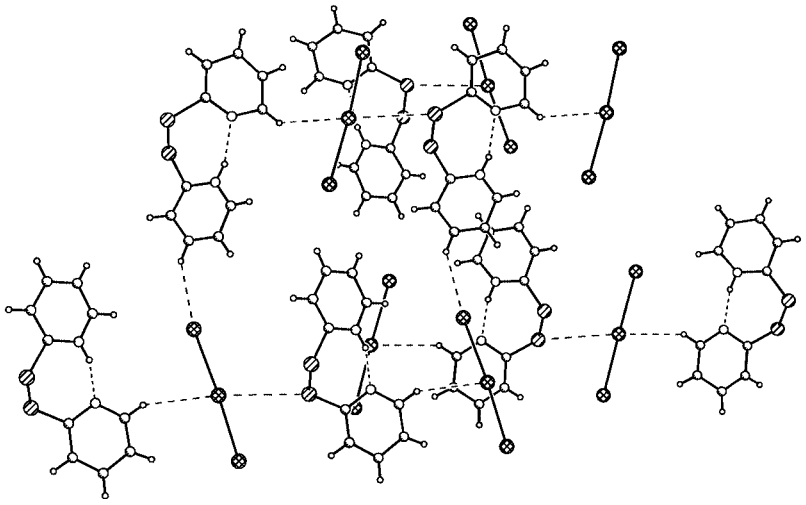


Figure 5. Crystal packing of **1** as seen approximately along the [100] direction, hydrogen bonds and S···I contacts are drawn as dashed lines

sponds to the nonprotonated ring and the shorter distance to the protonated one. The corresponding C−S bond lengths found in the monocation $[\{(C_4H_6N_2S-SN_2C_4H_5)_2\}^{2+}\cdot(I_3^-)\cdot(I_5^-)]$ ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione)[3] are 1.744(9) Å and 1.700(11) Å. The C−S bond lengths found in the doubly protonated rings of the dications are almost equal, 1.748(5) and 1.735(5) Å in $[\{(C_4H_6N_2S-)_2\}^{2+}\cdot 2I_3^-\cdot I_2]$ ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione),[3] 1.76(4) and 1.75(2) Å in $[\{(i\mathrm{Pr}_2\mathrm{timdt})_2\}^{2+}\cdot(\mathrm{IBr}_2^-)_2]$ (*i*Pr_2timdt = 1,3-diisopropylimidazolidine-2,4,5-trithione),[18] 1.76 and 1.78 Å in $[\{(H_2N)_2C-S-S-C(NH_2)_2\}^{2+}\cdot(2I^-)]$ $[(H_2N)_2C{=}S$ = thiourea],[14b] and 1.7281(2) Å in $[(L)_2{}^{2+}\cdot 2(I_3^-)]$ (L = 1,3-diisopropyl-4,5-dimethylimidazoldithiocarboxylate).[14c]

Both I−I bond lengths differ significantly from the corresponding I−I bond length of I_2 in the solid state (2.715 Å).[15] Thus, the two I−I bond lengths of I_3^- in the complex are I(11)−I(12) = 2.892(4) and I(12)−I(13) = 2.943(3) Å (**a**), I(21)−I(22) = 2.870(4) and I(22)−I(23) = 2.960(3) Å (**b**), I(31)−I(32) = 2.860(4) and I(32)−I(33) = 2.863(3) Å (**c**) and I(41)−I(42) = 2.855(4) and I(42)−I(43) = 2.928(3) Å (**d**), respectively (Figure 5), indicating a slight asymmetry of I_3^- in this complex (covalent linear asymmetric).[7b] In the following I_3^- adducts, however, the asymmetry seems to be stronger. Thus, in $[Et(NH_2)dtl]I_3^-$ [$Et(NH_2)$dtl = 3,5-bis(ethyllamino)-1,2-dithiolithium],[7b,16a] the I−I bond lengths are 2.74 and 3.14 Å, in CsI_3^- [7b,16b] 2.842 and 3.038 Å, in $Da_2I_3^-$ [7b,16c] (Da = 1,4-diazoniabicyclo[2.2.2]octane) 2.793 and 3.167 Å, and in [1-MethylcytosineH]I_3^- [7b,16d] 2.794 and 3.123 Å (see Table 1 and ref.[7b] for more examples).

According to Pauling,[17a] $d(\mathrm{I-I}) = d_o - 0.85\cdot\log(n)$ [Equation (2)], where d_o is the I−I bond length of I_2 in the gas phase, i.e. 2.67 Å,[17b] and *n* is the bond order. The calculated values of the bond orders for the I−I bonds of the complexes are listed in Table 1. Deplano et al.[7b] classi-

fied triiodide adducts into two types: (a) the $I^-\cdots I_2$ adducts which have a linear asymmetric geometry with one strong I−I bond (bond orders > 0.63 e) and one weaker I−I bond (bond orders < 0.30 e) and (b) the covalent I−I−I complexes which have (i) a linear symmetric geometry with two equal I−I bonds and bond order values around 0.50 e and those with (ii) a linear asymmetric geometry which have two nonequivalent I−I bonds with bond order values around 0.50 e (a stronger bond with bond order > 0.50 e and a weaker with bond order < 0.50 e). Thus, according to the values of the I−I bond lengths and bond orders, the I_3^- in this complex can be classified as a linear asymmetric $I^-\cdots I_2$ complex.[7b]

The mean value of the I−I−I bond angle is 175.4(1)° [(11)−I(12)−I(13) = 174.92(12)° (**a**), I(21)−I(22)−I(23) = 174.96(11)° (**b**), I(33)−I(32)−I(31) = 176.17(11)° (**c**) and I(41)−I(42)−I(43) = 175.58(13)° (**d**), respectively] (Figure 5) indicative of the involvement of both terminal iodine atoms in the interaction with the disulfide. These differ only slightly from linearity. In particular, the mean C···I and S···I contact distances of the two terminal iodine atoms of I_3^- species in the four symmetry-independent cation/anion pairs are 3.842 Å and 3.943 Å, respectively. Similar angles were observed in $[\{(C_4H_6N_2S-)_2\}^{2+}\cdot 2I_3^-\cdot I_2]$ ($C_4H_6N_2S$ = *N*-methylimidazole-2-thione) [178.87(4)°][3] and in $[(L)_2^{2+}\cdot 2(I_3^-)]$ (L = 1,3-diisopropyl-(4,5-dimethylimidazolyl)dithiocarboxylate) [175.71(4)°].[14c]

Strong intramolecular hydrogen bonds between the imino NH proton and the nonprotonated nitrogen atom are formed in the complex (mean value of the N···N bond is 2.74 Å, mean value of H···N is 1.91Å and the mean value of the N−H···N angle is 163°). In the crystal structure, the weak C−H···I, S···I, and S···S interactions organise the cations and anions in alternate layers (Figure 5).

Conclusion

Recently, a mechanism for the transformation of MMI to MMI disulfide was proposed by Isaia et al.[3] and Po et al.[18] based on crystallographic and electrochemical data. The proposed redox process involves the formation of a di- and a monocationic disulfide species of MMI prior to the full transformation of MMI to MMI disulfide. Thus, thioamides such as MMI[3] or tzdtH[2a] exhibiting antithyroidal activity against hyperthyroidism (Graves' disease) are either oxidised by the TPO-I system to form disulfides or act as strong donors towards diiodine forming iodonium salts, while activated iodine is reduced to the iodide anion simultaneously. On the other hand, thioamides such as PTU[2c] which are able to form weak charge transfer species with diiodine, interfere in other steps of the mechanism, either in the formation of thyroid peroxidase (TPO)−iodonium complex[4] or inhibit the activity of the iodothyronine deiodinase type I (ID-1), an enzyme responsible for the monodeiodination of the T4 prohormone to the T3 hormone[6] The easy oxidation of PYSH by I_2 to form the monocationic disulfide complex [(PYSPYSH)$^+\cdot I_3^-$] similar to the antithyroid drug methimazole (MMI)[3,18] may indicate that PYSH might also possess antithyroid properties like MMI.

Experimental Section

Materials and Instruments: All solvents used were reagent grade. Diiodine (Aldrich) and pyridine-2-thione (Merck) were used with no further purification. Elemental analyses for C, H, N, and S were carried out with a Carlo Erba EA model 1108 elemental analyser. Melting points were measured in open tubes with a Stuart scientific apparatus and are uncorrected. Infrared spectra in the region of 4000−370 cm^{-1} were obtained in KBr discs while far-infrared spectra in the region of 400−50 cm^{-1} were obtained in polyethylene discs with a Perkin−Elmer Spectrum GX FT-IR spectrophotometer. A Jasco UV/Vis/NIR V 570 series spectrophotometer was used to obtain the electronic absorption spectra. Conductivity titrations were carried out at 293 K in acetonitrile solutions with a WTF LF-91 conductivity meter.

Synthesis and Crystallisation: The complex was prepared by mixing a dichloromethane solution of diiodine with a suspension of 2-mercaptopyridine in dichloromethane in a 1:2 PYSH/I_2 molar ratio in air at 0 °C with continuous stirring for 5 h. The solution was then filtered and the resultant clear solution was kept in the refrigerator for several days. Dark crystals of the complex suitable for single-crystal X-ray analysis were obtained, yield 0.012 g (20%); m.p. 80−82 °C. $C_{10}H_9I_3N_2S_2$ (602.02): calcd. C 19.95, H 1.51, N: 4.65, S 10.65; found C 19.23, H 1.51, N 4.31, S 10.87. IR: $\tilde{\nu}$ = 3119 w, 1577 s, 1496 s, 1108 vs, 959 s, 765 vs, 731 s, 654 s, 463 s, 158 m, 112 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 500.5 (2.90), 367.5 (3.56), 292.5 (3.84) nm.

X-ray Structure Determination: Data were collected using the ω-scan technique in the range 2.90° < 2θ < 29.92° with a KUMA KM4CCD four-circle diffractometer[19a] with a CCD detector using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293(2) K. Cell parameters were determined by a least-squares fit.[19b] All data were corrected for Lorentz-polarisation and absorption effects.[19b,19c] The crystals of the compound were relatively poor in quality and the statistical indicators of the appropriate refinements are, therefore, not very good and the refinements were provided with constraints. Nevertheless, the quality of the data obtained allow for a reasonable discussion, especially of crystal packing and the constitution of the complex. The structure was solved by direct methods with SHELXS-97[19d] and refined by full-matrix least-squares procedures on F^2 with SHELXL-97.[19e] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in calculated positions and refined using the "riding model" with isotropic thermal parameters fixed at 1.2 times the U_{eq} values of the appropriate carrier atom. $C_{10}H_9I_3N_2S_2$, MW = 602.020, monoclinic in $P2_1$, a = 8.230(2) Å, b = 35.708(7) Å, c = 11.369(2) Å, β = 91.86(3)°, V = 3339.3(12) Å^3, Z = 8, ρ(calcd.) = 2.395 g cm^{-3}, μ = 5.849 mm^{-1}, reflections collected 21199, Final R ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$), $wR2$ $\{[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}\}$ [$I > 2\sigma(I)$] indices 0.0872 and 0.2028, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-230097 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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